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1 A century long sedimentary record of anthropogenic lead
2 (Pb), Pb isotopes and other trace metals in Singapore

3

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15

16 **Abstract**

17 Reconstructing the history of metal deposition in Singapore lake sediments contributes to
18 understanding the anthropogenic and natural metal deposition in the data-sparse Southeast
19 Asia. To this end, we present a sedimentary record of Pb, Pb isotopes and eleven other metals
20 (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) from a well-dated sediment core collected near the
21 depocenter of MacRitchie Reservoir in central Singapore. Before the 1900s, the sedimentary Pb
22 concentration was less than 2 mg/kg for both soil and sediment, with a corresponding
23 $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.20 . The Pb concentration increased to 55 mg/kg in the 1990s, and
24 correspondingly the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased to less than 1.14. The $^{206}\text{Pb}/^{207}\text{Pb}$ in the core top
25 sediment is concordant with the $^{206}\text{Pb}/^{207}\text{Pb}$ signal of aerosols in Singapore and other Southeast
26 Asian cities, suggesting that Pb in the reservoir sediment was mainly from atmospheric
27 deposition. Using the Pb concentration in the topmost layer of sediment, the estimated
28 atmospheric Pb flux in Singapore today is $\sim 1.6 \times 10^{-2} \text{ g/m}^2\text{-yr}$. The concentrations of eleven other
29 metals preserved in the sediment were also determined. A principal component analysis
30 showed that most of the metals exhibit an increasing trend towards 1990s with a local
31 concentration peak in the mid-20th century.

32

33 Keywords: Pb, Pb isotopes, heavy metals, Southeast Asia, Singapore, sediment.

34

35 **Capsule Abstract**

36

37 The sedimentary record from Singapore show that most metals increased during 20th century
38 with Pb isotopes implied atmospheric sources.

39

40 **Introduction**

41 Anthropogenic lead (Pb) has been an important contaminant in human history, especially after
42 the Industrial Revolution. The emission of anthropogenic Pb reached a level greater than 20
43 times the global natural Pb emissions in the 1980s (Nriagu 1989), mainly attributable to usage of
44 leaded gasoline, high-temperature industrial activities and incineration (Komárek 2008, Nriagu
45 1979). Anthropogenic Pb has been recorded in many environments, including the atmosphere
46 (e.g.: Patterson and Settle 1987; Duce et al. 1991; Bollhöfer and Rosman 2000, 2001; Zhu et al.
47 2002; Flegal et al. 2013); terrestrial (e.g.: Boutron et al 1995; Osterberg et al. 2008; De Deckker
48 et al. 2010; Kylander et al., 2010; Lee et al., 2011); aquatic (e.g.: Arnason and Fletcher 2003, Erel
49 and Patterson, 1994; Graney et al. 1995; Harrington et al. 1998; Kober et al. 1999; Li et al. 2000;
50 Eades et al. 2002;) and oceanic (Turekian, 1977; Schaule and Patterson, 1981; Boyle et al. 1986,
51 2005; Reuer, 1995; Flegal, 1986; Weiss et al., 2003; Kelly et al., 2009) environments.

52 Since the 1990s, the Asian contribution of Pb has received greater attention as the major Pb
53 contributors in 1970s and 1980s (North America and Western Europe) phased out leaded petrol
54 earlier than Asian countries. In addition, the increasing emissions of Pb from coal combustion
55 and other industrial sources have also received regional attention in Asia as a consequence of
56 the recent economic boom (e.g.: Díaz-Somoano et al. 2009; Hang et al. 2010; Flegal et al. 2013;
57 Zurbrick et al., 2014).

58 Therefore, the assessment of Asia's contribution of Pb to the global Pb flux is becoming
59 increasingly important . However, Southeast Asia remains data-sparse in terms of environmental
60 data on Pb emissions, despite being the last region in the Asia–Pacific to phase out leaded petrol
61 (Hirota 2006; USAID 2009). In addition to Pb petrol inputs, the rapid economic development in
62 Southeast Asia has also contributed to a dramatic increase in coal burning (International Energy
63 Statistics 2012), exacerbating the emission of Pb and many other metals. For example, the coal
64 consumption in Malaysia and Indonesia in 2012 was nearly 50 and 30 times the 1980s average
65 (International Energy Statistics 2012). Also, other metals could be co-released to the
66 environment, and the concentration of these metals is dependent on which raw materials were
67 used; which processes were involved in handling the metal-bearing materials; and which, if any,
68 emission controls were applied. A few Pb studies have reported Pb contents in Southeast Asian
69 environments that are higher than other parts of the world. For example, the Pb concentrations

70 of aerosols in Southeast Asian cities between 1994 and 1999 were much higher than Europe,
71 Australia and North America (Bollhöfer and Rosman 2000, 2001), and the Pb/Ca preserved in a
72 coral from southwest of Sumatra, Indonesia shows an increasing trend of Pb in the coastal
73 waters since the 1980s (Lee et al. 2014). In addition, the Pb content of lichens from the
74 Singapore Straits was found to be in the upper range of the recorded values around the world
75 (Ng et al. 2006). However, most of these studies do not shed light on the multi-decadal variation
76 of Pb in the environment of Southeast Asia or the isotopic composition of Pb in the environment.

77 Constraining the long term variation of Pb and other metals in a variety of environments is
78 important as it allows characterization of the long-term environmental response to
79 anthropogenic emissions (e.g: Kelly et al. 2009) and facilitates comparison of metals between
80 different environments and with different residence times (Alleman et al. 1999; Hamelin et al.
81 1997). The Pb isotope ratios ($^{206}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$) and the temporal variability of the
82 isotopes can differentiate Pb sources, and can be a further step in evaluating the source of the
83 Pb and its variation through time (Komárek et al. 2008).

84 One way to investigate the above two aspects is to study the variation of Pb and Pb isotopes in
85 well-dated lacustrine sediments. Lacustrine sediments are a sink for metals from the water
86 column (Foster and Charlesworth, 1996) and can be used as archives of century-scale Pb
87 variation (Komárek et al. 2008). The reliability of evaluating Pb and other metals from lacustrine
88 records has been demonstrated from studies carried out in Europe (e.g. Eades et al. 2002),
89 North America (e.g. Graney et al. 1995, Lima et al. 2009) and China (e.g. Eades et al. 2002; Cheng
90 and Hu 2010).

91 In order to assess the anthropogenic Pb input in Southeast Asia and to evaluate the relative
92 contribution of various Pb sources at different time periods, we determined the Pb
93 concentration ([Pb]) and Pb isotopes from a ^{210}Pb -dated sediment core recovered from the
94 MacRitchie Reservoir in the central catchment region of Singapore (Figure 1). The variations of
95 [Pb] and Pb isotopes are compared with historical Pb emissions from Southeast Asian countries
96 and the isotopic composition of Pb from potential sources.

97 Many metals are co-released during industrial activities (e.g. Cd and As are released during coal
98 combustion; Ba and Zn are released during waste incineration, ATSDR 2007, Salomons and
99 Förstner 1984), and some metals (e.g. Ag, Cu, Cr, Ni, Tl) are generally associated with electronics

100 industries, which have grown extensively over time in Singapore. For a more comprehensive
101 story on the changing release of metals over the last century, the temporal variability of eleven
102 other metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) from the sediment are also reported
103 and compared with the Pb record.

104

105

106 **Sampling and methodology**

107 **Site information and sampling**

108 Singapore is one of the most developed and densely populated cities in Southeast Asia (Statistics
109 Singapore 2014). Additionally, it houses one of the busiest ports in the world (American
110 Association of Port Authorities 2008). Singapore is a small city-state bordered to the north and
111 east by Malaysia and to the south by Indonesia. Singapore is dominated by a monsoonal climate,
112 with northeasterly winds prevailing between April and September and southwesterly winds
113 prevailing between November to March (National Environmental Agency, 2009, Figure 1a).
114 Despite monsoonal wind reversals, no clear seasonal variability has been observed in the
115 concentration of Pb in the aerosols or rain waters recovered from Singapore (personal
116 communications with Professor Richard Webster). MacRitchie Reservoir was chosen to
117 investigate the deposition of Pb (Figure 1) because it is located in a near pristine catchment, has
118 a very low dissolved oxygen concentration near the lake floor, which suggests that little
119 bioturbation of the lake floor sediment occurs (Chen et al. 1996). The MacRitchie Reservoir is
120 located in the Central Catchment Nature Reserve of Singapore, where over 20 km² of forested
121 area drains into four reservoirs (MacRitchie, Upper Seletar, Upper Peirce and Lower Peirce;
122 Public Utilities Board, 2015). The drainage basin lies on Triassic igneous granite containing 60-65%
123 feldspar and >30% quartz (Bukit Timah Granite, Pitts 1984, Zhao 1996). The MacRitchie
124 Reservoir was constructed by damming a creek valley in 1891 (Devi, 2002), and since then, the
125 catchment of the reservoir has remained relatively pristine (Public Utilities Board 2010).

126 A sediment freeze core was collected on the 6th August 2012 from the southeastern, and
127 deepest section (9m) of the MacRitchie Reservoir (Figure 1c). The coring site was away from the
128 major inlet of the catchment, and was also sufficiently distant from the dam so that the

129 sediments would not be affected by regular pumping activities (Figure 1d). During sampling, the
 130 core was collected by lowering a freeze-corer to the sediment-water interface and pushing into
 131 the underlying sediments (Shapiro 1958). In brief, a freeze corer consists a hollow rectangular
 132 cylinder filled with a slurry of dry ice and ethanol. While coring, the corer was lowered to ~1m
 133 above the bottom, and released to punch into the sediment layer by gravity. The dry ice and
 134 ethanol quickly froze sediment surrounding the corer, resulting in a slab of frozen sediment
 135 (including the sediment-water interface) freezing onto the corer's surface. The frozen slab of
 136 sediment was then carefully detached from the corer surface and sent back to the laboratory in
 137 a cooler box. During sub-sampling, the frozen core was stored horizontally at room temperature
 138 until soft (~10 min), and the preserved stratigraphy was sub-sampled at 2 to 8 cm increments
 139 (depending on the sediment density and water content) using a plastic spatula. A surface water
 140 sample was also collected on the day of sampling using a 1 litre trace-metal clean bottle
 141 attached to a plastic pole and dragged across the lake surface. The water sample was filtered
 142 through 0.4 µm Millipore filters within a few hours of collection and acidified in a class 100
 143 environment using trace metal clean reagents and lab-ware.

144

145

146 **Regional on Pb emissions**

147 For a better means of comparing the historical [Pb] recorded in our core, Pb emissions from
 148 Singapore coal burning were estimated based on the following equation (from Li et al., 2012):

$$149 E_{\text{coal}} = PP \times P_{\text{percap}} \times C \times [\text{Pb}]_{\text{coal}} \times EF \quad (1)$$

150 Where the E_{coal} is the Pb emitted from coal power plants (tons); the PP was the population
 151 (person), P_{percap} was the electricity consumption per capita (kwh/person); C was the amount of
 152 coal used to generate 1 kwh of electricity; $[\text{Pb}]_{\text{coal}}$ was the Pb content in the coal; and the EF was
 153 the emission factor, which was the amount of Pb released compared to the amount of the
 154 amount of Pb associated with coal burning. Singapore did not use coal for its electricity between
 155 1970 and 2010, however, there was a coal power plant in Singapore that operated between
 156 1927 and early 1970s (Ramlan 2014). The 1927-1959 population data came from Goldewijk et al.
 157 (2011) and the 1960 to 1970 population data came from Statistics Singapore (2014). The earliest

158 data on electricity consumption per capita for Singapore was recorded in 1971, as 1154.8
159 kwh/person (UN Data 2014). It is reasonable to expect that the per capita electricity
160 consumption between the 1920s and 1950s was lower and therefore the P_{percap} used in the
161 estimation only reflects an upper limit of the Pb emissions. The constants used in the coal
162 estimation in this study are 0.472 kg/kWh for C (e.g. Lee et al. 2014) and 15 mg/kg as the $[\text{Pb}]_{\text{coal}}$,
163 as an average Pb content in coal from Australia, Indonesia, China and India (Díaz-Somoano et al.
164 2009). The emission factor varies depending on the types and the efficiency of generators, and
165 was assumed to be 80% in this study (same as in Li et al. 2012 for consistency). The estimated Pb
166 emission is shown in Figure 2b.

167

168

169 **Determination of particle size and chronology**

170 The particle size distribution of the sediment core was examined to give an overview of the
171 physical properties of the sediment. For particle size analysis, HCl and H_2O_2 were applied to
172 remove the carbonates and organic components and to disassociate the clays. The treated
173 samples were analyzed by a laser diffraction particle size analyzer (Malven Mastersizer 2000)
174 using procedures outlined in Switzer (2013).

175 The chronology of the sediment was determined using the atmospherically-deposited
176 radionuclide ^{210}Pb (Krishnaswamy et al. 1971). The total activity of ^{210}Pb was measured using a
177 Canberra Broad Energy Germanium gamma counter at 46.5keV (Gäggeler et al. 1976). The
178 corrections for the combined effects of X-ray self-absorption, counter efficiency and
179 sample/counter geometry were established by first counting an untreated sample, and again
180 after mixing the sample with 100mg of US-DOE CRM 101 standard (a pitchblende-silica mixture
181 based on an aged uranium deposit that had come into radiochemical equilibrium for all of the
182 short-lived daughters). The signal enhancement for ^{210}Pb in the spiked mixture gave the product
183 of counting geometry and self-absorption. Similarly, the supported ^{210}Pb was estimated from its
184 long-lived ^{226}Ra parent by counting its short-lived daughter ^{214}Pb at 351.9 keV for the unspiked
185 and spiked samples to correct for counting geometry and minor self-absorption. The procedure,
186 assumptions and data reduction in this study is similar to that described by Appleby et al. (1986),

187 except that we used an empty-sample container for blanks rather than anti-coincidence
188 background correction.

189 In order to convert the ^{210}Pb data into estimated dates, the sedimentation rate was determined
190 by plotting the unsupported ^{210}Pb activity in a logarithmic scale with depth, as shown by
191 Tylmann (2004). The ^{210}Pb derived years are also shown in Figure 3b. It should be noted that
192 because the sediments were subsampled at 2-8cm increments, and because of the uncertainties
193 in the ^{210}Pb measurements, the age of a sample estimated from ^{210}Pb should be interpreted as
194 an average data over a period (c.a. ~10 years, e.g., a sample with a ^{210}Pb age of 1955 should be
195 interpreted as the 1950s).

196

197

198 **Sample preparation and metal analysis**

199 The sediment samples were leached by a combination of ultrapure grade 1.75 mol/L HNO_3 -3
200 mol/L HCl (distilled four times using a cleaned vycor glass still inside a class 100 clean room).
201 Samples were leached for 60 minutes in an ultrasonic bath following the method described by
202 Graney et al. (1995) and the samples were left at room temperature for another 24 hours to
203 complete the reaction. This method effectively extracts the metals adsorbed on the particle
204 surface without dissolving the mineral grains. Therefore, the leachate represents the
205 anthropogenic fraction of the metals with some of the mineral-bound metals. The recovery of
206 metal using this method was proven as [Pb] in the leachate were indistinguishable from 6 mol/L
207 HCl, 7 mol/L HNO_3 or Aqua Regia digestions (Graney et al. 1995). After acid leaching, the
208 samples were centrifuged and the supernatant was extracted. The supernatant was then filtered
209 through a 0.4 μm membrane using a syringe and diluted for metal analysis.

210 To determine the [Pb] of the sediments, both isotope dilution and internal standard methods
211 were applied. For isotope dilution, a known amount of ^{204}Pb enriched spike (Oak Ridge National
212 Laboratories) was added to each sample and the [Pb] in the sample was calculated from the
213 measured $^{204}\text{Pb}/^{208}\text{Pb}$ ratio (Wu and Boyle 1997). For the internal standard method, a known
214 amount of indium standard (In) was added to each sample and standard (SPEX CertiPrep), and
215 the [Pb] in the sample was calculated by comparing the Pb/In in the sample and the standard

216 (Vanhaecke et al. 1992). The accuracy of the data was cross-checked by measuring the same
217 sample using both isotope dilution and internal standard methods, which also showed a
218 consistent positive relationship suggesting a negligible offset between the two methods (see
219 supplementary material).

220 The metal concentrations of silver ([Ag]), arsenic ([As]), barium ([Ba]), cadmium ([Cd]), cobalt
221 ([Co]), chromium ([Cr]), Copper ([Cu]), nickel ([Ni]), thallium ([Tl]), uranium ([U]) and zinc ([Zn])
222 were determined applying a quadrupole inductively-coupled plasma mass spectrometry (Q-ICP-
223 MS, VG PlasmaQuad 2+) using the internal In standard method described above.

224 The iron concentrations ([Fe]) in the sediments were also analyzed by a Q-ICP-MS (PerkinElmer
225 ELAN DRC-e) following the same sample preparation method. The [Fe] was calculated by
226 comparing the signal intensity with a series of standards with various concentrations. The [Fe] in
227 the sediment was used to normalize other metals to provide a more objective view on the
228 variability of metals in the sediment (Supplementary Material S7).

229 Trace metal clean plasticware (leached from brand new vials using ultrapure acid and rinsed 5x
230 with 4x distilled deionized water), ultrapure acid and 4x distilled deionized water were used
231 throughout the sample preparation process. The procedural blanks were measured and ranged
232 from 0.04% to 4.1% of sample concentration and were corrected for the reported concentration.

233 Pb isotope ratios in the sediment were measured by multi-collector plasma mass spectrometry
234 (G/V IsoProbe). To prepare the samples for isotope analysis, an ion exchange column (Eichrom
235 AG-1X8 chloride form, 200 to 400 mesh) was employed to extract Pb from the sample matrices
236 (Reuer et al. 2003), which typically recovers 99.98% of the Pb from the sample. To ensure the
237 precision and accuracy of the Pb isotope measurement, a number of precautionary measures
238 were undertaken following the methods described in Reuer et al. (2003) and Boyle et al. (2012),
239 including the addition of a thallium spike to each sample and standard to constantly monitor the
240 mass fraction related to the instrument, monitoring the ^{202}Hg signal in each sample to correct
241 the isobaric interference of ^{204}Pb by ^{204}Hg , correcting the possible contamination from two
242 column procedural blanks, monitoring the instrumental acid blanks at the beginning and the end
243 of the day and every 10 samples to correct the ICP-MS background signal related to either the
244 acid or the instrument, correcting the tailing errors by measuring the monoisotopic element
245 bismuth at half masses, and calibrating the Pb isotopes measured in each sample by

246 normalization to NBS 981 standard reference material (Baker et al. 2004) measured during the
247 same day. The NBS-981 standard reference material is used during the correction procedure,
248 and an internal lab standard (BAB3deg) measured to ensure the accuracy of the NBS-981
249 standard. Measuring the BAB3deg standard calibrated to NBS-981 gave a 2 relative standard
250 deviation precision of $^{206}\text{Pb}/^{207}\text{Pb}$ of 160ppm (n=42), $^{208}\text{Pb}/^{207}\text{Pb}$ of 163ppm (n=42).

251 The [Pb] in the water was measured by isotope dilution after a single-batch resin adsorption
252 separation (Lee et al. 2011). In brief, an aliquot of cleaned Nitrilotriacetic resin was added to the
253 sample (final concentration ~ 2400 beads/1.3mL water sample) at pH=5.3. After four days of
254 resin uptake, the resins beads were rinsed three times using distilled deionized water and then
255 leached in 0.1 mol/L HNO_3 . The leachate was analyzed for [Pb] using Q-ICP-MS. The procedural
256 blanks averaged 3.7×10^{-4} $\mu\text{g}/\text{L}$ and was $\sim 3\%$ of our sample concentration.

257

258

259 **Principal component analysis on 11 metals in the sediments**

260 A principal component analysis (PCA) was carried out on the concentration of the metals in the
261 sediment to investigate the potential correlations among the metals. Eleven metals (Ag, As, Ba,
262 Cd, Co, Cr, Ni, Pb, Tl, U and Zn) , were included in the PCA. Because the metals in the sediment
263 vary at different scales (i.e., Ag varies from 0.008mg/kg to 0.228mg/kg and Zn varies from
264 2.5mg/kg to 122.5mg/kg), the concentration data for each metal was standardized by
265 subtracting its mean and then dividing by its standard deviation to provide equal weight for all
266 the elements. The standardized data were analyzed by the PCA function in Matlab (Jackson
267 1991), which returned the eigenvectors, the eigenvalues and the sample scores. Cu was not
268 included in the PCA as the highly skewed variation could potentially overwhelm the variation of
269 other metals. Instead, the variation of Cu is discussed separately.

270

271

272 **Results**

273 Sediment core description and ^{210}Pb chronology

274 Sediments in the upper part of the core (0 to 8 cm) were a slurry of silty clays, affirming the
275 collection of the sediment-water interface during the freeze core collection. Below the upper 8
276 cm lies denser dark grey silty clays. There was a distinct color change to reddish yellow at 33 cm
277 that extended to the base of the core and coincided with an increase in sand content to a sandy
278 silt.

279 The ^{210}Pb data was fit with a constant sedimentation model of 0.29 cm/yr (Figure 3b). As such,
280 the ^{210}Pb date at 34 cm was ca. 1895. It is likely that the color change at 33 cm marked the
281 damming of the creek valley and the formation of the reservoir in the year 1891, which is in
282 good agreement with the ^{210}Pb date. Using the date of sampling (year 2012) and the date of
283 reservoir's formation (year 1891) as the two end-member constraints, the ^{210}Pb dates
284 characterize the chronology of the sediments reasonably well (Figure 3b). After considering the
285 sampling resolution and uncertainties in ^{210}Pb measurements and sedimentation rates, we
286 suggest the age of each sample as an interval of time shown in Figure 3. The period each sample
287 represents is listed in the supplementary material. Samples were interpreted within the
288 timeframe of each period instead of an exact ^{210}Pb date (e.g. the 18-21cm sample with ^{210}Pb
289 year of 1955 would represent 1950-1960 and so was interpreted as 1950s).

290 The deeper portion of the core was classified as a paleo-soil because the material was formed
291 before the reservoir's construction. And as a result, the ^{210}Pb -derived dates are unlikely to be
292 applicable to the paleo-soil as they were formed in a different depositional setting. The paleo-
293 soil samples were all considered as "before 1895" without a specific date. Based on the
294 measured ^{210}Pb activity, the calculated calendar years are shown in Figure 3c (and the
295 representing periods were shown in the supplementary material).

296

297

298 Variation of Pb and Pb isotopes in the sediment

299 The [Pb] in the sediment core is shown in Figure 4(a). The general concentration of Pb was less
300 than or equal to 55 mg/kg, which was lower than the mid-range concentrations from various

301 guidelines around the world (82 to 530 mg/kg dry weight, above the concentration that would
302 likely cause adverse effects on benthic organisms, Burton 2002). The dissolved Pb in MacRitchie
303 Reservoir water was measured as $1.1 \pm 0.07 \times 10^{-2}$ $\mu\text{g/L}$, which was two orders of magnitude
304 lower than the legal safe level of Pb in the drinking water (10 $\mu\text{g/L}$, Attorney General's
305 Chambers Singapore 2008).

306 Before 1895, the [Pb] in the soils were 1.2 ± 0.6 mg/kg (Figure 4a). The sample dated as 1903
307 was the first sample after the reservoir was constructed, showing a concentration of 1.2 mg/kg,
308 comparable to the paleo-soil. The [Pb] started to increase in the 1920s and reached a peak of 53
309 mg/kg in the 1950s. After the 1950s peak, the concentration of Pb decreased to 41 mg/kg in the
310 1960s, remained stable over the next two decades (roughly 1960-1984), and then finally
311 increased to 55 mg/kg in the 1990s. Due to the decadal resolution sampling, events occurring in
312 2000s are not resolvable.

313 The temporal variation of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are shown in Figure 4b. In the paleo-soil
314 samples prior to 1895, the three $^{206}\text{Pb}/^{207}\text{Pb}$ data points were similar and >1.215 . Since 1895,
315 $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from >1.215 to ~ 1.140 . The decreasing trend was consistent throughout
316 the core.

317

318

319 **Concentration of other metals in the sediments**

320 The temporal variations of the other 11 metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) in the
321 sediments are shown in Figure 5. Since both the bulk metal concentrations and the metal-to-Fe
322 (Me/Fe) ratio clearly show similar patterns for each of the metals throughout the core
323 (Supplementary Material S7), we relate the high metal concentrations at the top of the core to
324 anthropogenic inputs. In the sediment, most of the metals had their lowest concentrations at
325 the bottom of the core (prior to 1895), and highest concentrations in 1990s. The concentrations
326 of Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn in the 1990s were significantly higher than during
327 the 1900s. Other than the high concentrations in the 1990s, the variability of the metals are
328 compared using PCA (Figure 6). The first principal component (PC) explains 77% of the metal
329 variance in the core and the second PC explains 18% of the variance (Table 2). Reconstructing

330 the time variability of PC1 shows that each metal concentration increased from the 1890s to
331 1950s, decreased during the 1960s and increased again from the 1970s to 1990s (Figure 6b).
332 PC2 shows that the concentration increased in the 1910s, plateaued from the 1920s to 1980s
333 and then decreased sharply in the 1990s (Figure 6b). This reconstruction of PCs closely matches
334 the measured changes of each metal in Figure 5.

335 By plotting first PC against the second PC, the metals can be divided into three different groups
336 (see Figure 6a): The first group of elements are positively correlated to PC1 at similar loadings
337 and weakly correlated to PC2. This group includes Pb, Ba, Cd, Ag, As and Co. The second group
338 positively correlates to PC1 but negatively correlates to PC2. This group includes Zn, Ni and Cr.
339 The third group positively correlates to PC1 and PC2. This group includes U and Tl.

340 The increase of Cu was the largest among all the metals (from less than 1 mg/kg to more than
341 300 mg/kg). Additionally, almost all the increase happened between the 1980s and 1990s. For
342 all these reasons, Cu was treated as a fourth group and is discussed separately.

343

344

345 **Discussion**

346 **Delivery of Pb to MacRitchie Reservoir sediments**

347 The Pb recorded in the sediment could be deposited through three pathways:

- 348 • direct dumping of Pb into the reservoir (e.g. Kersten et al. 1997 showed this in coastal
349 waters, but a similar process could happen in reservoirs);
- 350 • catchment input via river inflow or overland flow (e.g. Kober et al. 1999); or,
- 351 • atmospheric deposition via rainfall or dust deposition (e.g. Komárek et al. 2008).

352 It is improbable that Pb was directly discharged into the reservoir since the reservoir has
353 maintained a source of freshwater to the local community (Devi 2002) and it has been carefully
354 protected. Catchment input was not likely a major source either as it remained nearly pristine
355 (Public Utilities Board 2010) with no industries within the catchment. It is possible that the
356 atmospheric deposited Pb in the catchment could be incorporated in soil particles and

357 subsequently mobilized into sediment by weathering (Eades et al. 2002, Kober et al. 1999). In
358 this case the weathered soil particles should contain both geogenic Pb and atmospherically-
359 deposited Pb. However, the catchment input does not introduce additional sources (other than
360 atmospheric deposits) into the system. By excluding the other possibilities, atmospheric
361 deposition was likely the primary cause of Pb variability to the MacRitchie Reservoir sediments.

362 Atmospheric delivery time should not result in an observable lag between Pb emission and
363 subsequent deposition into sediment as the residence time of Pb in the lower troposphere is ~7
364 days (Poet et al. 1972). The residence time of Pb in MacRitchie Reservoir could potentially result
365 in some lag, which has not yet been investigated. However it is reasonable to expect that the
366 residence time to be less than a few years because a shallow reservoir with a high
367 sedimentation rate should scavenge Pb faster than an oligotrophic surface ocean (the average
368 residence time of Pb in surface oceans is ~2 yrs, Bacon et al., 1976, Nozaki et al., 1976). As a
369 result, the delivery time of Pb within the atmosphere and reservoir should be within a few years.
370 Compared to our sampling resolution (~10 yrs), this delivery time is small and the variation in
371 the delivery time to the core site cannot be resolved.

372

373

374 **The variability of Pb content and isotopic composition in the 20th century**

375 The lowest section of the core included three soil samples and one sediment sample deposited
376 prior to the 1900s. The four samples had invariant Pb concentrations and isotopic compositions
377 (1.9 ± 0.6 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.215 ± 0.001 , Figure 4). The [Pb] in the samples were the
378 lowest across the core, and are also in the lower range of the [Pb] found in published
379 pristine/unpolluted soils and sediments from Europe, North America and China (Table 1). The
380 $^{206}\text{Pb}/^{207}\text{Pb}$ in these samples is in good agreement with reported values in the Asian region,
381 including K-feldspar from Asian rivers (Bodet and Schärer 2001) and in the surface sediments in
382 the deep basin of the South China Sea (1.18 to 1.22; Zhu et al., 2010). Additionally the
383 $^{206}\text{Pb}/^{207}\text{Pb}$ in the sediment samples agree with the isotopic ratio of the upper continental crust
384 from across the globe (~1.2; Chow and Patterson, 1962; Hamelin et al., 1990). Thus, with [Pb]
385 and Pb isotope comparable to natural values, and with known limited development in Singapore

386 region before the 1900s (Kwa et al. 2009), it is reasonable to conclude that the bottom of the
387 core contains mainly natural, preindustrial Pb.

388 The [Pb] in the sediment increased 27 fold from the 1900s to the 1990s, which advocates for
389 anthropogenic sources. It is also noted that a local peak in Pb (53 mg/kg) content appeared in
390 the 1950s, decreased and remained ~43 mg/kg in the 1960s-1980s and then increased again to
391 55 mg/kg in the 1990s. Since lower consumption of leaded petrol was expected in the 1950s,
392 the high [Pb] in the core may not be solely caused by automobile emissions. Instead, it may be
393 attributed to a few local industrial sources described as “many small, unlicensed and backyard
394 type foundries and metal fabricating plants with poor ventilation or housekeeping”, “a number
395 of Pb recovery works which recover Pb from used batteries using a very crude form of furnace”,
396 “a big metal recovery work that recovers iron” and the coal-fired power station in the same
397 period (Figure 1b, Singapore Anti-pollution Unit, 1970-1972). These industries were asked to
398 install air pollution control facilities by June 1972 (Singapore Anti-Pollution Unit, 1970-1972) and
399 the coal power plant situated on the south of Singapore was decommissioned in early 1970s
400 (Ramlan 2014). The sediment core from MacRitchie Reservoir preserves a ~20% decline in [Pb]
401 and a significant decrease in the concentration of other metals (Ag, As, Cd and Zn) from the
402 1950s to the 1980s (Figures 5 and 6), which was likely due to the introduction/implementation
403 of the Clean Air Act in 1971 and the closure of the coal power plant.

404 The [Pb] in the sediment in the 1990s was 55 mg/kg, which was the highest throughout the core.
405 The high Pb content in the sediment likely reflects leaded petrol usage in the region. Leaded
406 petrol was the overwhelming source of Pb during the 1970s and 1980s in North America and
407 Western Europe (Flegal 1986; Nriagu 1989; Patterson and Settle 1987), while in Southeast Asia,
408 leaded petrol emissions peaked in the 1990s (see Figure 2). Besides leaded petrol usage in
409 Singapore, Pb emissions from Indonesia and Malaysia could be transported to Singapore during
410 the migration of the monsoon (Figure 1a). The leaded petrol emission from Singapore and
411 Malaysia started to decrease in the mid-1980s (Figure 2a), while the emission from Indonesia
412 continued to increase until 2006 (Hirota 2006; Lee et al. 2014, Figure 2a). The increasing Pb
413 emissions from the 1970s to 1990s are in agreement with the increasing Pb concentrations in
414 the MacRitchie Reservoir sediments during this period.

415 To better understand the variation of [Pb] in the Singapore region, the temporal [Pb] variability
416 in MacRitchie Reservoir sediments were compared to a 50-year-long coral record from an
417 undeveloped island in the Singapore Straits (Jong Island, Figure 1b, Chen et al. 2015), a sediment
418 core from Nee Soon Swamp (Koh 2014, Figure 1d) and a sediment core from Lower Peirce
419 Reservoir (Ee 2000, Figure 1d). Comparing the MacRitchie Reservoir Pb record to the Jong Island
420 coral Pb record is difficult due to the low resolution of the sedimentary record (3 sediment data
421 points versus 46 coral data points), however, both records show an increasing Pb concentration
422 from the 1960s to 1990s (Figure 4). It was noted that the coral Pb/Ca started to decrease after
423 2003, in parallel to the general phasing out the leaded petrol in Southeast Asia (Chen et al.
424 2015). Such a drop in Pb content was not seen in the sediment due to the lower temporal
425 resolution of the sediment core. Comparing the MacRitchie Reservoir sediments to the other
426 sedimentary records, all show an increase in [Pb] towards the top of the respective cores. The
427 Nee Soon Swamp core preserved an increase in [Pb] from 40 cm upwards (Koh 2014), and the
428 Lower Peirce Reservoir sediments (Figure 1) showed an increase in [Pb] in the top 10 cm (Ee
429 2000). The comparison of MacRitchie Reservoir sediments to the Nee Soon Swamp and Lower
430 Peirce Reservoir sediments is also difficult as the ^{210}Pb -dating for the Nee Soon Swamp and
431 Lower Peirce Reservoir sediments are not available. However, the general agreement between
432 the sediment core sites supports the inference that the increase of [Pb] in the sediments was in
433 parallel to the regional increase of atmospheric Pb sources.

434

435

436 **Sources of Pb in the sediment implied by Pb isotopes**

437 There are four potential sources of Pb into the sediment: leaded petrol, industrial emissions,
438 incineration and coal burning. For leaded petrol, the $^{206}\text{Pb}/^{207}\text{Pb}$ from aerosols across Southeast
439 Asian cities is 1.141 ± 0.001 for Kuala Lumpur, 1.127 ± 0.001 for Bangkok, 1.156 ± 0.001 for Ho
440 Chi Minh City and 1.131 ± 0.001 for Jakarta in the 1990s, when leaded petrol was still in use
441 (Bollhöfer and Rosman 2000). Although Singapore was not included in Bollhöfer and Rosman's
442 study, the Pb isotopes in the MacRitchie Reservoir sediment from the 1970s to 1990s (~ 1.137 ,
443 Figures 4 and 7) fall well within the range of other measured Southeast Asian city aerosol ratios
444 during the peak in leaded petrol emissions. The agreement in Pb isotope data between the

445 sediments and regional aerosols supports the hypothesis that atmospheric deposition from
446 leaded petrol was the dominant source of Pb to the sediments in MacRitchie Reservoir.

447 Industrial sources might also contribute large amounts of Pb to the environment (e.g. Flegal et al.
448 2013). Industrial Pb emissions from mining, smelting, waste incineration and coal combustion
449 were found to be significant in many cities (e.g. Ragaini et al. 1977, Shi et al. 2008, Jackson et al.
450 2004), especially after the phasing out of leaded petrol (Díaz-Somoano et al. 2009). In the
451 Singaporean context, recent aerosol measurements show that $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore aerosol
452 was ~ 1.145 (Lee et al. 2014). Since these aerosols were measured in 2012 and 2013, 10 years
453 after Singapore concluded phasing out of leaded petrol, the Pb isotopes in Singapore aerosols
454 should be interpreted as of predominantly industrial origin. Unfortunately the $^{206}\text{Pb}/^{207}\text{Pb}$ in
455 Singapore aerosol in 2013 was indistinguishable from the aerosols measured in other major
456 Southeast Asian cities in the 1990s, when leaded petrol was still in use. Thus, it is still difficult to
457 differentiate the Pb from industrial sources from leaded petrol using Pb isotopic measurements.
458 More precise Pb isotope measurements of leaded petrol could potentially provide a more
459 quantitative solution in differentiating these sources.

460 Incineration might also contribute Pb to the sediment (e.g: Nriagu 1979). The fly ash collected
461 from all four incineration plants from Singapore showed $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.148 ± 0.005 (Chen et
462 al.2015), slightly higher than isotope ratios in the top of the sediment core (1.137), but
463 comparable to Singapore aerosols (~ 1.145 , Lee et al. 2014). It was difficult to differentiate the
464 relative contribution of Pb from petrol and incineration as they have very similar isotopic ratios
465 (Chen et al., 2014). However, the isotopic agreement between incineration fly ash and the
466 sediment suggested that incineration might be a major source of Pb to the sediment from the
467 1970s to the 1990s, although the relative contributions of these two sources could not be
468 determined.

469 Coal combustion might also be a possible Pb source to the sediments (Díaz-Somoano et al. 2009).
470 Coal-generated Pb emitted from Malaysia and Indonesia has increased since the 1970s (Figure
471 2b), in conjunction with the increasing Pb concentration in the MacRitchie Reservoir sediments.
472 However, the Pb isotope ratios from Australian and Indonesian coal (the type of coal most
473 commonly used in the region, COMTRADE 2012; Hargraves 1993; Lucarelli 2000) has $^{206}\text{Pb}/^{207}\text{Pb}$
474 ~ 1.184 and $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.477$ for Indonesian coals (Díaz-Somoano et al. 2009), and $^{206}\text{Pb}/^{207}\text{Pb}$

475 ~ 1.195 and $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.473$ for Australian coals (Díaz-Somoano et al. 2009), which is much
 476 higher than the ratio in the sediments deposited between the 1970s and 1990s (~ 1.140 for
 477 $^{206}\text{Pb}/^{207}\text{Pb}$, Figure 4). Therefore, coal combustion is not a dominant source of Pb to the
 478 MacRitchie Reservoir sediments. However, coal has been used for electricity generation in
 479 Singapore from 1927 to the 1970s (Ramlan, 2014; Wan and Lau, 2009). During the earlier period
 480 when the petrol consumption was limited, coal combustion may have been a significant
 481 contributor to the Pb in the sediments. The sediments deposited during the 1910s to 1940s had
 482 a $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.185 and $^{208}\text{Pb}/^{207}\text{Pb}$ of ~ 2.466 , similar to Indonesian and Australian coals
 483 (Figure 4 and Figure 7), implying the burning of coal as a possible source of Pb in the 1910 to
 484 1940s period.

485 It should also be noted that a mix of natural ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.215$, $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.507$) and
 486 atmospheric Pb ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.138$, $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.414$) could result in an isotopic composition
 487 comparable to the 1910s to 1940s sediments (Figure 4). Although the hypothesis of mixing does
 488 not exclude the possible contribution from Indonesian and Australian coals that have isotope
 489 ratios close to the Pb in MacRitchie Reservoir sediment between the 1910s and 1940s, the Pb
 490 isotopes in the MacRitchie Reservoir sediment showed high linearity on the triple isotope plot
 491 (Figure 7), which would likely be a result of mixing between the natural Pb and atmospheric Pb
 492 sources.

493

494

495 **An estimation of recent atmospheric Pb flux into the Singapore region**

496 Since the atmospheric deposition is the main cause of Pb in recent MacRitchie Reservoir
 497 sediment, the atmospheric Pb deposition could be calculated using the actual aerosol and
 498 rainwater data using the following equation.

$$499 \text{ Pb Flux} = (C_{\text{aerosol}} \times v)_{\text{wet}} + (C_{\text{rain}} \times d)_{\text{dry}} \quad (3),$$

500 The *Pb flux* is calculated as a sum of wet deposition and dry deposition in equation 3, where
 501 C_{aerosol} is the atmospheric concentration of Pb (10 ng/m^3 , measured from 2009 to 2012, pers.
 502 comm. Prof. Webster); v is the settling velocity of particulate matter in the atmosphere (1 cm/s ;

503 Grönholm et al. 2007); C_{rain} is the rainwater Pb concentration (4.7 $\mu\text{g/L}$, measured from 2009 to
 504 2012, pers. comm. Prof. Webster), and d is the annual rainfall in Singapore (2400 mm/yr; Public
 505 Utilities Board 2011). With the aerosol and rainwater data, the calculated Pb flux is 1.4×10^{-2}
 506 $\text{g/m}^2\text{-yr}$.

507 Alternatively, the atmospheric Pb flux into Singapore region could be estimated using the
 508 equation modified from Kober et al. (1999):

$$509 \quad Pb \text{ Flux} = S \times \rho \times (C_{measured} - C_{baseline}) \quad (4),$$

510 where S is the sedimentation rate, ρ is the dry bulk density of the sediment ($1.05 \times 10^{-3} \text{ g/mm}^3$),
 511 and $C_{measured}$ and $C_{baseline}$ are the concentrations of Pb in the sediment from measured sample and
 512 baseline value (assumed 1.9 mg/kg, as the average of the four points from the bottom of the
 513 core), respectively. The estimated Pb flux using the concentration from the top of the core (55
 514 mg/kg) is $1.6 \times 10^{-2} \text{ g/m}^2\text{-yr}$. The annual atmospheric Pb flux estimated from MacRitchie
 515 Reservoir sediment [Pb] agrees well with the calculations using current atmospheric
 516 measurements.

517

518

519 **Variation of other metals compared to Pb**

520 The PCA analysis of the metals grouped the metals by their covariability (Figure 6). The first PC
 521 signifies an increase towards 1990s with a local peak in ~1950s. This feature is shown in many
 522 elements and contributes more than 75% of the variance. The second PC signifies the mid-
 523 century peak and decrease since 1970s. This feature is less common as it contributes ~18% of
 524 the variance. Based on the two PCs, the elements were divided into three groups with each
 525 group of metals having very similar loadings on the PCA biplot (see section 3.3 and Figure 6a).

526 The first group of metals contains Pb, Ba, Cd, Ag, As and Co. The variations of these metals can
 527 be summarized as increasing concentration over the 20th century with a decline in the 1970s.
 528 One possible explanation for the increasing trend over the 20th century was that the production
 529 of these metals has all increased (e.g. Foster and Charlesworth 1996) and their use by Singapore
 530 industry has also increased significantly. Although emissions of different metals may be the by-

531 product of different industries, on the large scale all of these metals follow an increasing trend
532 (Foster and Charlesworth 1996; Salomons and Förstner 1984). Another possible explanation for
533 the similarity in the PC1 pattern is that other metals were co-released during Pb emission, for
534 example, Pb, Cd and As can be released during coal combustion (Salomons and Förstner 1984),
535 and Ba can be released as a result of fossil fuel combustion and waste incineration (ATSDR 2007).
536 Similar trace metal trends would be observed if the metals were released during similar
537 processes. The decrease in concentration of the metals in the 1970s could be explained as a
538 result of the introduction of the Clean Air Act (Singapore Anti-Pollution Unit, 1970-1972). The
539 decrease in Pb content in the 1970s accompanied by little change in the Pb isotopic composition
540 could be the result of improved emission control.

541 The second group recognized in the PCA includes Zn, Ni and Cr. These elements recorded little
542 decrease in 1970s followed by a sharp increase from the 1980s to 1990s. The decrease in the
543 concentration of Group 1 elements in the 1970s was not clearly observed in this group, because
544 Zn, Ni or Cr were not included in the emission control guidelines (Singapore Anti-Pollution Unit
545 1970-1972). This group signifies less harmful metals as Zn and Ni are essential nutrients to
546 human health (ATSDR 2012, EPA 2005, Cempel and Nickel 2006), but could increase to toxic
547 levels due to anthropogenic activity (e.g.: Zayed and Terry 2003, Cempel and Nickel 2006). Zn can
548 be released by various processes, but most Zn is released by industrial activities (including metal
549 production), wood combustion and waste incineration (Nriagu 1979). Ni is mainly released by oil
550 combustion and industrial activities (Nriagu 1979). Cr is released by a variety of industrial
551 processes (Zayed and Terry 2003), but also from natural sources such as wind-borne soil
552 particles (Nriagu 1989). Although various sources could contribute Zn, Ni and Cr to MacRitchie
553 Reservoir sediments, the sharp increase in these elements from the 1980s to 1990s suggests
554 that they may be linked to urbanization and industrialization of the Singapore region.

555 The third group discerned by the PCA analysis included Tl and U, which recorded an increase in
556 concentration from the 1890s to 1950s and a decrease from the 1950s to 1990s. The decreasing
557 concentration from the 1950s to 1990s differs from the behavior of other metals. The U
558 concentrations in MacRitchie Reservoir sediments (0.4 to 2.4 mg/kg) are lower than local
559 granitic rocks (3.0 mg/kg), and within the range of sedimentary rocks (0.45-2.2 mg/kg, Turekian
560 and Wedpohl 1961). It is more reasonable to compare U concentrations to sedimentary rocks
561 due to the soluble characteristics of uranium. It is unclear whether the variation of Tl was

562 caused by anthropogenic activities since the concentration of Tl varied from 0.01 to 0.23 mg/kg
563 and is within the range of the Earth's mean crustal concentration of 0.1 to 1.7 mg/kg (Peter and
564 Viraraghavan 2005). Therefore, based on this evidence, U and Tl cannot be attributed clearly to
565 anthropogenic activities.

566 Copper had the largest magnitude and most rapid increase of all of the metals measured from
567 MacRitchie Reservoir sediments (Figure 5). Such increases could only be caused by
568 anthropogenic activities. Copper sulfate (CuSO_4) had been used as an algaecide in reservoirs
569 around the globe for decades (e.g. Hawkins et al. 1987). Such application has remained the most
570 common method for controlling cyanobacteria because it was effective, economical and relative
571 safe to human health (Chorus and Bartram 1999). CuSO_4 treatment could be a possible source
572 explaining the increase in Cu in the MacRitchie Reservoir sediments as the same order of
573 increase has been observed in other reservoirs across the worlds that have employed CuSO_4
574 treatment (e.g. AWWA 1995, Haughey et al. 2000). Singapore is no longer using CuSO_4
575 treatment in the reservoirs (personal communication with PUB), and the Cu concentration in
576 Singapore drinking water is firmly within the safe level recommended by the World Health
577 Organization (Public Utilities Board 2014).

578

579

580 **Conclusions**

581 The temporal variation of Pb and Pb isotopes was reconstructed from a sediment freeze core
582 retrieved from MacRitchie Reservoir, located in the Central Catchment Nature Reserve of
583 Singapore. The core spans the period from 1895 to 2012 as measured by ^{210}Pb dating. The
584 variation of Pb was compared with the historical Pb emissions from neighboring countries, the
585 isotopic composition of Pb from potential sources, and the variation of eleven other metals (Ag,
586 As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) in the sedimentary record., From the reconstruction, the
587 following conclusions can be drawn:

- 588 1. The Pb content in the sediment increases from 1.9 mg/kg in the 1910s to 53 mg/kg
589 in the 1950s. From the 1950s to the 1960s, the Pb in the sediment decreased by 20%
590 (41 mg/kg) and stayed ~42 mg/kg until the 1980s. From the 1980s to 1990s, the Pb

591 content increased to 55 mg/kg. The corresponding decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ from
592 1.199 in the 1910s to 1.137 in 1990s, suggested an atmospheric input of Pb to the
593 reservoir. The recent estimated atmospheric Pb flux in Singapore region is $\sim 1.6 \times 10^{-2}$
594 $\text{g}/\text{m}^2\text{-yr}$.

595 2. The dissolved [Pb] in MacRitchie Reservoir water was $1.1 \pm 0.07 \times 10^{-2}$ $\mu\text{g}/\text{L}$, far lower
596 than the allowable drinking water standards. The highest Pb content in MacRitchie
597 Reservoir sediments were within the range of threshold values of global sediment
598 guidelines.

599 3. The $^{206}\text{Pb}/^{207}\text{Pb}$ in recent sediments (1970s to 1990s) was ~ 1.14 , similar to the
600 aerosol ratios previously reported in several Southeast Asian countries/cities. The
601 possible sources included leaded petrol, industrial sources and incineration. The Pb
602 recorded in the sediment between the 1910s and 1940s had a $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.18
603 consistent with a combination of natural and atmospheric Pb sources and/or from
604 the combustion of coal.

605 4. The Ag, As Ba, Cd, Co, Cr, Ni and Zn content in the sediment have all increased
606 significantly from the 1910s to 1990s. The increase was parallel to the urbanization
607 and industrialization of Singapore. The decrease in concentration of Ag, As Ba, Cd,
608 Co and Pb in the 1970s and 1980s may be a result of stricter emission controls since
609 1971. The Tl and U content in the sediment shows a decrease from the 1950s to
610 1990s, but may not be caused by anthropogenic activities. The Cu content in the
611 sediment shows a large increase in 1980s, which probably caused by CuSO_4
612 treatment in the reservoir.

613 This study signifies the importance of identifying Pb and other metal concentrations and Pb
614 isotopes from terrestrial archives to reconstruct the history of Pb and trace metals, and
615 provides the history of metals in the data-sparse South East Asian region.

616

617

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629

630 **Figure captions:**

631 Figure 1: Map of MacRitchie Reservoir and its relative location in the central catchment natural
632 reserve of Singapore. The inset map shows: a. Singapore's relative location within Southeast
633 Asia with the monsoonal wind directions illustrated (see section 2.1); b. A map of Singapore and
634 its neighboring countries with Central Catchment Nature Reserve (CCNR) highlight in a square
635 box, the two dots are Jong island with coral record and St James Power Station (STPS, the
636 former coal power station closed in early 1970s) respectively; c. A close view of CCNR with the
637 name of reservoirs inside the nature reserve are shown in italic letters. Within the MacRitchie
638 Reservoir, the sampling site (black star); major inlet (black arrow); and the dam (thick black bar)
639 are also illustrated. The satellite image of CCNR is included in the bottom right corner with the
640 nature reserve shown in dark areas and the residential and/or commercial area shown in light
641 areas; d. An illustration of the reservoir's sedimentology layout, including the major inlet, the
642 delta area near the major inlet, and the muddy-lake area near the dam. The possible sources of
643 Pb to the reservoir are also illustrated in the figure.

644 Figure 2: Estimated historical Pb emissions from gasoline usage and coal combustion including
645 Singapore (white open diamonds), Malaysia (grey filled triangles), Thailand (black filled squares,
646 Lee et al. 2014) and Indonesia (white open circles, Lee et al. 2014). Dotted lines are for the years
647 that data are unavailable. (a) from vehicle gasoline combustion. The decline of Indonesian

648 emission in 2006 illustrates the announced total phase out of leaded gasoline. (b) from power
649 generation-based coal combustion. The decline of Singapore emission in 1971 illustrates the
650 closure of Singapore's only coal power plant.

651 Figure 3: The illustration of: (a)The picture of the sediment core. The top, bottom of the core
652 and the change in color during reservoir's construction were marked. (b) Unsupported ^{210}Pb
653 (black diamonds) in Bq/kg of dry sample plotted at the mid-depth of each subsample. The
654 dotted curve is the 0.29cm/yr fit using a constant sedimentation rate model (see text). The
655 vertical axis on the left shows the depth of the sediment and the axis on the right shows the
656 converted calendar years from the ^{210}Pb activities. (c) the sediment composition change
657 throughout the core, includes clay (light grey); silt (dark grey) and sand (white).

658 Figure 4: (a) The bulk Pb concentration in the sediments (grey filled diamonds) compare to the
659 Pb/Ca in the Jong island coral (open diamonds, Lee et al. 2014). The GPS location for the coral is
660 $1^{\circ}12'54.25''\text{N}$, $103^{\circ}47'11.17''\text{E}$. (b) the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (grey filled circles) and $^{208}\text{Pb}/^{207}\text{Pb}$ (open
661 triangles) in the sediment. Note that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for natural Pb is ~ 1.20 and for local
662 aerosol is ~ 1.14 . The error bars of Pb isotopes are within the size of each point.

663 Figure 5: The concentrations in mg/kg of all the metals (Pb, As, Ag, Ba, Cd, Co, Cr, Ni, Zn, Tl, U, Ba
664 and Cu) measured in the sediment are plotted.

665 Figure 6: The plots show the results from principal component analysis. The first and second
666 principal components explain $\sim 95\%$ of the total variations in the core. (a) The PCA bi-plot
667 showing PC1 versus PC2. The directions and expressing powers of each metal in the PC space are
668 expressed in vectors. (b) The first 2 eigenvectors (PCs) from the principal component analysis.
669 Horizontal axis is a dimensionless unit to express the variation of the principal component; and
670 the vertical axis is the calendar year.

671 Figure 7: The plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios against $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in the MacRitchie sediments
672 (white open triangles) together with a panel of possible end-members. The Singapore aerosols
673 (Lee et al. 2014) and incineration fly ashes are shown as grey filled circles; the Indonesian coals
674 (Diaz-Somoano et al. 2009) are shown as grey filled squares; the Australian coals (Diaz-Somoano
675 et al. 2009) are shown as grey filled triangles; the South China Sea (SCS) sediments (Zhu et al.
676 2010) are shown as small grey filled crosses; the south Chinese Pb ore are shown as grey open

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677 crosses; the Singapore corals are shown as dark grey dots; and the Chinese aerosols, Thai
678 aerosols, Indonesian aerosols are shown as black open squares; grey open diamonds; black open
679 circles correspondingly. The dashed line illustrates the binary mixing scenario between natural
680 and atmospheric Pb sources.

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