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

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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   $^{206}Pb/^{207}Pb$ of ~1.20. The Pb concentration increased to 55 mg/kg in the 1990s, and

24   correspondingly the $^{206}Pb/^{207}Pb$ decreased to less than 1.14. The $^{206}Pb/^{207}Pb$ in the core top

25   sediment is concordant with the $^{206}Pb/^{207}Pb$ 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 ~1.6 x $10^{-2}$ g/m$^2$-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-20$^{th}$ century.

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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 ($^{206}$Pb/$^{208}$Pb and $^{207}$Pb/$^{208}$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.

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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 km$^2$ 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 6$^{th}$ 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.

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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    $E_{coal} = PP \times P_{percap} \times C \times [Pb]_{coal} \times EF$    (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; $[Pb]_{coal}$ 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 at al. 2014) and 15 mg/kg as the $[Pb]_{coal}$,

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.

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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).

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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 $^{204}$Pb/$^{208}$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 $^{206}Pb/^{207}Pb$ of 160ppm (n=42), $^{208}Pb/^{207}Pb$ 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 $3.7x10^{-4}\mu g/L$ and was ~3% of our sample concentration.

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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 nd 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 $1.1 \pm 0.07 \times 10^{-2}$ µg/L, which was two orders of magnitude

304    lower than the legal safe level of Pb in the drinking water (10 µg/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 $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ are shown in Figure 4b. In the paleo-soil

314    samples prior to 1895, the three $^{206}Pb/^{207}Pb$ data points were similar and >1.215. Since 1895,

315    $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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]Pb/[207]Pb from aerosols across Southeast

439    Asian cities is1.141 ± 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$

474    ~ 1.184 and $^{208}Pb/^{207}Pb$ ~ 2.477 for Indonesian coals (Díaz-Somoano et al. 2009), and $^{206}Pb/^{207}Pb$

475　~ 1.195 and $^{208}$Pb/$^{207}$Pb ~ 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　$^{206}$Pb/$^{207}$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 $^{206}$Pb/$^{207}$Pb of ~1.185 and $^{208}$Pb/$^{207}$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 ($^{206}$Pb/$^{207}$Pb ~ 1.215, $^{208}$Pb/$^{207}$Pb ~2.507) and

486　atmospheric Pb ($^{206}$Pb/$^{207}$Pb ~1.138, $^{208}$Pb/$^{207}$Pb ~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　$Pb\ Flux = (C_{aerosol} \times v)_{wet} + (C_{rain} \times d\ )_{dry}$　　　(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 µg/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 x $10^{-2}$

506     $g/m^2$-yr.

507     Alternatively, the atmospheric Pb flux into Singapore region could be estimated using the

508     equation modified from Kober et al. (1999):

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

510     where $S$ is the sedimentation rate, $\rho$ is the dry bulk density of the sediment (1.05 x $10^{-3}$ $g/mm^3$),

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 x $10^{-2}$ $g/m^2$-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 Nikel 2006), but could increase to toxic

547    levels due to anthropogenic activity (e.g.: Zayed and Terry 2003, Cempel and Nikel 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 $^{206}Pb/^{207}Pb$ 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 ~1.6 x 10$^{-}$

594      $^{2}$ g/m$^{2}$-yr.

595    2.    The dissolved [Pb] in MacRitchie Reservoir water was $1.1\pm0.07 \times 10^{-2}$ µg/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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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

618    **Acknowledgements**

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°12'54.25"N, 103°47'11.17"E. (b) the $^{206}$Pb/$^{207}$Pb ratio (grey filled circles) and $^{208}$Pb/$^{207}$Pb (open

661  triangles) in the sediment. Note that the $^{206}$Pb/$^{207}$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 ~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 $^{206}$Pb/$^{207}$Pb ratios against $^{208}$Pb/$^{207}$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

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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Figure 3

(a)

Pb in sediment, mg/kg

(b)
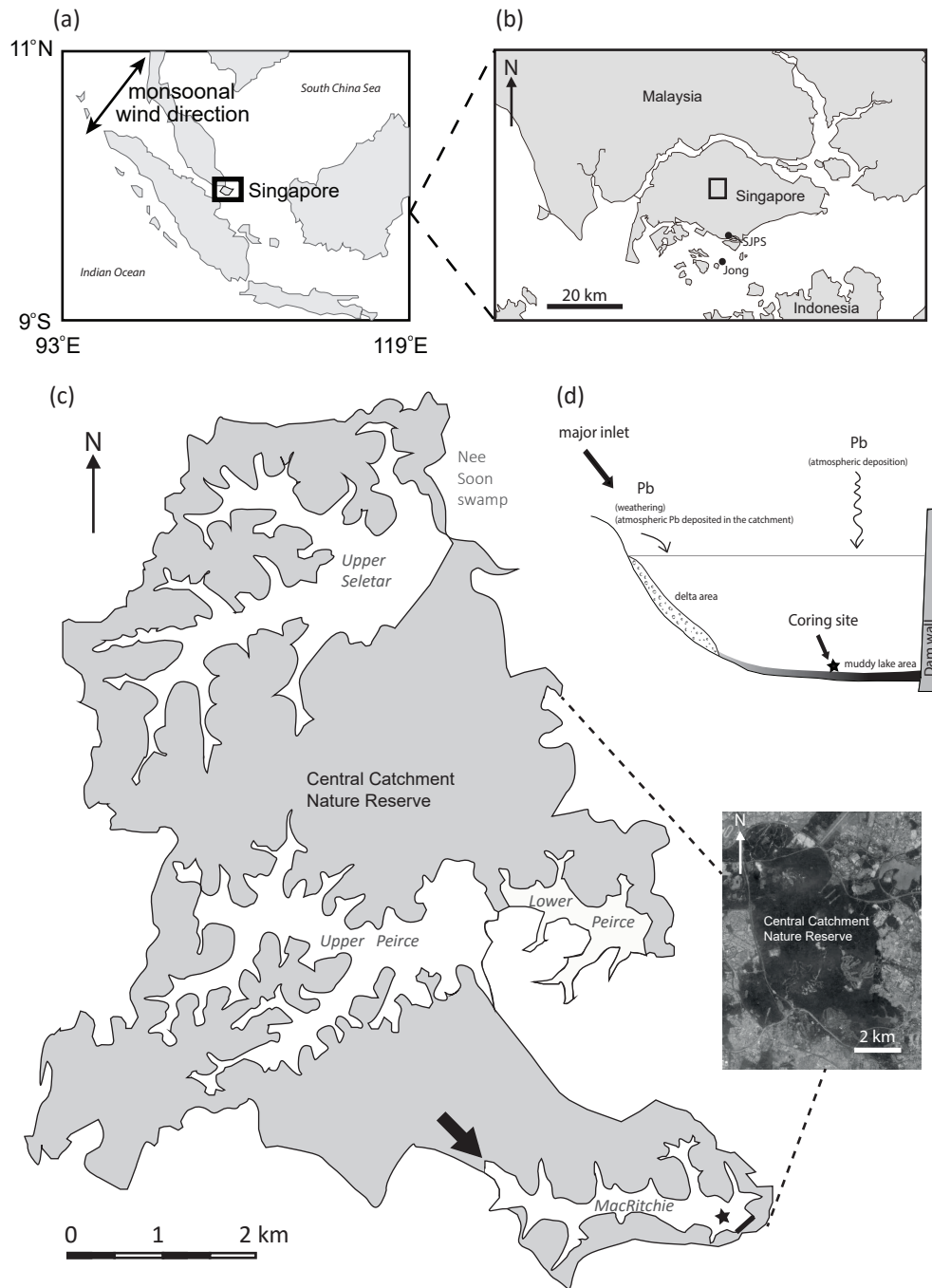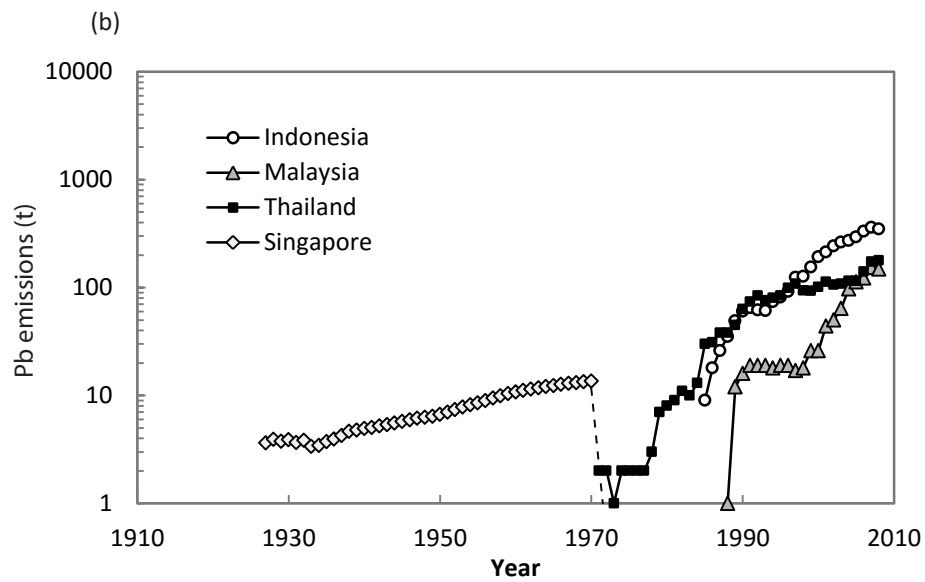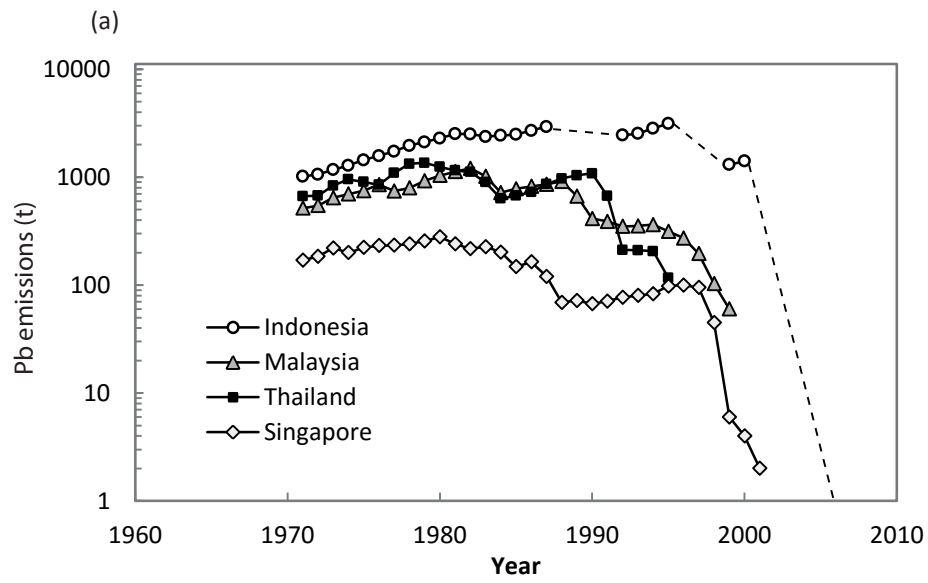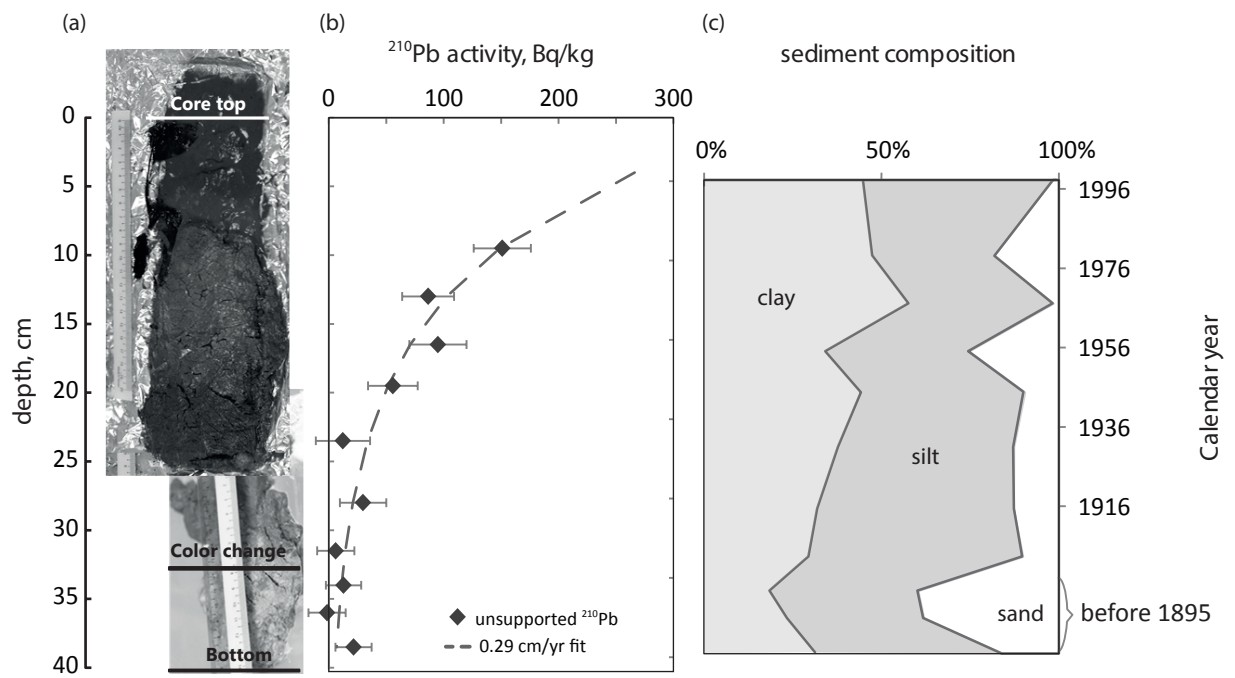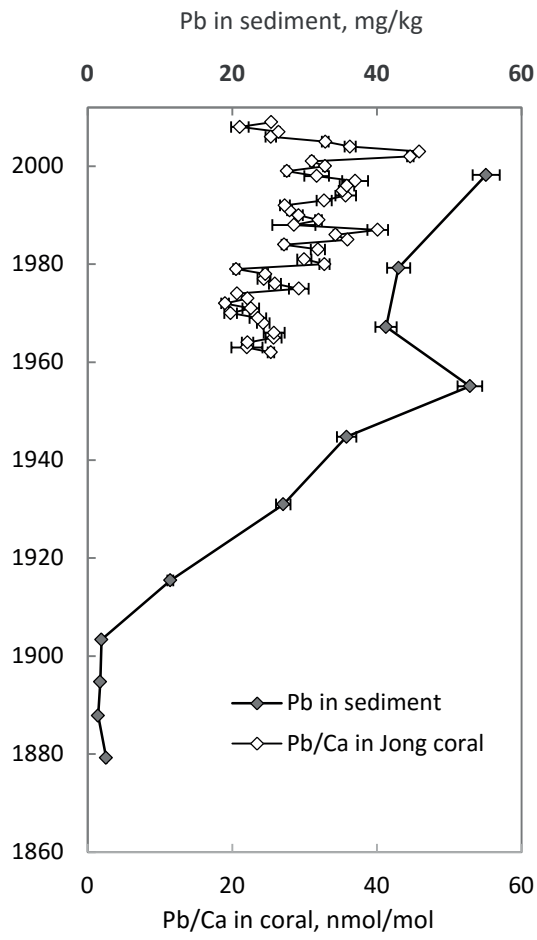
$^{206}Pb/^{207}Pb$

**Figure 5**
**Click here to download Figure: Figure 5 ME.pdf**

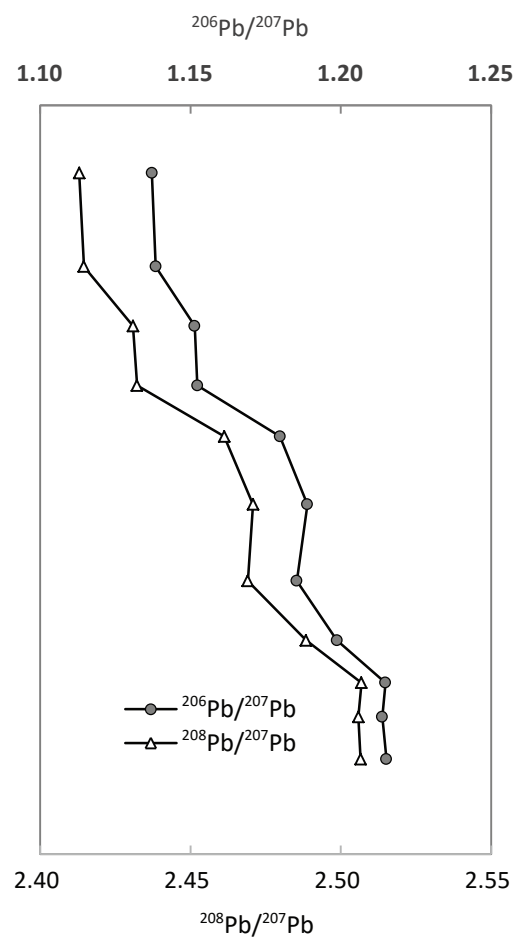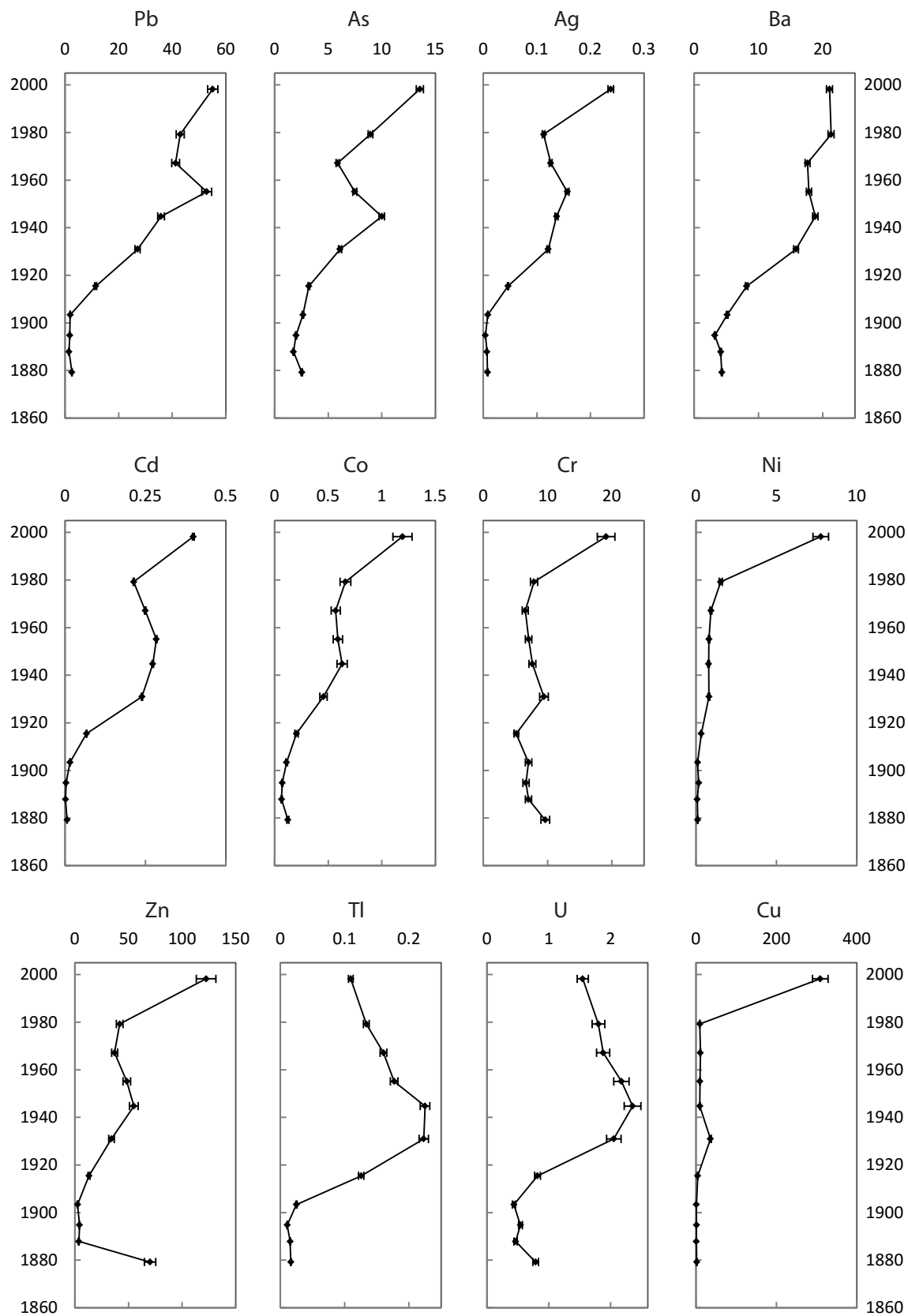**Figure 6**
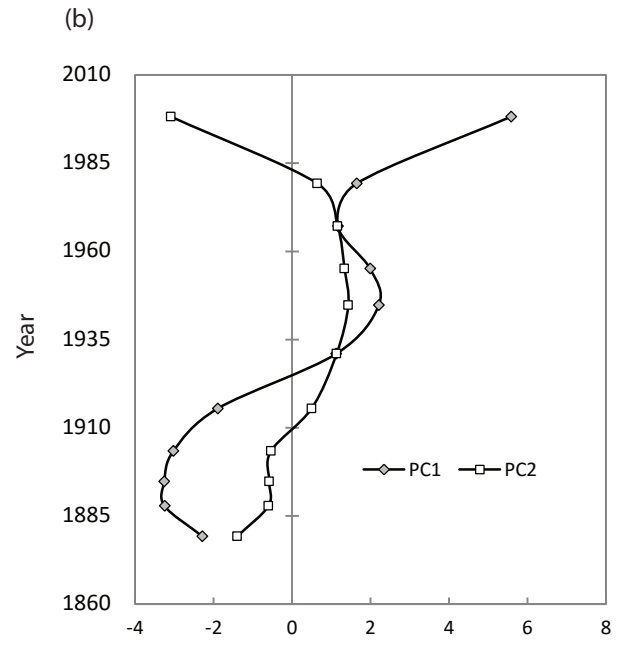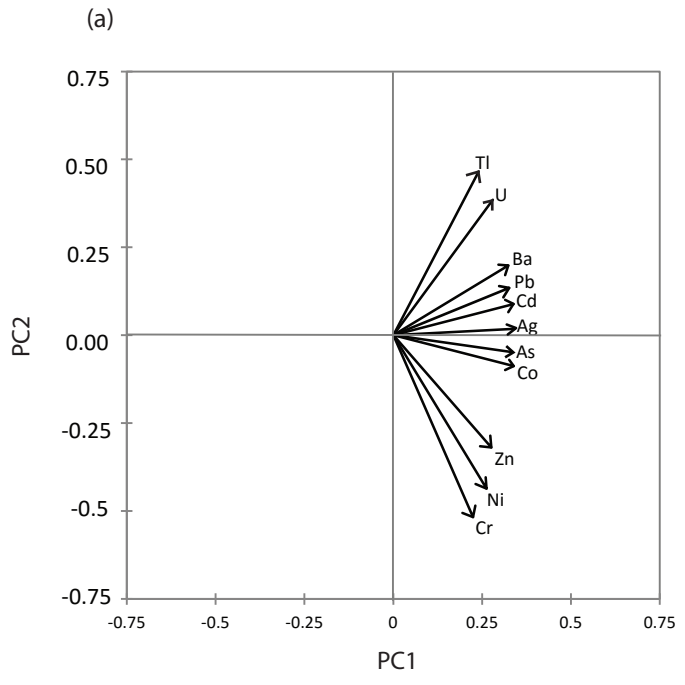**Click here to download Figure: figure 6 PCA.pdf**

**Figure 7**
**Click here to download Figure: figure 7 triple iso bw.pdf**
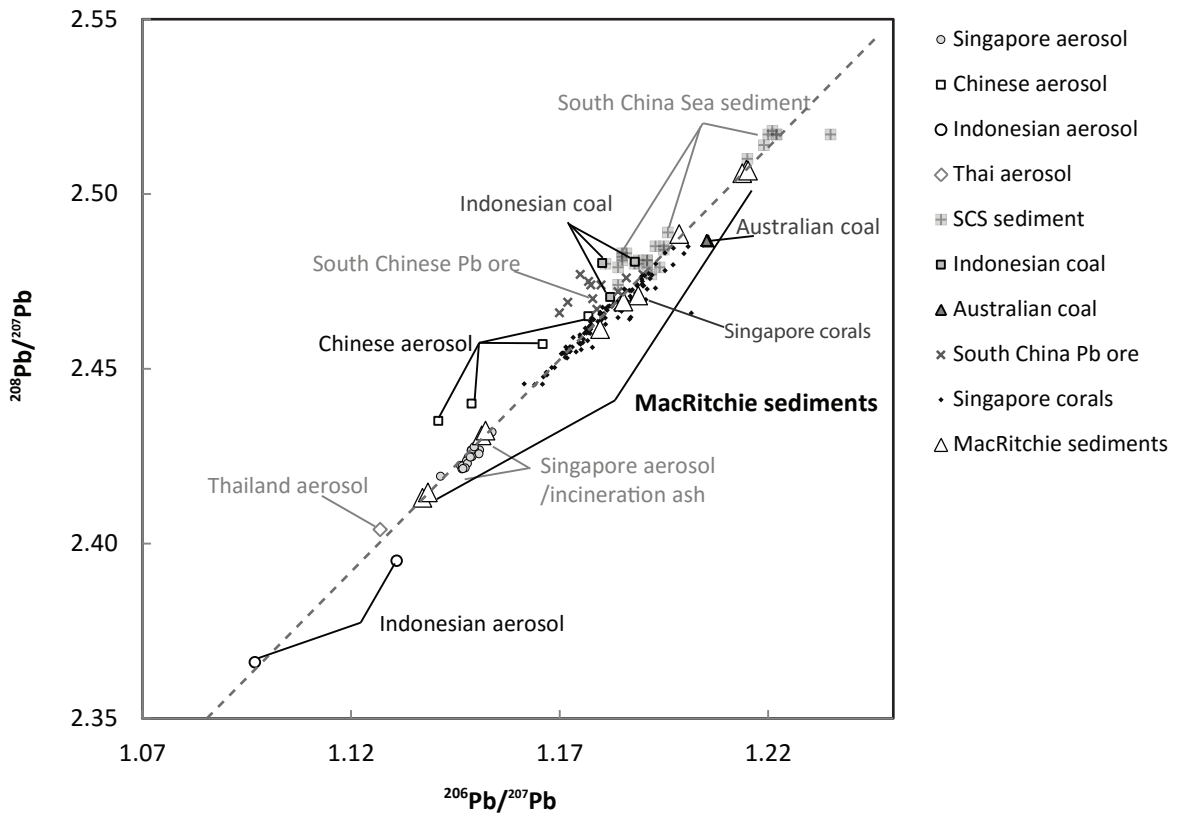
Figure 7

Table 1: Lead concentrations and isotope ratios in MacRitchie bottom core compare to natural soils and sediments

*Soil*

| Location | Methodology | [Pb] range (mg/kg) | 206/207 | 208/207 | 208/206 | Source |
|---|---|---|---|---|---|---|
| Macritchie reservoir (Singapore) | HNO3-HCl leach | 1.451-2.560 | 1.214-1.215 | 2.506-2.507 | 2.063-2.065 | this study |
| Rural south central Ontario (Canada) | HNO3 leach | ~6-7 | 1.31-1.32 | | | Watmough and Hutchinson (2004) |
| Pearl River Delta (China) | HNO3 + HCLO4 leach | 7.7-54.7 | 1.195 | 2.499 | 2.091 | Wong et al. (2002) |
| Jerusalem (Israel) | HNO3 + HCLO4 + HF leach | 17.0-19.0 | 1.206-1.219 | | 2.051-2.066 | Teutsch et al. (2001) |
| pristine forest soil (Sweden) | HNO3 + HCLO4 leach | <0.1 | | | | Bindler et al. (1999) |
| Swedish pre-industrialization forest soil (Sweden) | HNO3 + HCLO4 leach | 2.4-6.7 | 1.372-1.455 | | | Bindler et al. (1999) |
| Swiss unpolutted soil (Switzerland) | HNO3 leach | 5.4-17.5 | 1.209 | 2.472 | 2.044 | Hansmann and Koppel (2000) |

*Sediments*

| Location | Methodology | [Pb] range (mg/kg) | 206/207 | 208/207 | 208/206 | Source |
|---|---|---|---|---|---|---|
| Macritchie reservoir (Singapore) | HNO3-HCl leach | 1.911 | 1.199 | 2.488 | 1.019 | this study |
| Lake Constance (Central Europe) | HNO3-HCl leach | 20.5-21.7 | 1.197 | 2.472 | 2.065 | Kober et al. (1999) |
| Lake Erie and other lakes (Northeastern US) | HNO3-HCl leach | 11.3-13.3 | 1.252 | 2.492 | 1.990 | Graney et al. (1995) |
| Loch Lomond north (Scotland) | HNO3-HCl leach | 23-29 | 1.160 | | | Eades et al. (2002) |
| Loch Lomond south (Scotland) | HNO3-HCl leach | 11.0-19.0 | 1.174 | | | Eades et al. (2002) |
| Loch Ness (Scotland) | HNO3-HCl leach | 10.4-13.4 | 1.215 | | | Eades et al. (2002) |
| Swedish lakes (Sweden) | HNO3 + HCLO4 leach | ~2-17 | 1.28-2.01 | | | Renberg et al. (2002) |
| Lake Tantaré (Canada) | HNO3 + HCLO4 + HF leach | 4.14-9.12 | 1.161 | 2.444 | 2.105 | Gallon et al. (2006) |

| Lake Despériers and other lakes (Canada) | HNO3+HF leach | ~5-8 | 1.221 | | 2.118 | Gallon et al. (2005) |
|---|---|---|---|---|---|---|
| Hongfeng Lake (southwest China) | HNO3 leach | 29.04 | 1.233 | 2.478 | 2.009 | Zhao et al. (2011) |
| Liangzhi Lake (central China) | HNO3 + HCLO4 leach | 15.5 | 1.193 | 2.495 | 2.091 | Lee et al. (2008) |

Table 2: Eigenvalues and variance contribution in principal component analysis

| Principal compoment | eigenvalue | variance contribution |
|---|---|---|
| PC1 | 8.452 | 76.84% |
| PC2 | 1.961 | 17.83% |
| PC3 | 0.263 | 2.39% |
| PC4 | 0.164 | 1.49% |
| PC5 | 0.083 | 0.75% |
| PC6 | 0.043 | 0.39% |
| PC7 | 0.025 | 0.23% |
| PC8 | 0.006 | 0.05% |
| PC9 | 0.002 | 0.02% |
| PC10 | 0.000 | 0.00% |
| PC11 | 0.000 | 0.00% |

**Supplementary Material**