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

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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

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

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

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

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

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

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

Sampling and methodology

Site information and sampling

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

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

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

Regional on Pb emissions

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

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

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

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

Determination of particle size and chronology

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

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

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

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

Sample preparation and metal analysis

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

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

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

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

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

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

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

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

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

Principal component analysis on 11 metals in the sediments

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

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

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

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

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 samples prior to 1895, the three $^{206}\text{Pb}/^{207}\text{Pb}$ data points were similar and >1.215 . Since 1895, $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from >1.215 to ~ 1.140 . The decreasing trend was consistent throughout the core.

Concentration of other metals in the sediments

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

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

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

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

Discussion

Delivery of Pb to MacRitchie Reservoir sediments

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

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

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

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

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

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

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

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

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

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

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

Sources of Pb in the sediment implied by Pb isotopes

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

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

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

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

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

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

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 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 comparable to the 1910s to 1940s sediments (Figure 4). Although the hypothesis of mixing does not exclude the possible contribution from Indonesian and Australian coals that have isotope ratios close to the Pb in MacRitchie Reservoir sediment between the 1910s and 1940s, the Pb isotopes in the MacRitchie Reservoir sediment showed high linearity on the triple isotope plot (Figure 7), which would likely be a result of mixing between the natural Pb and atmospheric Pb sources.

An estimation of recent atmospheric Pb flux into the Singapore region

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

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

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

Grönholm et al. 2007); C_{rain} is the rainwater Pb concentration (4.7 µg/L, measured from 2009 to 2012, pers. comm. Prof. Webster), and d is the annual rainfall in Singapore (2400 mm/yr; Public Utilities Board 2011). With the aerosol and rainwater data, the calculated Pb flux is 1.4×10^{-2} g/m²-yr.

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

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

where S is the sedimentation rate, ρ is the dry bulk density of the sediment (1.05×10^{-3} g/mm³), and $C_{measured}$ and $C_{baseline}$ are the concentrations of Pb in the sediment from measured sample and baseline value (assumed 1.9 mg/kg, as the average of the four points from the bottom of the core), respectively. The estimated Pb flux using the concentration from the top of the core (55 mg/kg) is 1.6×10^{-2} g/m²-yr. The annual atmospheric Pb flux estimated from MacRitchie Reservoir sediment [Pb] agrees well with the calculations using current atmospheric measurements.

Variation of other metals compared to Pb

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

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

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

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

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

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

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

Conclusions

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

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

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

2. The dissolved [Pb] in MacRitchie Reservoir water was $1.1 \pm 0.07 \times 10^{-2} \text{ } \mu\text{g/L}$, far lower than the allowable drinking water standards. The highest Pb content in MacRitchie Reservoir sediments were within the range of threshold values of global sediment guidelines.
3. The $^{206}\text{Pb}/^{207}\text{Pb}$ in recent sediments (1970s to 1990s) was ~ 1.14 , similar to the aerosol ratios previously reported in several Southeast Asian countries/cities. The possible sources included leaded petrol, industrial sources and incineration. The Pb recorded in the sediment between the 1910s and 1940s had a $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.18 consistent with a combination of natural and atmospheric Pb sources and/or from the combustion of coal.
4. The Ag, As Ba, Cd, Co, Cr, Ni and Zn content in the sediment have all increased significantly from the 1910s to 1990s. The increase was parallel to the urbanization and industrialization of Singapore. The decrease in concentration of Ag, As Ba, Cd, Co and Pb in the 1970s and 1980s may be a result of stricter emission controls since 1971. The Ti and U content in the sediment shows a decrease from the 1950s to 1990s, but may not be caused by anthropogenic activities. The Cu content in the sediment shows a large increase in 1980s, which probably caused by CuSO_4 treatment in the reservoir.

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

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Figure captions:

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

Figure 2: Estimated historical Pb emissions from gasoline usage and coal combustion including Singapore (white open diamonds), Malaysia (grey filled triangles), Thailand (black filled squares, Lee et al. 2014) and Indonesia (white open circles, Lee et al. 2014). Dotted lines are for the years 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

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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