Century scale variation of elemental Pb and Pb isotopes in the South China Sea region

Chen, Mengli

2015

Chen, M. (2015). Century scale variation of elemental Pb and Pb isotopes in the South China Sea region. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/65667>

<https://doi.org/10.32657/10356/65667>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Century scale variation of
elemental Pb and Pb isotopes in the
South China Sea region**

Chen Mengli

Asian School of the Environment

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2015

Acknowledgements

I like to take this opportunity to thank all the people that made this work possible. Firstly I wish to thank my MIT advisor Ed Boyle for constantly guiding me through 5-years' of PhD study, providing thoughtful suggestions whenever I could not figure out what's going on. I also wish to thank my NTU advisor Adam Switzer for questioning me and shaping my directions when I didn't know what to do. Also for endeavoring to arrange the endless laboratory and administration matters to get the work done. I'm also grateful for my thesis committee members Nathalie Goodkin for generously providing me the Vietnam coral, having lengthy discussions on interpreting the findings. I also owe a big thanks to the geochemistry team, for showing me how to fabricate essential devices for my lab work, and for always being open when I was puzzled.

A major part of my laboratory work was done at MIT where Rick Kayser gave me terrific laboratory and instrument support, which was essential for every piece of my data. Jong-Mi Lee was a great teacher showing me coral cleaning and many other essential cleaning/purifying techniques towards a reliable measurement. I also need to thank Gonzalo Carrasco, Simone Moos, Cheryl Zurbrick and Abigail Noble for teaching me various techniques in sediment dating; measuring metals in seawater and sediment leachates.

I also owe a sincere thank you to Christos Gouramanis for help in the sediment core collection; Intan Nurhati and Jani Tanzil for collecting the Singapore corals and seawater samples; Konrad Huguen, Justin Ossolinski and the Nha Trang Institute of Oceanography for assistance with the Vietnam coral collection; Wenshu Yap for help in analyzing the grain size of the MacRitchie sediment. I also need to thank the Singapore National Environmental Agency (NEA) for providing the incineration fly ash samples, and the Public Utilities Board (PUB) for granting me the access to sample in Singapore reservoirs.

I'm also grateful to Alan Ziegler, Annette Bolton, Bahareh Khezri, Bob Wasson, Hans Eikaas, Hong-Wei Chiang, Pavel Adamek, Ole Larsen, Richard Webster and Xinhao Cheng for having lengthy discussion on the metals in Singapore environments, or giving constructive criticism during my manuscripts' preparation. I also appreciate Jocelyn Sales for constantly helping me through the tedious administration work involved in traveling to MIT.

Last I like to thank my husband Yongxiang Lin, my parents and my parents-in-law for always being supportive to my PhD study. I deeply appreciate my husband for understanding the need for my regular trips to MIT. I would also like to thank Bo Duan, Ning Zhao and Teng Teng Yang for their friendship. This dissertation would never have been completed without the support from my family and friends.

Funding of this work was provided by the Singapore National Research Foundation (NRF) through the Singapore-MIT Alliance for Research and Technology (SMART) Center for Environmental Sensing and Modeling (CENSAM) and through the Singapore NRF Fellowships scheme awards to Adam Switzer (National Research Fellow Award No. NRF-RF2010-04) and Nathalie Goodkin (National Research Fellow Award No. NRF-RF2012-03).

Table of Contents

Acknowledgements.....	2
Summary.....	13
Chapter 1 : Introduction.....	14
1.1 Pb cycling in the ocean	15
1.2 Anthropogenic Pb in the ocean	16
1.3 Pb isotope geochemistry	17
1.4 Thesis outline	18
References for Chapter 1	21
Chapter 2 : Ocean Circulation contributes to the rise and fall of lead in the western South China Sea over the past two centuries	26
Abstract.....	26
2.1 Introduction	27
2.2 Sampling and Analysis	28
2.3 Temporal variability of Pb/Ca and Pb isotopes in the Vietnam coral	29
2.4 Possible mechanisms for Pb delivery to the western SCS.....	29
2.5 Sources of Pb to the western SCS interpreted from isotope records	32
2.6 Conclusion	33
References for Chapter 2	38
Chapter 3 : Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities	44
Abstract.....	44
3.1 Introduction	45
3.1.1 Leaded petrol usage in neighboring countries and regions	46
3.1.2 Pb isotope studies from the Asia-Pacific and Eastern Indian Ocean regions	47
3.2 Sampling and methodology.....	48
3.2.1 Site settings of the Singapore Strait	48
3.2.2 Methodology	49
3.3 Results	50
3.3.1 Pb/Ca Variabilities in Singapore corals	50

3.3.2	Pb isotope variabilities in Singapore corals	51
3.4	Discussion.....	52
3.4.1	The Pb/Ca variation in Singapore corals	52
3.4.2	Pb isotopes variation in Singapore corals	53
3.4.3	Possible attribution of different Pb sources	57
3.5	Conclusion	58
	References for Chapter 3	68
Chapter 4 : A century long sedimentary record of anthropogenic lead (Pb), Pb isotopes and other trace metals in Singapore		73
	Abstract.....	73
4.1	Introduction	74
4.2	Sampling and methodology.....	76
4.2.1	Sediment coring	76
4.2.2	Sediment core description and chronology.....	76
4.2.3	Sample preparation and metal analysis	77
4.2.4	Regional settings on Pb emission	78
4.2.5	Principal component analysis on 12 metals in the sediments	79
4.3	Results	79
4.3.1	Sediment core description and ²¹⁰ Pb chronology	79
4.3.2	Variation of Pb and Pb isotopes in the sediment.....	80
4.3.3	Concentration of other metals in the sediments.....	80
4.4	Discussion.....	81
4.4.1	The Pb content and isotopic composition in the natural background	81
4.4.2	The variation of Pb content and isotopic composition in 20th century	82
4.4.3	The variation of Pb isotope ratios in the sediment.....	85
4.4.4	An estimation of Pb flux into the Singapore region	86
4.4.5	Variation of other metals compared to Pb	87
4.5	Conclusion	88
	References for Chapter 4	100
Chapter 5 : Isotope exchange of Pb by riverine input of particulate matters: a preliminary study on the Johor River mouth		108
	Abstract.....	108

5.1	Introduction	109
5.2	Sampling and methodology.....	111
5.2.1	Closed system isotope exchange experiment	111
5.2.2	Aerosol sampling.....	112
5.2.3	Seawater sampling	112
5.2.4	Methods for analyzing Pb and Pb isotopes.....	112
5.3	Results.....	113
5.4	Discussion.....	114
5.4.1	Pb isotopes in Singapore seawater and aerosol	114
5.4.2	Mechanisms inferred from the closed-system isotope exchange experiment.....	115
5.4.3	A model for Pb isotope exchange.....	117
5.4.4	Comparison between batch experiment and field measurements in Singapore Strait water	119
5.4.5	The potential role of Pb isotope exchange for ocean chemistry	120
5.5	Conclusion.....	120
	References for Chapter 5	129
	Chapter 6 : Conclusion	133
6.1	Summary of the works	133
6.2	Discussions on the environmental perspective of the records.....	134
6.3	Implications to the ocean Pb cycle	134
6.4	Limitations and recommendations to future research.....	135
	References for Chapter 6	138
	Appendix.....	139
	Appendix A: Measured data involved in this thesis	139
	Appendix A-1: Vietnam coral Pb/Ca measurements	139
	Appendix A-2: Singapore corals Pb/Ca measurements	141
	Appendix A-3: MacRitchie sediment trace metal measurements	143
	Appendix A-4: Vietnam coral Pb isotope measurements	145
	Appendix A-5: Singapore corals Pb isotope measurements	147
	Appendix A-6: MacRitchie sediment Pb isotope measurements	149
	Appendix A-7: Singapore Strait water Pb isotope measurements.....	150

Appendix A-8: Singapore incineration ash Pb isotope measurements	150
Appendix A-9: Observed Pb concentration and Pb isotopes in isotope exchange experiment.....	151
Appendix B: Estimated data involved in this thesis.....	152
Appendix B-1: The isotopic composition in average Chinese Pb ores as of 1996 ...	152
Appendix B-2: The estimated isotopic composition of Chinese emitted Pb as of 2000 (peak petrol emission) and 2008 (more recent, leaded petrol phased out)	153
Appendix C: Methods for making mini-columns	154
Appendix D: X-ray and luminesce images of the coral slabs used in this thesis	155
Appendix D-1: X-ray image of the Vietnam coral with annual bands identified	155
Appendix D-2: X-ray image of the Kusu coral	156
Appendix D-3: X-ray image of the Hantu coral	157
Appendix D-4: Luminescence image of the Hantu coral.....	158
Appendix E: Formatted version of the published Marine Chemistry paper (chapter 3)	159

List of Figures

Figure 1.1: World's map on published Pb and Pb isotope studies as of March 2015. Blue dots denote one-time samples and red dots denote continuous records. Yellow arrows indicate the sites in this thesis. 20

Figure 1.2: Distribution of dissolved Pb in the present-day Atlantic Ocean (GEOTRACES GA02 transect). The inset figure on the bottom right shows the map of GA02 transect. Figure adapted from GEOTRACES intermediate data product 2014 (http://www.geotraces.org/sections/GA02_Pb_D_CONC_BOTTLE.html). 20

Figure 2.1: The atmospheric and oceanographic conditions of the coral site: a. ocean circulation patterns (black arrows) in the South China Sea and adjacent western Pacific with summer sea surface temperature (color) contour replotted from Botlon et al. 2015. The white dashed line indicates the upwelling region, and KC = Kuroshio Current, NEC = North Equatorial Current. b. The locations of other adjacent corals published in the literature. 1 = Hainan coral, 2 = Hongkong coral, 3 = Ishigaki coral, 4 = Jakarta coral (Inoue et al. 2006, 2008). Arrows indicates directional seasonal winds. c. Sampling location of the Vietnam coral (black cross) and its relative location in the South China Sea in the inset map. Major currents of the site are shown (black arrows). The black dot denotes for the location of the coral from a previous study (Nguyen et al. 2013). Dredging sites on the Tac River are also shown in shaded areas (Nguyen et al. 2013). 35

Figure 2.2: The variation of Pb/Ca in the Vietnam coral. The three grey bars mark the beginning of the record (1858); beginning of Second Indochina War (1959); and midpoint of China phasing out of leaded petrol (1998.85). 36

Figure 2.3: (a) Triple isotope plot of the Pb in the Vietnamese corals, together with potential Pb sources in the South China Sea region, including: aerosols (Bollhöfer and Rosman 2000, Chen et al. 2014, Mukai et al. 2001, Wang et al. 2006), sediments (Zhu et al. 2010), corals (Inoue and Tanimizu 2008), coals (Cheng and Hu 2000), petroleum (Lee et al. 2011) and Pb ores (Mukai et al. 1993, Sangster et al. 2000). The two possible end-members are highlighted in bold letters with the average Chinese Pb estimated based on 2008 emissions (see text). Regression of Pb isotope values in the Vietnam coral after 1959 (dashed line, $r^2 = 0.83$). The inset figure shows a close view of the Pb isotopes with major end members. The key dates are identified and explained in part b. (b) The variation of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in the Vietnam coral. Errors associated with isotope ratios are within the size of the points. The three grey bars mark the timing of beginning of the core (1858); beginning of Second Indochina War (1959); and midpoint of China phasing out leaded petrol (1998.85). 37

Figure 3.1: Map of the study site. On the top left corner is a map of Singapore Strait and its relative location in Southeast Asia; on the bottom left corner is a zoomed map of Singapore Strait with respect to the countries and regions in its vicinity, the adjacent countries and ocean basins are denoted. The large map on the right shows a close view of coral sites in this study. The coral sites are highlighted in dots. The figure also shows Singapore's major industrial areas (Jurong and Bukom/Busing); the landfill (Semakau); and the city center (around Singapore River). 60

Figure 3.2: The estimated Pb emission from petrol in Malaysia (white open rectangles), Singapore (black filled diamonds) and Batam (grey filled triangles). Data are estimated by the product of: road sector petrol emissions; the allowable Pb content in the petrol; the market share of the leaded petrol; and the tailpipe emission factor. Maximum consumption of leaded petrol occurred in 1980 for Singapore; 1984 for Malaysia; and 2003 for Batam. 61

Figure 3.3: The Pb/Ca in corals from multiple islands in the Singapore Strait. The average error of Pb/Ca in Singapore corals is 2.59 nmol/mol, taken from one standard deviation of triplicate sample measurements. The Pb/Ca are arranged geographically with Kusu on the east, Jong in the middle, and Hantu on the west. Grey open arrows indicate a period of Bukom/Busing development (an industrial Island 400m from Hantu, covering the period of 1984-1989, the location of Bukom/Busing is illustrated in Figure 3.1) and the black filled arrows indicate the period of Jurong island development (the largest industrial island in Singapore, 5km from Hantu, 1991-1998, Figure 3.1). The small figure on the bottom left corner illustrates the Pb/Ca in corals on the same scale. 62

Figure 3.4: The Pb/Ca from Jong coral (longest record and similar as Kusu, in black filled squares) is correlated with local annual rainfall (in grey open squares) with a lag time of 2 years, possibly due to the residence time of Pb in Surface Ocean. Annual precipitation data retrieved from IRI/LDEO Climate data library. 63

Figure 3.5: The variation of Pb/Ca (black diamonds) and 206/207 ratio (open squares) in the Hantu coral from 1990 to 1994. Wet seasons (December to March, also called Northeast Monsoon season) are marked in darker color. Such seasonal variation is not clearly seen in other corals. 63

Figure 3.6: The temporal variation of 206/207 ratio in Singapore corals. From east to west in the Strait, the sites are Kusu (grey filled circles), Jong (black filled squares), and Hantu (white open diamonds). The average two standard error is 0.0001. Note the Singapore aerosol 206/207 ratio is around 1.14 (measured over a year in 2012), the Southeast Asian aerosol 206/207 ratio is around 1.145, taken between 1994 and 1999 (Bollhöfer and Rosman,2000). The dotted line shows the point of separation between period one and period two. The two periods are differentiated by the magnitude of spatial variability among sites (see text). 64

Figure 3.7: Triple-isotope plot for Pb isotopes in Singapore coral and selected sources around the region of study, including various Pb ores (Inoue and Tanimizu 2008), aerosols (Bollhöfer and Rosman 2001, Lee et al. 2014), coals (Diaz-Somoano et al. 2009), and the South China Sea sediments (Zhu, et al. 2010). The Kusu water is the seawater sample taken near the coral site in this study. 65

Figure 3.8: The triple-isotope plot of Pb isotopes in corals (filled squares) compare to the most possible end members suggested in this study, including Singapore aerosol(open circle, Lee et al. 2014); South Chinese Pb ore (open triangle, Inoue et al. 2006); natural regional soil (open diamonds, from central catchment reserve of Singapore, unpublished data). The coral data are divided by every 10 years. The dash line illustrates the linearity of these possible sources to Singapore corals. 66

Figure 4.1: A map of the sampling site in this study. (a) Map of Macritchie Reservoir with the major inlet and the dam. The black star denotes the coring location. The relative location of Macritchie Reservoir in Singapore is shown on the rectangular map on the bottom left corner. The black area in the rectangular map on the bottom left corner indicates the Macritchie Reservoir. Singapore's relative location within Southeast Asia is shown by the latitude and longitude beside the map. (b) 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, including the direct discharge, the atmospheric deposition, and the natural/anthropogenic Pb from the catchment. The coring site in this study is highlight as a black star. 90

4.2: Estimated historical Pb emissions from petrol usage and coal combustion in the countries around Singapore. Including Singapore (white open diamonds), Malaysia (grey filled triangles), Thailand (black filled squares) and Indonesia (white open circles). Dotted lines are for the years there data are unavailable. (a) the estimated Pb emissions in tons from petroleum Pb usage (Lee et al. 2014). (b) the estimated Pb emission from coal burning for electricity production (Lee et al. 2014). 91

Figure 4.3: The illustration of: (a)The picture of the sediment core. The top, bottom of the core and the change in color during reservoir's construction were all marked. (b)Unsupported ^{210}Pb activities (black diamonds) in Bq/kg of dry sample. The blue dotted line is the 0.29cm/yr fit using a constant sedimentation rate model (see section 2.2). The vertical axis on the left shows the depth of the sediment and the axis on the right shows the converted calendar years from the ^{210}Pb data. (c) the sediment composition change throughout the core, includes clay (light grey); silt (dark grey) and sand (white). The red horizontal bar across (b) and (c) highlights the time when the reservoir was constructed..... 92

Figure 4.4: The comparison between the Pb concentrations measured by 2 methods. The horizontal axis is the concentration measured by isotope dilution method and the vertical axis is by Indium spike method. The dashed line is the least square regression from the method comparison, which records a significant positive relationship between the two methods..... 93

Figure 4.5: (a) The Pb concentration in the sediments (grey filled diamonds) compare to the Pb/Ca in the Jong island coral (open diamonds, Lee et al. 2014). The GPS location for the coral is $1^{\circ}12'54.25''\text{N}$, $103^{\circ}47'11.17''\text{E}$. (b) the 206/207 ratio (grey filled circles) and 208/207 (open triangles) in the sediment. Note that the 206/207 ratios for natural Pb is ~ 1.20 and for local aerosol is ~ 1.14 94

Figure 4.6: The concentrations of all the metals (As, Pb, Cu, Ag, Cd, Zn, Cr, Co, Ni, U, Tl, and Ba) measured in the sediment are plotted. The horizontal axes are all in mg/kg and the vertical axes are the corresponding years of each sample. 95

Figure 4.7: The plots show the results from principal component analysis. The first and second principal components could explain around 95% of the total variabilities in the core. (a) The PCA bi-plot showing PC1 versus PC2. The directions and expressing powers

of each metal in the PC space are expressed in vectors. (b) The first 2 eigenvectors (PCs) from the principal component analysis (PCA). The horizontal axis is a dimensionless unit to express the variation of the principal component; and the vertical axis is the calendar year. 96

Figure 4.8: The plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios against $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in Singapore sediments (white open triangles) together with a panel of possible end-members. The Singapore aerosols (Lee et al. 2014) and incineration fly ashes are shown in grey filled circles; the Indonesian coals (Diaz-Somoano et al. 2009) are shown in grey filled squares; the Australian coals (Diaz-Somoano et al. 2009) are shown grey filled triangles; the South China Sea sediments (Zhu et al. 2010) are shown in small grey filled crosses; the south Chinese Pb ore are shown in grey open crosses; the Singapore corals are shown in dark grey dots; and the Chinese aerosol, Thailand aerosol, Indonesian aerosols are shown in black open squares; grey open diamonds; black open circles correspondingly. The dashed line illustrates the binary mixing scenario between natural and atmospheric Pb sources. 97

Figure 5.1: Map of the Singapore Strait and the Johor River. The sampling sites are denoted as red boxes. The sampling sites include: 1. Johor River mouth for isotope exchange water samples; 2. National University of Singapore for aerosol samples; 3. Kusu for seasonal seawater samples; 4. Hantu for seasonal seawater samples. 122

Figure 5.2: Schematics of the isotope exchange experiments 123

Figure 5.3: The Pb isotope time series in Singapore aerosols (grey filled diamonds) and seawater (squares). The seawater samples were taken from the Singapore Strait near either Hantu (black filled squares) or Kusu (open squares). The dashed line illustrates an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Singapore Strait water. The aerosol samples were taken on top of the S16 building and CREATE building (courtesy to Dr. Lee J.M.). 124

Figure 5.4: The measured Pb concentration in seawater after spiking with NBS-981 standard reference material. Bottle A (filled triangles) is the unfiltered seawater; Bottle B (open triangles) is the $0.4\mu\text{m}$ filtered seawater; and the unspiked sample is shown in a blue open triangle. The main figure shows the detail change in Pb concentration in Bottle A within first 200 hours and the inset figure shows the 2-month-long variation of Pb concentration in both Bottle A and B. 125

Figure 5.5: The measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of seawater after spiking with NBS-981 standard reference material (red open triangle). The main figure shows the detailed change in $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A (filled squares) after spike addition. The inset figure shows the overview of the $^{206}\text{Pb}/^{207}\text{Pb}$ in unfiltered sample (blue open triangle); spike (red open triangle); the calculated $T = 0$ (green open triangle, calculated 18.3 pM initial dissolved + 10.5 pM NBS-981 point) and change in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Bottle A and Bottle B (filtered at $t=0$, open squares). 126

Figure 5.6: The modelled $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (dashed grey line) compared to measured values from the close-system experiment (filled squares). 127

Figure 5.7: The modelled dissolved Pb concentration (dashed grey line) compared to measured values from the close-system experiment (filled squares)..... 128

Figure 6.1: A comparison of the Pb content in MacRitchie sediment record (grey filled diamonds) with Pb/Ca in Vietnam coral (blue filled squares). The y-axes are not in the same scale. The three arrows indicate major emission control measures for Pb in the history, including: introducing of “Clean Air Act” (for Singapore), reducing the Pb content in leaded petrol (all major countries in Southeast Asia and China), and phasing out of leaded petrol..... 137

List of Tables

Table 3.1: General information about the Singapore coral cores used in this study.....67

Table 4.1: Lead concentrations and isotope ratios of the natural soils and sediments.....98

Table 4.2: Eigenvalues and variance contribution in principal component analysis99

Summary

The contribution of Asian Pb to the global Pb cycle is increasingly important now that Asian countries have experienced intensive development and phased out leaded petrol decades later than Europe or North America. To assess the Asian Pb, this study investigates the spatial and temporal variation of Pb and Pb isotopes in the South China Sea (SCS) region.

This study focuses on two sites: Nha Trang Bay represents an open ocean environment in western SCS and Singapore resembles a typical emerging Asian city. As seen from the 200-year-long coral off the Nha Trang Bay, central Vietnam, Pb was low in the western SCS until the late 1950s, and then increased $\sim 4\times$ from the late 1950s to 2000s. The peak Pb/Ca in the Vietnam coral lags peak Pb emission by at least 4-7 years, implying that upwelling in the western SCS might have transported older water masses to the coral. As suggested by Pb isotopes, Chinese emitted Pb accounts for $\sim 46\%$ of the Pb in the recent western SCS.

Moving on to a typical emerging Asian city, the temporal variability of Pb and Pb isotopes in Singapore was reconstructed using: a) three corals located along an east-west transect of the Singapore Strait and b) a 40cm-long sediment core from MacRitchie Reservoir (Singapore's central catchment reserve). The Pb content in the MacRitchie sediment has increased $\sim 30\times$ over the 20th century, and the Pb isotopes changes from natural composition to the composition found in Southeast Asian aerosols.

$^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore corals deviate from aerosols and I have not been able to find any direct source causing this deviation. I propose that the anomalous Pb isotope ratios are likely a result of isotope exchange between anthropogenic dissolved Pb and natural crustal particulates. The exchange process has been demonstrated through a closed-system isotope exchange experiment using waters from the Johor River mouth (the largest river discharging to Singapore Strait). The results presented in this dissertation provide new perspectives on Asian Pb emissions and improves our understanding of ocean Pb cycling.

Chapter 1 : Introduction

Pb is a naturally-occurring toxic element, and is found in the modern environment from both natural and anthropogenic sources. Natural Pb is released mainly by weathering processes; erosion of Pb-bearing rocks; and volcanic eruptions [e.g.: *Foster and Charlesworth*, 1996; *Nriagu*, 1989]. In contrast, anthropogenic Pb is mainly released during the combustion of fossil fuels (coal, leaded petrol); high temperature industrial activities involving Pb compounds and waste incineration [*Foster and Charlesworth*, 1996]. Since the industrial revolution, the Pb in the environment is primarily anthropogenic (~90% of global Pb emission, *Nriagu*, 1979; 1996).

Among the anthropogenic sources, leaded petrol was the largest Pb source in the 20th century *Nriagu*, 1979]. Leaded petrol involves introducing tetraethyl lead (TEL, or $(\text{CH}_3\text{CH}_2)_4\text{Pb}$) into petrol as an antiknock reagent [*Nriagu*, 1990]. During combustion, TEL is oxidized into Pb or PbO, reacts with halogenated scavengers, and then is released into the atmosphere in volatile bromide or chloride form [*Thomas et al.*, 1997]. Other major anthropogenic sources include releasing of Pb to the atmosphere by coal combustion, high temperature industrial activities and incineration [*Nriagu*, 1989].

The atmosphere is the first and major recipient of anthropogenic Pb [*Komárek et al.*, 2008]. Following atmospheric circulation, Pb has been traced in aerosols and precipitation over long distances [e.g.: *Bollhöfer and Rosman*, 2000, 2001; *Church et al.*, 1990; *Duce et al.*, 1991; *Erel et al.*, 2006; *Kusunoki et al.*, 2012]. Removal of Pb from the atmosphere occurs mainly by particulate fall out (dry deposition) and precipitation (wet deposition) [*Church et al.*, 1990; *Foster and Charlesworth*, 1996; *Settle and Patterson*, 1982]. Based on analysis of atmospheric ^{210}Pb and ^{210}Po radionuclide activity, the residence time of Pb in the lower troposphere is ~7 days [*Poet et al.*, 1972].

Atmospheric deposition is the primary pathway for anthropogenic Pb into many environments. The invasion of anthropogenic Pb into these environments has been assessed using snow and ice cores [*Boutron*, 1995; *Lee et al.*, 2011; *Murozumi et al.*, 1969]; aquatic sediments [*Eades et al.*, 2002; *Graney et al.*, 1995]; soil and peat bogs [*Bindler et al.*, 1999; *Kylander et al.*, 2009]; and corals [*Kelly et al.*, 2009; *Lee et al.*, 2014]. These natural archives have shown that anthropogenic Pb started to appear at ~3100 BP in a Canadian ice core [*Zheng et al.*, 2007], at ~3500 years ago in Swedish lake sediments [*Renberg et al.*, 2002], and became dominant as time progressed. The increase in Pb content in these environments has been noted in many other places, for example, the Pb content has increased for ~200 times over the past 3000 years in a Greenland ice core [*Murozumi et al.*, 1969], and has increased by ~10 times over the past 200 years in a sediment core from Rhode Island [*Lima et al.*, 2005]. It is also evident that the sharpest

increase of Pb in these environments resulted from the introduction of leaded petrol [Boutron, 1995; Graney *et al.*, 1995; Kelly *et al.*, 2009; Renberg *et al.*, 2002; Settle and Patterson, 1980].

In terms of leaded petrol usage, North America and Europe have been the major petroleum Pb consumers between the 1940s and 1970s [Reuer, 2002]. From the 1970s, countries in North America and Europe started to phase out leaded petrol, while countries in Asia and Africa continued using leaded petrol until late the ~1990s [UNEP, 2011]. As of April 2014, countries still using leaded petrol include Afghanistan, Algeria, Myanmar, Iraq, North Korea and Yemen [UNEP, 2014]. The difference in petroleum Pb emissions over space and time was one of the main reasons for changing regional contributions to the global Pb cycle. Besides petroleum Pb emissions, the increasing industrialization in Asian countries has elevated the relative importance of Asian Pb. Despite the emerging Asian Pb sources, most of the Pb studies (particularly those including Pb isotopes) are still limited within North America and Europe (Figure 1.1). Studies quantifying the emerging Asian Pb sources are still sparse.

1.1 Pb cycling in the ocean

Pb speciation in seawater may be dominated by chloride and carbonate complexes [Long and Angino, 1977; Powell *et al.*, 2009], although the mixing seawater and freshwater could change its complexes [Long and Angino, 1977]. As suggested by some speciation studies, Pb in seawater should not show much biological utilization [Schaule and Patterson, 1983]. Instead, Pb exhibits a particle-active behavior in the water column [Flegal and Patterson, 1983; Murray *et al.*, 2005], which shows decreasing concentration from the mixed layer to intermediate depths during times of peak emissions. Particle scavenging is the main mechanism for Pb removal as suggested by ^{210}Pb studies in both the surface and Deep Ocean [Bacon *et al.*, 1976; Nozaki *et al.*, 1976]. It is also shown that within the mixed layer, regeneration of ^{210}Pb from particulate to dissolved phase is small (<10%, Bacon *et al.*, 1976; Boyle *et al.*, 1986). Based on the observed distribution of ^{210}Pb relative to atmospheric deposition and particle removal, the residence time of Pb in the near-surface oligotrophic ocean is estimated as ~2 years [Bacon *et al.*, 1976; Nozaki *et al.*, 1976] and on the order of ~100 years in deep water [Bacon *et al.*, 1976; Cochran *et al.*, 1983,1990].

Ocean circulation can also be important in transporting Pb through the ocean. For example, Pb dominantly of North American origin has been found in the deep eastern subtropical Atlantic, suggesting the advective transport of Pb through subtropical North

Atlantic gyre (Figure 1.2, *Hamelin et al.*, 1997). Evidence for the oceanic transport of Pb have also been found in the North Atlantic [*Véron et al.*, 1994], South Atlantic [*Alleman et al.*, 2001], the Southern Oceans [*Flegal et al.*, 1993] and the Pacific [*Flegal et al.*, 1989]. Moreover, the temporal variability of dissolved Pb in the surface North Atlantic can be later traced in North Atlantic Deep Water (*Alleman et al.*, 1999; *Lee*, 2013). Based on this evidence, with a relatively known and recent injection of anthropogenic Pb into oceans, Pb can illustrate the pathways of ocean circulation [*Boyle et al.*, 2014].

1.2 Anthropogenic Pb in the ocean

Pb in the present-day ocean is dominated by anthropogenic sources [*Duce et al.*, 1991; *Flegal*, 1986; *Schaule and Patterson*, 1981; *Settle and Patterson*, 1982]. Since sources and fluxes of anthropogenic Pb have been constantly changing, Pb in the oceans follows a temporal and spatial dependent pattern that reflects the regional historical evolution of anthropogenic Pb emissions [*Alleman et al.*, 1999; *Weiss et al.*, 2003]. The temporal and spatial variation of Pb in the ocean is important for various purposes, including the interpreting the recent distribution of Pb within a historical context; assessing the relative contribution of different Pb sources; and understanding the movement mechanism of Pb through the marine environment.

In surface oceans, the temporal variation of Pb can be inferred from corals. Pb is inadvertently substituted into the calcium carbonate structure while corals secrete their skeletons [*Shen and Boyle*, 1987]. Although the exact mechanism for coral calcification is still debatable [e.g.: *Sinclair*, 2005; *Tambutté et al.*, 2011], Pb in corals appears to record the variation of dissolved Pb in seawater faithfully [*Shen and Boyle*, 1988]. For example, the variation of Pb/Ca in Bermuda in corals over the last century suggests the dissolved Pb in surface North Atlantic follows closely with the metal production, coal combustion and leaded petrol consumption [*Kelly et al.*, 2009; *Shen and Boyle*, 1987]. Although contributions of these sources to the coral vary in time and space, it is evident that the greatest increase of Pb in the North Atlantic coral happened between 1940s and 1970s, and is primarily attributed to the increased usage of leaded petrol from North America and Europe [*Kelly et al.*, 2009]. Besides Bermuda, the temporal variabilities of Pb in Indian Ocean [*Lee et al.*, 2014], Western Pacific [*Inoue and Tanimizu*, 2008], and Caribbean Sea (*Desenfant et al.*, 2006) have been investigated using corals. The coral from Chagos Island (central Indian Ocean) shows that a Pb/Ca increase of ~4 times from the mid-1980s to mid-1990s, reflecting the petroleum and coal emissions from India and other countries [*Lee et al.*, 2014]. The coral from Ogasawara (western Pacific) also shows that Pb increased significantly over the last century [*Inoue and Tanimizu*, 2008]. Besides

coral Pb investigations, the distributions of Pb in the ocean have also been explored through water sampling on research cruises (Figure 1.1, *e.g.*: *Alleman et al.*, 1999; *Boyle et al.*, 1986; *Boyle et al.*, 2014; *Echegoyen et al.*, 2014; *Sherrell et al.*, 1992; *Véron et al.*, 1994; *Weiss et al.*, 2003; *Wu et al.*, 2010).

1.3 Pb isotope geochemistry

Pb has four stable isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb . Among the stable Pb isotopes, ^{204}Pb is the only non-radiogenic isotope, while ^{206}Pb , ^{207}Pb and ^{208}Pb are radiogenic with an evolving abundance [Brown, 1962]. The abundance of radiogenic Pb isotopes follow the uranium and thorium decay chain as:

The half-life of ^{238}U is 4.47 billion years, while that of ^{235}U is 0.704 billion years. With the radiogenic growth of ^{206}Pb , ^{207}Pb and ^{208}Pb , the relative abundance of Pb isotopes is dependent on the initial U/Th/Pb composition in the reservoir where Pb ore was extracted, and the age of the reservoir from which the Pb is extracted [Cumming and Richards, 1975]. The relative abundance of radiogenic Pb isotopes compare to ^{204}Pb is generally used to investigate the geochemical origin of mineral grains [Brown, 1962] and has been widely used in geological mapping in Asia [Wang et al., 2013; Zhu et al., 2003]. For example, high $^{208}\text{Pb}/^{204}\text{Pb}$ in the feldspar grains from Southeast Asian rivers suggests Th-enriched crust [Bodet and Schärer, 2001].

As little isotope fractionation occurs during environmental processes (compared to its source variability), Pb isotopes can be utilized as a fingerprint tracing the source and pathways of anthropogenic Pb to the environment [Cheng and Hu, 2010; Komárek et al., 2008]. For historical reasons (resulted from the precision and accuracy of early mass spectrometers), $^{206}\text{Pb}/^{207}\text{Pb}$ was preferred as a norm while ratios using any two isotopes among ^{206}Pb , ^{207}Pb and ^{208}Pb are used for supplementary information. Many studies have used isotopes in identifying Pb sources in the environment [e.g., Bollhöfer and Rosman, 2002; Flegal et al., 2013; Komárek et al., 2008]. For example, the relatively high mid-20th century $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Bermuda coral in 1970s results from the Pb petrol which predominantly used Pb ores from the Mississippi Valley [Kelly et al., 2009]. The decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Bermuda coral since the 1970s reflects the increasing

relative contribution of European leaded petrol [Kelly *et al.*, 2009], which used Pb additives mainly from ores with low $^{206}\text{Pb}/^{207}\text{Pb}$ [Komárek *et al.*, 2008]. It should be noted that the Pb isotope ratios found in the environment need to be interpreted within a framework of the Pb-containing products used in the region and the mechanisms that transport Pb to the region (including import and export of Pb containing materials).

1.4 Thesis outline

In order to assess the emerging Asian Pb sources, this study has examined Pb and Pb isotope records from 2 sites: Singapore and Nha Trang, Vietnam. While Singapore is likely to resemble the Pb record of emerging Asian cities, Nha Trang is expected to indicate a far field contamination record and a natural baseline level of Pb in western South China Sea (SCS).

First, the variation of Pb and the Pb isotopic composition from the western SCS are discussed in Chapter 2, using a 170-year-long coral from a near pristine environment off the Nha Trang Bay, Vietnam. The result demonstrates that the anthropogenic Pb started to increase in western SCS since the 1950s. Pb isotopes in the Vietnam coral indicate a Chinese contribution of Pb to the SCS region. Moreover, the skeletal Pb/Ca variation implies the variation of Pb in the coral was modulated by the summer upwelling in western SCS, suggesting the temporal variation of Pb could potentially be used to illustrate aspects of changing oceanic circulation.

Moving from the western SCS to a coastal environment, the variabilities of Pb and Pb isotopes in the Singapore Strait are discussed in Chapter 3. Three annually banded coral records were recovered along an East-West transect of the strait. These records provide new perspectives on how Pb and Pb isotopes change in a coastal area that has been developed intensively over the last few decades. The Pb isotopes deviate from typical Southeast Asian aerosols, which implies either non-atmospheric sources or an isotopic exchange processes has regulated the Pb isotopic composition in the Singapore Strait water.

In order to construct the atmospheric contribution of Pb in Singapore environments during the past century, the sedimentary variation of Pb, Pb isotopes and eleven other metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) from the MacRitchie Reservoir (central Singapore) are presented in Chapter 4. As the sediment core was collected from a near pristine catchment, the sedimentary record provides an insight on the variation of Pb and Pb isotopes mainly from atmospheric deposition. This chapter provides a

complement to the coral records in Chapter 3, and sets up a baseline level of metals in Singapore reservoir sediments prior to industrialization.

In order to resolve the mysterious Pb isotopes in Singapore corals, a batch isotope exchange experiment is presented in Chapter 5. The isotope exchange experiment was implemented by adding an anomalous Pb spike into unfiltered water samples taken in proximity to Johor River mouth, and constantly monitoring its change in isotopic composition. The results of the experiment clearly show a rapid isotope exchange process. The isotope exchange experiment provides evidence for the mysterious isotope signature in Singapore corals. It also provides insights on the mechanisms involved in changing Pb isotopes in coastal environments, and enhances our understanding on the marine Pb cycle.

Figure 1.1: World's map on published Pb and Pb isotope studies as of March 2015. Blue dots denote one-time samples and red dots denote continuous records. Yellow arrows indicate the sites in this thesis.

Figure 1.2: Distribution of dissolved Pb in the present-day Atlantic Ocean (GEOTRACES GA02 transect). The inset figure on the bottom right shows the map of GA02 transect. Figure adapted from GEOTRACES intermediate data product 2014 (http://www.geotraces.org/sections/GA02_Pb_D_CONC_BOTTLE.html).

References for Chapter 1

- Alleman, L. Y., A. J. Véron, T. M. Church, A. R. Flegal, and B. Hamelin (1999), Invasion of the abyssal North Atlantic by modern anthropogenic lead, *Geophysical Research Letters*, 26(10), 1477-1480.
- Alleman, L. Y., T. M. Church, P. Gangulic, A. J. Véron, B. Hamelin, and A. R. Flegal (2001), Role of oceanic circulation on contaminant lead distribution in the South Atlantic, *Deep-Sea Res.*, 48, 2855–2876.
- Bacon, M. P., D. W. Spencer, and P. G. Brewer (1976), $^{210}\text{Pb}/^{226}\text{Ra}$ and $^{210}\text{Po}/^{210}\text{Pb}$ disequilibria in seawater and suspended particulate matter, *Earth and Planetary Science Letters*, 32(2), 277-296.
- Bindler, R., M. L. Brännvall, I. Renberg, O. Emteryd, and H. Grip (1999), Natural lead concentrations in pristine boreal forest soils and past pollution trends: A reference for critical load models, *Environmental Science and Technology*, 33(19), 3362-3367.
- Bodet, F., and U. Schärer (2001), Pb isotope systematics and time-integrated Th/U of SE-Asian continental crust recorded by single K-feldspar grains in large rivers, *Chemical Geology*, 177(3-4), 265-285.
- Bollhöfer, A., and K. J. R. Rosman (2001), Isotopic source signatures for atmospheric lead: The Northern Hemisphere, *Geochimica et Cosmochimica Acta*, 65(11), 1727-1740.
- Bollhöfer, A., and K. J. R. Rosman (2002), The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres, *Geochimica et Cosmochimica Acta*, 66(8), 1375-1386.
- Bollhöfer, A., and K. J. R. Rosman (2000), Isotopic source signatures for atmospheric lead: The Southern Hemisphere, *Geochimica et Cosmochimica Acta*, 64(19), 3251-3262.
- Boutron, C. F. (1995), Greenland snow and ice cores: Unique archives of large-scale pollution of the troposphere of the Northern Hemisphere by lead and other heavy metals, *Science of the Total Environment*, 160-161, 233-241.
- Boyle, E. A., S. D. Chapnick, G. T. Shen, and M. P. Bacon (1986), TEMPORAL VARIABILITY OF LEAD IN THE WESTERN NORTH-ATLANTIC, *Journal of Geophysical Research-Oceans*, 91(C7), 8573-8593.
- Boyle, E. A., et al. (2014), Anthropogenic lead emissions in the ocean: The evolving global experiment, *Oceanography*, 27(1), 69-75.
- Brown, J. S. (1962), Ore leads and isotopes, *Economic Geology*, 57(5), 673-720.
- Cheng, H., and Y. Hu (2010), Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review, *Environmental Pollution*, 158(5), 1134-1146.
- Church, T. M., A. Véron, C. C. Patterson, D. Settle, Y. Erel, H. R. Maring, and A. R. Flegal (1990), Trace elements in the North Atlantic troposphere: shipboard results of precipitation and aerosols, *Global Biogeochemical Cycles*, 4, 431-443.

- Cochran, J. K., M. P. Bacon, S. Krishnaswami, and K. K. Turekian (1983), ^{210}Po and ^{210}Pb distributions in the central and eastern Indian Ocean, *Earth and Planetary Science Letters*, 65(2), 433-452.
- Cochran, J. K., T. McKibbin-Vaughn, M. Dornblaser, D. Hirschberg, H. D. Livingston, and K. O. Buesseler (1990), ^{210}Pb scavenging in the North Atlantic and North Pacific Oceans, *Earth and Planetary Science Letters*, 97, 332-352.
- Cumming, G. L., and J. R. Richards (1975), Ore lead isotope ratios in a continuously changing earth, *Earth and Planetary Science Letters*, 28(2), 155-171.
- Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., and Zhou, M., (1991). The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5(3): 193-259.
- Eades, L. J., J. G. Farmer, A. B. MacKenzie, A. Kirika, and A. E. Bailey-Watts (2002), Stable lead isotopic characterisation of the historical record of environmental lead contamination in dated freshwater lake sediment cores from northern and central Scotland, *Science of the Total Environment*, 292(1-2), 55-67.
- Echegoyen, Y., E. A. Boyle, J. M. Lee, T. Gamo, H. Obata, and K. Norisuye (2014), Recent distribution of lead in the Indian Ocean reflects the impact of regional emissions, *Proceedings of the National Academy of Sciences of the United States of America*, 111(43), 15328-15331.
- Erel, Y., U. Dayan, R. Rabi, Y. Rudich, and M. Stein (2006), Trans boundary transport of pollutants by atmospheric mineral dust, *Environmental Science and Technology*, 40(9), 2996-3005.
- Flegal, A. R. (1986), Lead in tropical marine systems: A review, *Science of the Total Environment*, 58(1-2), 1-8.
- Flegal, A. R., and C. C. Patterson (1983), Vertical concentration profiles of lead in the Central Pacific at 15N and 20S, *Earth and Planetary Science Letters*, 64, 19-32.
- Flegal, A. R., T. F. Duda, and S. Niemeyer (1989), High gradients of lead isotopic composition in north-east Pacific upwelling filaments, *Nature*, 339(6224), 458-460.
- Flegal, A. R., H. Maring, and S. Niemeyer (1993), Anthropogenic lead in Antarctic sea water, *Nature*, 365(6443), 242-244.
- Flegal, A. R., C. Gallon, P. M. Ganguli, and H. C. Christopher (2013), All the Lead in China, *Critical Reviews in Environmental Science and Technology*, 43(17), 1869-1944.
- Foster, I. D. L., and S. M. Charlesworth (1996), Heavy metals in the hydrological cycle: Trends and explanation, *Hydrological Processes*, 10(2), 227-261.
- Graney, J. R., A. N. Halliday, G. J. Keeler, J. O. Nriagu, J. A. Robbins, and S. A. Norton (1995), Isotopic record of lead pollution in lake sediments from the northeastern United States, *Geochimica et Cosmochimica Acta*, 59(9), 1715-1728.
- Hamelin, B., J. L. Ferrand, L. Alleman, and E. Nicolas (1997), Isotopic evidence of pollutant lead transport from North America to the subtropical North Atlantic gyre, *Geochim. Cosmochim. Acta*, 61, 4423.

Inoue, M., and M. Tanimizu (2008), Anthropogenic lead inputs to the western Pacific during the 20th century, *Science of the Total Environment*, 406(1-2), 123-130.

Kelly, A. E., M. K. Reuer, N. F. Goodkin, and E. A. Boyle (2009), Lead concentrations and isotopes in corals and water near Bermuda, 1780-2000, *Earth and Planetary Science Letters*, 283(1-4), 93-100.

Komárek, M., V. Ettler, V. Chrastný, and M. Mihaljevič (2008), Lead isotopes in environmental sciences: A review, *Environment International*, 34(4), 562-577.

Kusunoki, K., M. Sakata, Y. Tani, Y. Seike, and K. Ayukawa (2012), Evaluating the contribution of long-range transport of heavy metals from the Asian continent to their concentrations in sediment cores from Lake Shinji, Western Japan, *Water, Air, and Soil Pollution*, 223(3), 1151-1160.

Kylander, M. E., D. J. Weiss, and B. Kober (2009), Two high resolution terrestrial records of atmospheric Pb deposition from New Brunswick, Canada, and Loch Laxford, Scotland, *Science of the Total Environment*, 407(5), 1644-1657.

Lee, J.-M., E. A. Boyle, I. Suci Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014), Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century, *Earth and Planetary Science Letters*, 398(0), 37-47.

Lee, J.M. (2013), Evolution of anthropogenic Pb and Pb isotopes in the deep North Atlantic Ocean and the Indian Ocean, Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.

Lee, K., S. D. Hur, S. Hou, L. J. Burn-Nunes, S. Hong, C. Barbante, C. F. Boutron, and K. J. R. Rosman (2011), Isotopic signatures for natural versus anthropogenic Pb in high-altitude Mt. Everest ice cores during the past 800 years, *Science of the Total Environment*, 412-413, 194-202.

Lima, A. L., B. A. Bergquist, E. A. Boyle, M. K. Reuer, F. O. Dudas, C. M. Reddy, and T. I. Eglington (2005), High-resolution historical records from Pettaquamscutt River basin sediments: 2. Pb isotopes reveal a potential new stratigraphic marker, *Geochimica et Cosmochimica Acta*, 69(7), 1813-1824.

Long, D. T., and E. E. Angino (1977), Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions, *Geochimica et Cosmochimica Acta*, 41(9), 1183-1191.

Murozumi, M., T. J. Chow, and C. Patterson (1969), Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, *Geochimica et Cosmochimica Acta*, 33, 1247-1294.

Murray, J. W., B. Paul, J. P. Dunne, and T. Chapin (2005), ²³⁴Th, ²¹⁰Pb, ²¹⁰Po and stable Pb in the central equatorial Pacific: Tracers for particle cycling, *Deep-Sea Research Part I: Oceanographic Research Papers*, 52(11), 2109-2139.

Nozaki, Y., J. Thomson, and K. K. Turekian (1976), The distribution of ²¹⁰Pb and ²¹⁰Po in the surface waters of the Pacific Ocean, *Earth and Planetary Science Letters*, 32(2), 304-312.

Nriagu, J. O. (1979), Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere [7], *Nature*, 279(5712), 409-411.

- Nriagu, J. O. (1989), A global assessment of natural sources of atmospheric trace metals, *Nature*, 338(6210), 47-49.
- Nriagu, J. O. (1990), The rise and fall of leaded petrol, *Science of the Total Environment*, 92, 13-28.
- Nriagu, J. O. (1996), A history of global metal pollution, *Science*, 272(5259), 223-224.
- Poet, S. E., H. E. Moore, and E. A. Martell (1972), Lead 210, bismuth 210, and polonium 210 in the atmosphere: Accurate ratio measurement and application to aerosol residence time determination, *Journal of Geophysical Research*, 77(33), 6515-6527.
- Powell, K. J., P. L. Brown, R. H. Byrne, T. Gajda, G. Hefter, A. K. Leuz, S. Sjöberg, and H. Wanner (2009), Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The $Pb^{2+} + OH^-$, Cl^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} systems (IUPAC Technical Report), *Pure and Applied Chemistry*, 81(12), 2425-2476.
- Renberg, I., M. L. Brännvall, R. Bindler, and O. Emteryd (2002), Stable lead isotopes and lake sediments - A useful combination for the study of atmospheric lead pollution history, *Science of the Total Environment*, 292(1-2), 45-54.
- Reuer, M. K. (2002), Centennial-scale Elemental and Isotopic Variability in the Tropical and Subtropical North Atlantic Ocean, 187 pp. Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.
- Schaule, B., and C. C. Patterson (1983), Perturbations of the natural lead depth profile in the Sargasso Sea by Industrial Lead, in *Trace Metals in Seawater*, edited by C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg, pp. 487-504, Plenum, N.Y.
- Schaule, B. K., and C. C. Patterson (1981), Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations, *Earth and Planetary Science Letters*, 54(1), 97-116.
- Settle, D. M., and C. C. Patterson (1980), Lead in albacore: guide to lead pollution in Americans, *Science*, 207(4436), 1167-1176.
- Settle, D. M., and C. C. Patterson (1982), Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewatak, *Journal of Geophysical Research*, 87(C11), 8857-8869.
- Shen, G. T., and E. A. Boyle (1987), Lead in corals: reconstruction of historical industrial fluxes to the surface ocean, *Earth and Planetary Science Letters*, 82(3-4), 289-304.
- Shen, G. T., and E. A. Boyle (1988), Determination of lead, cadmium and other trace metals in annually-banded corals, *Chemical Geology*, 67(1-2), 47-62.
- Sherrell, R. M., E. A. Boyle, and B. Hamelin (1992), Isotopic equilibration between dissolved and suspended particulate lead in the Atlantic Ocean: evidence from ^{210}Pb and stable Pb isotopes, *Journal of Geophysical Research*, 97(C7), 11,257-211,268.
- Sinclair, D. J. (2005), Correlated trace element "vital effects" in tropical corals: A new geochemical tool for probing biomineralization, *Geochimica et Cosmochimica Acta*, 69(13), 3265-3284.

Tambutté, S., M. Holcomb, C. Ferrier-Pagès, S. Reynaud, T. Tambutté, D. Zoccola, and D. Allemand (2011), Coral biomineralization: From the gene to the environment, *Journal of Experimental Marine Biology and Ecology*, 408(1-2), 58-78.

Thomas, V. M., J. A. Bedford, and R. J. Cicerone (1997), Bromine emissions from leaded petrol, *Geophysical Research Letters*, 24, 1371-1374.

UNEP (2011), Study on the possible effects on human health and the environment in Asia and the Pacific of the trade of products containing lead, cadmium and mercury, *United Nations Environmental Programme*.

UNEP (2014), Leaded Petrol Phase-out: Global Status April 2014, *United Nations Environmental Programme*.

Véron, A. J., T. M. Church, C. C. Patterson, and A. R. Flegal (1994), Use of stable lead isotopes to characterize the sources of anthropogenic lead in North Atlantic surface waters, *Geochimica et Cosmochimica Acta*, 58(15), 3199-3206.

Wang, X. C., Z. X. Li, X. H. Li, J. Li, and Y. G. Xu (2013), Identification of an ancient mantle reservoir and young recycled materials in the source region of a young mantle plume: Implications for potential linkages between plume and plate tectonics, *Earth and Planetary Science Letters*, 377-378, 248-259.

Weiss, D., A. B. Boyle, J. Wu, V. Chavagnac, A. Michel, and M. K. Reuer (2003), Spatial and temporal evolution of lead isotope ratios in the North Atlantic Ocean between 1981 and 1989, *Journal of Geophysical Research C: Oceans*, 108(10), 4-1.

Wu, J., R. Rember, M. Jin, E. A. Boyle, and A. R. Flegal (2010), Isotopic evidence for the source of lead in the North Pacific abyssal water, *Geochimica et Cosmochimica Acta*, 74(16), 4629-4638.

Zheng, J., W. Shotyk, M. Krachler, and D. A. Fisher (2007), A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: Natural and anthropogenic enrichments, isotopic composition, and predominant sources, *Global Biogeochemical Cycles*, 21(2).

Zhu, B. Q., Y. W. Chen, and X. Y. Chang (2003), Application of Pb isotopic mapping to environment evaluation in China, *Chemical Speciation and Bioavailability*, 14(1-4), 49-56.

Chapter 2 : Ocean Circulation contributes to the rise and fall of lead in the western South China Sea over the past two centuries

(manuscript submitted to Geophysical Research Letters)

Abstract

In recent decades, rapid developments have increased Pb inputs to the South China Sea (SCS). To quantify the increasing input, we investigated 170 years of skeletal Pb and Pb isotopes from an open-ocean coral off central Vietnam. The Pb/Ca in the coral was ~14.15 nmol/mol before the mid-1950s and increased to ~30 nmol/mol by 2000. While leaded-petrol phase-out across the region commenced in 2000, coral Pb/Ca continued increasing until 2004, possibly due to regional upwelling and the transport of previously emitted Pb from tropical Pacific waters. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the coral was 1.191-1.195 before mid-1950s, suggesting natural sources. The ratio decreased since then and reached ~1.176 in 2004. Pb isotopes show high linearity between natural and Chinese emitted Pb, with the latter contributing ~46% of the skeletal Pb after 2000.

Keywords: Pb, Pb isotopes, coral, South China Sea, Asia, Vietnam

2.1 Introduction

Lead (Pb) in the present ocean is dominated by anthropogenic sources [Echegoyen *et al.*, 2014; Flegal, 1986; Patterson and Settle, 1987] such as leaded petrol, coal and high-temperature industrial activities. The variation of Pb content and isotopes in oceans depend on regional historical anthropogenic Pb emissions, and atmospheric and oceanic transports [Alleman *et al.*, 1999; Weiss *et al.*, 2003]. Therefore the temporal and spatial dependent pattern of Pb in oceans could be used as a tracer demonstrating how metals move through the ocean [Boyle *et al.*, 2014]. Due to such non-uniformity, directly determining Pb variation in ocean Pb (10^{-10} - 10^{-12} mol/kg) requires extensive cruise efforts, contamination control measures and advanced analytical instruments [Boyle *et al.*, 2012; Reuer *et al.*, 2003; Schaule and Patterson, 1981; Wu and Boyle, 1997], which is why long-term continuous monitoring of Pb in the ocean remains sparse. Fortunately, the temporal variation of surface ocean Pb can be inferred from corals, which has been demonstrated in the North Atlantic [Kelly *et al.*, 2009; Reuer, 2002], the Indian Ocean [Lee *et al.*, 2014], the Caribbean Sea [Desenfant *et al.*, 2006], the Singapore Strait [Chen *et al.*, 2015], and the western Pacific [Inoue and Tanimizu, 2008; Inoue *et al.*, 2006]. These studies have demonstrated the change in Pb in various ocean basins in response to historical Pb emissions.

The SCS is an important site characterizing the injection of anthropogenic Pb into the ocean from emerging Asian economies that experienced intensive development over the last few decades. During the East Asian Winter Monsoon, Vietnam is downwind of China, the world's largest Pb producer since late 1990s [Flegal *et al.*, 2013; International Lead and Zinc Study Group, 1999; Keating, 1997]. Because of the recent emissions, the Pb content in SCS surface is (~ 100 pmol/L in 115.7°E; 18.2°N, [Ho *et al.*, 2010]) much higher than the present-day surface Atlantic (~ 20 pmol/kg, [Boyle *et al.*, 2012; Kelly *et al.*, 2009]). Despite these facts, only a few coral-derived records from coastal environments next to large cities have been reported (e.g.: Chen *et al.*, 2015; Chen *et al.*, 2010; Inoue *et al.*, 2006; Wang *et al.*, 2011]). Reliable temporal variabilities of Pb in the SCS remain sparse.

To address this issue, we reconstructed the temporal variation of Pb and Pb isotopes in the western SCS. We report the Pb/Ca and Pb isotopes variation over the last 170 years from a coral in open water environments to the east of central Vietnam. The Pb/Ca in the coral is compared to historical and recent Pb emissions of the region and the Pb isotopes in the coral are compared with potential sources such as leaded petrol, coal and Pb ore.

2.2 Sampling and Analysis

Hon Tre island (12°12'49.90"N, 109°18'17.51"E, Figure 2.1) lies in the open water of the western SCS [Bolton *et al.*, 2014] and is within the influence of East Asian Monsoon [Chang, 2004]. From November to March, the location is under the influence of the northeast prevailing wind [Dippner *et al.*, 2007; Xie *et al.*, 2003], from China and northern part of Vietnam; whereas from June to September, the southwest prevailing wind is from Southeast Asian countries and southern part of Vietnam. Co-currently, during the southwest monsoon, upwelling occurs at ~12°N off Vietnamese coast [Xie *et al.*, 2003], bringing deeper water [Dippner *et al.*, 2013], and possibly older Pb to the site.

A 2.4m-long *Porities lutea* coral core was obtained off the northeastern side of Hon Tre Island on March 2011. The chronology of the coral core was primarily determined by counting the annual density bands under x-ray imaging and was confirmed by paired seasonal paleoclimate analysis [Bolton *et al.*, 2014]. The coral was subsampled at 1-2 year increments using a diamond coated saw and the samples were cleaned using the method laid out in Shen and Boyle [1987] and then described in [Lee *et al.*, 2014] and [Chen *et al.*, 2015]. In brief, corals were crushed into small fragments (2-4 mm for primary and 280-700 µm for final cleaning) and were cleaned extensively using alternating NaOH-H₂O₂ oxidant, HNO₃ and hydrazine-based reductant. During the cleaning process, each sample was divided into three subsamples. The cleaned coral fragments were then dissolved in ultrapure HNO₃ for Pb/Ca and Pb isotope analysis. The three subsamples were analyzed separately for Pb/Ca to ensure the precision. Trace metal clean laboratory, reagents and plasticware were used throughout the process to ensure no contamination of Pb induced during sample preparation.

Pb in the coral was analyzed on Quadrupole Inductive Coupled Plasma Spectrometer (Q-ICP-MS, VG Plasma Quad 2+) by isotope dilution. Pb isotopes were measured by multiple collector ICP-MS (MC-ICP-MS, GV IsoProbe) after purifying the dissolved coral samples using an HCl-HBr anion exchange column. Pb isotope data calibration, including mass fractionation by the instrument, isobaric interferences, procedural/instrumental blanks, tailing error and accuracy adjustment were all performed as described in Reuer *et al.* [2003] and Boyle *et al.* [2012].

An estimation of Pb isotopes for average Chinese emitted Pb is necessary as large range of Pb isotopes were found among Chinese Pb sources [Cheng and Hu, 2010; Flegal *et al.*, 2013]. The Pb isotopes from Chinese emitted Pb were estimated from a weighted average of the Pb isotopes in Chinese petroleum, coal and Pb ores with respect to their consumption. The emission of automobile exhausts and coal combustion were adopted from Lee *et al.* [2014], while the emission of Pb smelting were estimated by the amount of Pb produced [International Lead and Zinc Study Group, 2014] multiply by the general government's emission guidelines. The ²⁰⁶Pb/²⁰⁷Pb in Chinese leaded petrol was ~1.134 [Lee *et al.*, 2011] since China used alkyl-lead additives mainly from Australian ores

[Cheng and Hu, 2010]. The $^{206}\text{Pb}/^{207}\text{Pb}$ in Chinese coal was adopted as ~ 1.166 , which is an average of values reported by [Cheng and Hu, 2010; Díaz-Somoano et al., 2009]. The average isotopic value of Pb emitted by Chinese Pb ore smelting is $^{206}\text{Pb}/^{207}\text{Pb} = 1.151$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.133$, which was calculated as the weighted average with respect to the Pb production from Liaoning, Hunan, Guangdong, Guangxi and Yunnan provinces ($\sim 85\%$ of the country's total production, *Ministry of Land and Resources of the People's Republic of China and China Mining(eds); Mukai et al., 1993; Sangster et al., 2000*). With the specifics above, the weighted average Pb isotope ratios for Chinese emitted Pb in 2008 was calculated as $^{206}\text{Pb}/^{207}\text{Pb} = 1.159$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.123$.

2.3 Temporal variability of Pb/Ca and Pb isotopes in the Vietnam coral

The variation of Pb/Ca in the Vietnam coral is shown in Figure 2.2. From the 1840s to mid-1950s, the Pb/Ca was low and stable, at 14.15 ± 1.96 (1σ) nmol/mol. The Pb/Ca increased abruptly from 14.16 nmol/mol in 1958 to 22.09 nmol/mol in 1959, and then plateaued at 19.74 ± 1.42 (1σ) nmol/mol until the late 1970s. After the late 1970s, Pb/Ca increased steadily from 17.62 nmol/mol in 1976 to 24.02 nmol/mol in 1999, and then increased sharply to 44.20 nmol/mol in 2004. The rate of increase was ~ 0.27 nmol/mol-year for 1975-1999 and was ~ 4.04 nmol/mol-year for 1999-2004. From 2004 to 2010, Pb/Ca in the coral decreased to 33.94 nmol/mol.

The variabilities of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are shown in Figure 2.3. From mid-1910s to mid-1950s, $^{206}\text{Pb}/^{207}\text{Pb}$ was 1.190-1.194 and $^{208}\text{Pb}/^{207}\text{Pb}$ was 2.478-2.486. $^{206}\text{Pb}/^{207}\text{Pb}$ decreased to 1.178 at ~ 1958 and then plateaued at 1.185 ± 0.003 (1σ) until the late 1980s. Over the same period, $^{208}\text{Pb}/^{207}\text{Pb}$ decreased to 2.462 and then plateaued at 2.467 ± 0.003 (1σ). From the late 1980s to 2004, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 1.185 to 1.174. $^{208}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 2.47 to 2.45 in 2004. The decrease in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ coincided with the sharp increase in Pb/Ca from the late 1990s to 2004. Pb/Ca is negatively correlated with $^{206}\text{Pb}/^{207}\text{Pb}$ in the coral with $r^2 = 0.71$. The correlation is also observed between Pb/Ca and the other isotope ratios.

2.4 Possible mechanisms for Pb delivery to the western SCS

The variation of Pb/Ca and Pb isotopes in the Vietnam coral implies that anthropogenic Pb has invaded the western SCS. The contamination of Pb in the western SCS began to appear in quantitatively during late-1950s. This is earlier than the “take-off” of the

regional economy and industrial development (since 1970s in this region, *UN Data*, 2014]. The elevated Pb/Ca in late-1950s coincides with the Vietnamese war (1955-1975, *DOD*, 1998). Petroleum consumption in Vietnam during the war (1971-1975) was ~4 times higher than immediately following the war (1976-1979) [*International Energy Agency*, 2014]. The elevated leaded petrol consumption certainly resulted in increased Pb emissions since unleaded petrol was not available in 1950s [*Balce*, 2000]. Besides leaded petrol, scraps from leaded paint due to military activity could also be a possible source for the Pb in coral [*Wang et al.*, 2011] as the US air force and navy base was located ~30km south of Nha Trang during the Vietnamese war [*Storey and Thayer*, 2001]. Both elevated leaded petrol consumption and scrap from leaded paint could be possible sources for the Pb in the Vietnam coral during 1958-1975.

From late 1970s to 2004, the Pb/Ca increased strongly in the coral, implying increased Pb concentrations in surface seawater. The increase in Pb contamination was most prominent between the late 1990s and mid-2000s, with the highest Pb/Ca value ~3 fold higher than pre-1950 values. These results are in line with the rise of the regional economy since the 1970s (particularly China) [*UN Data*, 2014]. However, the usage of leaded petrol [*Lee et al.*, 2014; *Yao et al.*, 2013] in this region does not seem to correlate with the variation of Pb/Ca. From the estimations from previous studies, peak petroleum-Pb emission happened from 1997-2000 in China [*Chen et al.*, 2005; *Cheng and Hu*, 2010; *Lee et al.*, 2014], 1977 in Thailand [*Hirota*, 2006], 1980 in Malaysia [*Afroz et al.*, 2003] and 1994 in Vietnam [*Balce*, 2000]. However, Pb/Ca in the Vietnam coral was still increasing until 2004 (Figure 2.2), several years later than any of the peak petroleum-Pb emissions. China used ~20 times more leaded petrol than Vietnam, Thailand or Malaysia [*Lee et al.*, 2014], therefore the primary source of the Pb in Vietnam coral is likely China. In this case, the peak Pb/Ca in coral was 4-7 years later than the phase-out of leaded petrol in China. The residence time of Pb in oligotrophic surface waters is ~2 yrs [*Bacon et al.*, 1976; *Nozaki et al.*, 1976]. Evidence from ^{210}Pb has shown a ~1.8 yr residence time of Pb in surface SCS (calculated using data from 18°N, 116°E, *Wei et al.*, 2011). Because the late arrival of Pb/Ca peak was significantly longer (4-7 yrs later than the peak Pb emission) than the residence time (~2 yrs), the late arrival of Pb/Ca is not accounted for by the residence time of Pb in the surface SCS. Additionally, no significant correlation was observed between Pb/Ca in the Vietnam coral and leaded petrol Pb emission from China, Thailand, Malaysia or Vietnam, implying that the usage of leaded petrol alone does not fully explain the variation of Pb/Ca in the Vietnam coral.

There are several other possible sources of Pb to the surface ocean at this site including: 1) coal combustion, 2) run-off from urban and industrial processes or 3) advective transport of anthropogenic lead from other regions will modify the temporal variability of Pb on the western SCS region.

Industrial processes like coal combustion and metal smelting could also contribute Pb to the Vietnam coral. As noted from atmospheric monitoring, the concentration of Pb in

Chinese aerosols remained relatively high after phasing out leaded petrol [Chen *et al.*, 2005; Wang *et al.*, 2006]. An atmospheric monitoring study in Hanoi also concluded that coal combustion could be a major Pb source besides leaded petrol [Gatari *et al.*, 2005]. Pb emissions related to coal combustion or metal smelting (or both) from these countries have been estimated in various studies [Cheng *et al.*, 2014; Lee *et al.*, 2014; Li *et al.*, 2012; Niisoe *et al.*, 2010; Yao *et al.*, 2013]. Estimated Pb emissions differ greatly (e.g. from ~9000t/year to 56,500t/yr in 2008) because of the choices of emission factor in different studies. It was difficult to justify which emission factor is more appropriate because of the significant improvements on emission controls over the last decade [Cheng *et al.*, 2014]. As a result, it is difficult to compare skeletal Pb/Ca and atmospheric emissions quantitatively. Qualitatively speaking, all these estimates show an increasing trend since 2000, which is contrary to the decrease in Pb/Ca since 2004. Industrial Pb sources could have some influence on Pb in the Asian region in general, but do not appear likely the major source for the Pb in coral.

In coastal environments, runoff from urban and industrial used catchments could potentially contribute Pb to corals [Chen *et al.*, 2015]. A series of coastal projects has been carried out in the nearest city, Nha Trang, including the construction of Nha Trang port, several resorts and dredging of the Tac River (Figure 2.1, Nguyen *et al.*, 2013). As suggested by a coral taken from the reefs facing the river, local constructions started to influence the metal content in the coral in 2003. The influence was most intensive at 2006-2008 [Nguyen *et al.*, 2013]. However, in this study, the Pb/Ca in coral began to decrease in 2004; implying construction activities did not heavily influence the Pb in the coral. In Nguyen *et al.*'s study, the coral was sampled from a reef facing the river discharge; while in this study the coral was sampled from a reef facing the SCS, where corals may respond differently to local construction activities [Chen *et al.*, 2015]. The differences between these two studies show that construction activities started to influence the local water after the coral Pb/Ca in our study began to decrease, and therefore should not have significantly influenced our site.

Advective transport of Pb is likely modulating the surface ocean Pb at this site. Ocean circulation has been shown to be important in advecting Pb [Alleman *et al.*, 1999; Boyle *et al.*, 1986]. In the coral site, a strong southwestward current prevails from October to April and a northeastward current from May to September [Mitsuguchi *et al.*, 2008; Nguyen *et al.*, 2013]. During mid-summer (June to August), the prevailing winds, the topography and ocean dynamics together develop an upwelling zone [Xie *et al.*, 2003] at ~12°N in the SCS encompassing this study site. Previous studies demonstrated that water masses segregated from the atmosphere (ie below the thermocline ~150m) transport anthropogenic Pb signals over decades [Boyle *et al.*, 2014; Bridgestock *et al.*, 2014]. As suggested by field measurements, the upwelled water mass contains high salinity North Pacific Tropical Water (NPTW) mixed with the SCS Open Sea Water [Dippner and Loick-Wilde, 2011; Dippner *et al.*, 2007]. The NPTW originates near the center of North Pacific

subtropical basin [Cannon, 1966], and intrudes into the SCS from the Kurushio current [Qu *et al.*, 2000] below the surface (~100-200m, [Suga *et al.*, 2000]). No direct measurement was made in the remote tropical Pacific where NPTW was formed, however Chinese Pb is likely the main contributor to NPTW as it accounts for ~60% of Pb input to the western Pacific since 1990s [Inoue and Tanimizu, 2008] and ~30% of Pb in urban Californian aerosols [Ewing *et al.*, 2010]. In this case, the temporal variation pattern of Pb in NPTW could be similar to the Chinese leaded petrol emissions and similar to surface SCS. While the frequency and strength of the Kurushio intrusion varies [Centurioni *et al.*, 2004], the transport time of NPTW from the Pacific to Vietnam could be a possible explanation for the 4-7 year offset from the main features of petrol emissions, indicating that a substantial volume of NPTW is regularly surfacing off western Vietnam. Since our site receives water both from surface SCS and NPTW, the transport time of NPTW should be at least 2-5 years to account for the 4-7 years lag between the peak Chinese Pb emission and the peak Pb/Ca in the Vietnam coral, as the residence time of Pb in the upper SCS is ~2 years [Wei *et al.*, 2011]. Further work on corals from non-upwelling regions in SCS or using other oceanographic tracer can be done to better constrain the intensity of upwelling and the timescale of the advection of NPTW into the SCS.

2.5 Sources of Pb to the western SCS interpreted from isotope records

Pb isotopes provide information on the sources of Pb to the region, allowing for further interpretations of the mechanisms proposed previously. Before the mid-1950s, $^{206}\text{Pb}/^{207}\text{Pb}$ in the coral was 1.191-1.195 and $^{208}\text{Pb}/^{206}\text{Pb}$ was 2.078-2.081. The isotope ratios were invariable and agree with averages from SCS Holocene sediments (avg $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.196, $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.079, Figure 2.3, [Zhu *et al.*, 2002; Zhu *et al.*, 2010]). Considering the limited industrial development in the SCS region during that period [Hirschman and Bonaparte, 2012], Pb in the Vietnam coral clearly originates primarily from natural sources.

From the mid-1950s to 2010, $^{206}\text{Pb}/^{207}\text{Pb}$ decreased to <1.170, suggesting low $^{206}\text{Pb}/^{207}\text{Pb}$ sources to the western SCS. $^{206}\text{Pb}/^{207}\text{Pb}$ was negatively correlated with Pb/Ca in the coral, with low $^{206}\text{Pb}/^{207}\text{Pb}$ consistently associated with high Pb/Ca, supporting an anthropogenic Pb source into the region with low $^{206}\text{Pb}/^{207}\text{Pb}$. Pb isotope ratios in the Vietnam coral show high linearity in a triple isotope plot (Figure 2.3), which suggests that Pb in the Vietnam coral results from a mixture between the natural Pb with high $^{206}\text{Pb}/^{207}\text{Pb}$ (low $^{208}\text{Pb}/^{206}\text{Pb}$) and an anthropogenic Pb with a low $^{206}\text{Pb}/^{207}\text{Pb}$ (high $^{208}\text{Pb}/^{206}\text{Pb}$). Since 2000, Pb isotopes in the coral were $^{206}\text{Pb}/^{207}\text{Pb}=1.176\pm0.001$,

$^{208}\text{Pb}/^{206}\text{Pb} = 2.092 \pm 0.002$, in agreement with both Chinese aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges 1.141-1.177, $^{208}\text{Pb}/^{206}\text{Pb}$ ranges 2.094-2.134) and Vietnamese aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges 1.155-1.167, $^{208}\text{Pb}/^{206}\text{Pb}$ ranges 2.101-2.103, Figure 2.3) [Bollhöfer and Rosman, 2001; Bollhöfer and Rosman, 2000; Chen *et al.*, 2005; Wang *et al.*, 2006]. It should be noted that the isotope ratio in Chinese and Vietnamese aerosols are similar (Figure 2.3).

Pb isotopes in the most recent part of Vietnam coral (from the 1990s) are similar in ratio to corals from the northern part of SCS, including a coral from Hainan ($^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.172 , $^{208}\text{Pb}/^{206}\text{Pb}$ of ~ 2.135) and a coral from Hong Kong ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.172, $^{208}\text{Pb}/^{206}\text{Pb}$ of ~ 2.070) from comparable periods [Inoue *et al.*, 2006] and to sediments from Yangtze River Delta [Yao *et al.*, 2013] and Pearl River Delta [Li *et al.*, 2001] ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.166-1.176). In contrast, Pb isotopes in aerosols from countries to the south of Vietnam show lower $^{206}\text{Pb}/^{207}\text{Pb}$ (1.127-1.147 for Singapore, Kuala Lumpur, Bangkok and Jakarta, Bollhöfer and Rosman, 2000; Lee *et al.*, 2014) and hence cannot be the dominant source of Pb to the Vietnam coral.

Little was known about the isotopic composition in NPTW as no direct Pb isotope measurements have been made in the remote Pacific. However, studies on both western Pacific [Inoue and Tanimizu, 2008], north Pacific [Zurbrick *et al.*, submitted] and Californian aerosols [Ewing *et al.*, 2010] all showing significant Chinese Pb contribution. Inferring from these studies on the neighboring basins, Chinese Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.159$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.123$) could be the dominant source to NPTW (see section 2.4). Pb isotopes in the Vietnam coral would be in good agreement with the Chinese Pb even though we see a delayed time stamp caused by upwelling.

A linear fit between the average emitted Pb and natural Pb in the SCS passes within error of the values obtained from the Vietnam coral (Figure 2.3), supporting the previous argument that Chinese Pb is the major source of anthropogenic Pb in the region. Using the Chinese emitted Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.151$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.133$) and natural SCS ($^{206}\text{Pb}/^{207}\text{Pb} = 1.193$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.079$) as the two end members, the weightage calculation shows that the Pb into the Vietnamese coral after 2000 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.176$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.092$) contains $\sim 46\%$ of Chinese emitted Pb.

2.6 Conclusion

The temporal variation of Pb and Pb isotopes in the western SCS over the last 170 years was inferred from a coral east of Nha Trang Bay, central Vietnam. From 1840s to mid-1950s, the Pb/Ca in the coral was 14.15 ± 1.96 nmol/mol and the $^{206}\text{Pb}/^{207}\text{Pb}$ was ~ 1.195 , inferring natural Pb sources. Since the late-1950s, Pb/Ca started increasing and reaching 44.20 nmol/mol in 2004. Correspondingly, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 1.195 to

1.174, suggesting the invasion of anthropogenic Pb sources. The variation in Pb in the coral involved several periods, including natural variabilities, the Vietnamese war, increasing development and usage of leaded petrol, and then the phasing out of leaded petrol. The decrease in Pb/Ca was 4-7 years later than peak emissions of Pb in this region, possibly due to the upwelling in the western SCS. The delayed Pb peak in the coral also implies the transport time of NPTW into Vietnamese upwelling region is at least 2-5 years. The Pb isotopes in the Vietnam coral showed high linearity on the triple isotope plot, suggesting Pb in the coral was a mix between natural Pb and Chinese emitted Pb. The average Chinese Pb contributes to ~46% of the Pb in the coral in 2000s. This is the first study addressing the century scale variation of Pb in the South China Sea using both the Pb/Ca and Pb isotopes.

Figure 2.1: The atmospheric and oceanographic conditions of the coral site: a. ocean circulation patterns (black arrows) in the South China Sea and adjacent western Pacific with summer sea surface temperature (color) contour replotted from Botlon et al. 2015. The white dashed line indicates the upwelling region, and KC = Kuroshio Current, NEC = North Equatorial Current. b. The locations of other adjacent corals published in the literature. 1 = Hainan coral, 2 = Hongkong coral, 3 = Ishigaki coral, 4 = Jakarta coral (Inoue et al. 2006, 2008). Arrows indicates directional seasonal winds. c. Sampling location of the Vietnam coral (black cross) and its relative location in the South China Sea in the inset map. Major currents of the site are shown (black arrows). The black dot denotes for the location of the coral from a previous study (Nguyen et al. 2013). Dredging sites on the Tac River are also shown in shaded areas (Nguyen et al. 2013).

Figure 2.2: The variation of Pb/Ca in the Vietnam coral. The three grey bars mark the beginning of the record (1858); beginning of Second Indochina War (1959); and midpoint of China phasing out of leaded petrol (1998.85).

Figure 2.3.: (a) Triple isotope plot of the Pb in the Vietnamese corals, together with potential Pb sources in the South China Sea region, including: aerosols (Bollhöfer and Rosman 2000, Chen et al. 2014, Mukai et al. 2001, Wang et al. 2006), sediments (Zhu et al. 2010), corals (Inoue and Tanimizu 2008), coals (Cheng and Hu 2000), petroleum (Lee et al. 2011) and Pb ores (Mukai et al. 1993, Sangster et al. 2000). The two possible end-members are highlighted in bold letters with the average Chinese Pb estimated based on 2008 emissions (see text). Regression of Pb isotope values in the Vietnam coral after 1959 (dashed line, $r^2 = 0.83$). The inset figure shows a close view of the Pb isotopes with major end members. The key dates are identified and explained in part b. (b) The variation of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in the Vietnam coral. Errors associated with isotope ratios are within the size of the points. The three grey bars mark the timing of beginning of the core (1858); beginning of Second Indochina War (1959); and midpoint of China phasing out leaded petrol (1998.85).

References for Chapter 2

- Afroz, R., M. N. Hassan, and N. A. Ibrahim (2003), Review of air pollution and health impacts in Malaysia, *Environmental Research*, 92(2), 71-77. doi:10.1016/S0013-9351(02)00059-2
- Alleman, L. Y., A. J. Véron, T. M. Church, A. R. Flegal, and B. Hamelin (1999), Invasion of the abyssal North Atlantic by modern anthropogenic lead, *Geophysical Research Letters*, 26(10), 1477-1480. DOI: 10.1029/1999GL900287
- Bacon, M. P., D. W. Spencer, and P. G. Brewer (1976), $^{210}\text{Pb}/^{226}\text{Ra}$ and $^{210}\text{Po}/^{210}\text{Pb}$ disequilibria in seawater and suspended particulate matter, *Earth and Planetary Science Letters*, 32(2), 277-296. doi:10.1016/0012-821X(76)90068-6
- Balce, G. R. (2000), Overview of Regional Fuel Market and Fuel Quality Standards in ASEAN, *ASEAN CENTRE FOR ENERGY, Jakarta, Indonesia*.
- Bollhöfer, A., and K. J. R. Rosman (2001), Isotopic source signatures for atmospheric lead: The Northern Hemisphere, *Geochimica et Cosmochimica Acta*, 65(11), 1727-1740. doi:10.1016/S0016-7037(00)00630-X
- Bollhöfer, A., and K. J. R. Rosman (2000), Isotopic source signatures for atmospheric lead: The Southern Hemisphere, *Geochimica et Cosmochimica Acta*, 64(19), 3251-3262. doi:10.1016/S0016-7037(00)00436-1
- Bolton, A., N. F. Goodkin, K. Huguen, D. R. Ostermann, S. T. Vo, and H. K. Phan (2014), Paired Porites coral Sr/Ca and $\delta^{18}\text{O}$ from the western South China Sea: Proxy calibration of sea surface temperature and precipitation, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 410(0), 233-243. doi:10.1016/j.palaeo.2014.05.047
- Boyle, E. A., S. D. Chapnick, G. T. Shen, and M. P. Bacon (1986), Temporal variability of lead in the western North Atlantic, *Journal of Geophysical Research-Oceans*, 91(C7), 8573-8593. DOI: 10.1029/JC091iC07p08573
- Boyle, E. A., J.-M. Lee, Y. Echegoyen, A. Noble, S. Moos, G. Carrasco, N. Zhao, R. Kayser, J. Zhang, T. Gamo, H. Obata, and K. Norisuye. (2014), Anthropogenic lead emissions in the ocean: The evolving global experiment, *Oceanography*, 27(1), 69-75. <http://dx.doi.org/10.5670/oceanog.2014.10>.
- Boyle, E. A., S. John, W. Abouchami, J. F. Adkins, Y. S. Echegoyen, M. Ellwood, R. A. Flegal, K. Fornace, C. Gallon, S. Galer, M. Gault-Ringold, F. Lacan, A. Radic, M. Rehkamper, O. Rouxel, Y. Sohrin, C. Stirling, C. Thompson, D. Vance, Z. Xue, Y. Zhao,. (2012), GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration, *Limnology and Oceanography: Methods* 10, 653-665. DOI: 10.4319/lom.2012.10.653
- Bridgestock, L., M. Paul, T. van de Flierdt, M. Rehkamper, and E. Achterberg (2014), Understanding the Marine Biogeochemical Cycle of Pb in the Equatorial Atlantic, presented at 2014 Ocean Sciences Meeting, Hawaii USA.

- Cannon, G. A. (1966), Tropical waters in the western Pacific Ocean, August-September 1957, *Deep-Sea Research and Oceanographic Abstracts*, 13(6), 1139-1148. doi:10.1016/0011-7471(66)90705-4
- Centurioni, L. R., P. P. Niiler, and D. K. Lee (2004), Observations of inflow of Philippine sea surface water into the South China Sea through the Luzon strait, *Journal of Physical Oceanography*, 34(1), 113-121. Observations of inflow of Philippine sea surface water into the South China Sea through the Luzon strait
- Chang, C.-P. (Ed.) (2004), *East Asian Monsoon*, 564 pp., World scientific publishing Co. Pte. Ltd. Singapore.
- Chen, J., M. Tan, Y. Li, Y. Zhang, W. Lu, Y. Tong, G. Zhang and Y. Li (2005), A lead isotope record of shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded petrol, *Atmospheric Environment*, 39(7), 1245-1253. doi:10.1016/j.atmosenv.2004.10.041
- Chen, M., J.-M. Lee, A. D. Switzer, I. S. Nurhati, and E. A. Boyle (2015), Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities, *Marine Chemistry*, 168, 49-59. doi:10.1016/j.marchem.2014.10.007
- Chen, T. R., K.-F. Yu, S. Li, G. J. Price, Q. Shi, and G.-J. Wei (2010), Heavy metal pollution recorded in Porites corals from Daya Bay, northern South China Sea, *Marine Environmental Research*, 70(3-4), 318-326. doi:10.1016/j.marenvres.2010.06.004
- Cheng, H., and Y. Hu (2010), Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review, *Environmental Pollution*, 158(5), 1134-1146. doi:10.1016/j.envpol.2009.12.028
- Cheng, K., Y. Wang, H. Tian, X. Gao, Y. Zhang, X. Wu, C. Zhu, and J. Gao (2014), Atmospheric emission characteristics and control policies of five precedent-controlled toxic heavy metals from anthropogenic sources in China, *Environmental Science and Technology*, 49(2), 1206-1214. DOI: 10.1021/es5037332
- Desenfant, F., A. J. Véron, G. F. Camoin, and J. Nyberg (2006), Reconstruction of pollutant lead invasion into the tropical North Atlantic during the twentieth century, *Coral Reefs*, 25(3), 473-484. doi: 10.1007/s00338-006-0113-x
- Díaz-Somoano, M., M. E. Kylander, M. A. López-Antón, I. Suárez - Ruiz, M. R. Martínez-Tarazona, M. Ferrat, B. Kober, and D. J. Weiss (2009), Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing, *Environmental Science and Technology*, 43(4), 1078-1085. DOI: 10.1021/es801818r
- Dippner, J. W., and N. Loick-Wilde (2011), A redefinition of water masses in the Vietnamese upwelling area, *Journal of Marine Systems*, 84(1-2), 42-47. doi:10.1016/j.jmarsys.2010.08.004
- Dippner, J. W., D. Bombar, N. Loick-Wilde, M. Voss, and A. Subramaniam (2013), Comment on "current separation and upwelling over the southeast shelf of Vietnam in the South China Sea" by Chen et al, *Journal of Geophysical Research: Oceans*, 118(3), 1618-1623. DOI: 10.1002/jgrc.20118

Dippner, J. W., K. V. Nguyen, H. Hein, T. Ohde, and N. Loick (2007), Monsoon-induced upwelling off the Vietnamese coast, *Ocean Dynamics*, 57(1), 46-62. DOI: 10.1007/s10236-006-0091-0

DOD (1998), NAME OF TECHNICAL SERGEANT RICHARD B. FITZGIBBON TO BE ADDED TO THE VIETNAM VETERANS MEMORIAL, *U.S. Department of Defense*. Retrived on April 22nd, from: <http://www.defense.gov/releases/release.aspx?releaseid=1902>

Echegoyen, Y., E.A. Boyle, J.-M. Lee, T. Gamo, H. Obata, and K. Norisuye (2014), Recent distribution of lead in the Indian Ocean reflects the impact of regional emissions, *Proceedings of the National Academy of Sciences of the United States of America*, 111(43), 15328-15331. doi: 10.1073/pnas.1417370111

Ewing, S. A., J. N. Christensen, S. T. Brown, R. A. Vancuren, S. S. Cliff, and D. J. Depaolo (2010), Pb isotopes as an indicator of the Asian contribution to particulate air pollution in urban California, *Environmental Science and Technology*, 44(23), 8911-8916. DOI: 10.1021/es101450t

Flegal, A. R. (1986), Lead in tropical marine systems: A review, *Science of the Total Environment*, 58(1-2), 1-8. doi:10.1016/0048-9697(86)90071-9

Flegal, A. R., C. Gallon, P. M. Ganguli, and C. H. Conaway (2013), All the Lead in China, *Critical Reviews in Environmental Science and Technology*, 43(17), 1869-1944. DOI:10.1080/10643389.2012.671738

Gatari, M., A. Wagner, and J. Boman (2005), Elemental composition of tropospheric aerosols in Hanoi, Vietnam and Nairobi, Kenya, *Science of the Total Environment*, 341(1-3), 241-249. doi:10.1016/j.scitotenv.2004.09.031

Hirota, K. (2006), Review of Lead Phase Out for Air Quality Improvement in the Third World Cities Lessons from Thailand and Indonesia. *Studies in Regional Science Part C: Sustainable Cities and Transport*, 36(2), 527-541, <http://doi.org/10.2457/srs.36.527>

Hirschman, C., and S. Bonaparte (Eds.) (2012), *Population and Society in Southeast Asia*, Cornell University, Ithaca, NY.

Ho, T. Y., C. T. Chien, B. N. Wang, and A. Siriraks (2010), Determination of trace metals in seawater by an automated flow injection ion chromatograph pretreatment system with ICPMS, *Talanta*, 82(4), 1478-1484. doi: 10.1016/j.talanta.2010.07.022

Inoue, M., and M. Tanimizu (2008), Anthropogenic lead inputs to the western Pacific during the 20th century, *Science of the Total Environment*, 406(1-2), 123-130. doi:10.1016/j.scitotenv.2008.07.032

Inoue, M., A. Hata, A. Suzuki, M. Nohara, N. Shikazono, W. W. S. Yim, W. S. Hantoro, D. Sun, and H. Kawahata (2006), Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons, *Environmental Pollution*, 144(3), 1045-1052. doi:10.1016/j.envpol.2005.11.048

International Energy Agency (2014), Vietnam - Road sector petrol fuel consumption, *International Road Federation, World Road Statistics and electronic files*.

International Lead and Zinc Study Group (1999), Lead and zinc statistics. Monthly bulletin.*Rep*.

International Lead and Zinc Study Group (2014), View of the global development of the world non-ferrous metals and commodities, paper presented at 8th Asia-Pacific Economic Cooperation(APEC) Mining Task Force meeting, Beijing.

Keating, J. (1997), *Lead; Canadian minerals yearbook*, Ottawa, Canada: Natural Resources Canada.

Kelly, A. E., M. K. Reuer, N. F. Goodkin, and E. A. Boyle (2009), Lead concentrations and isotopes in corals and water near Bermuda, 1780-2000, *Earth and Planetary Science Letters*, 283(1-4), 93-100. doi:10.1016/j.epsl.2009.03.045

Lee, J.-M., E. A. Boyle, I. Suci Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014), Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century, *Earth and Planetary Science Letters*, 398(0), 37-47. doi:10.1016/j.epsl.2014.04.030

Lee, K., S. D. Hur, S. Hou, L. J. Burn-Nunes, S. Hong, C. Barbante, C. F. Boutron, and K. J. R. Rosman (2011), Isotopic signatures for natural versus anthropogenic Pb in high-altitude Mt. Everest ice cores during the past 800 years, *Science of the Total Environment*, 412-413, 194-202. doi:10.1016/j.scitotenv.2011.10.002

Li, Q., H. Cheng, T. Zhou, C. Lin, and S. Guo (2012), The estimated atmospheric lead emissions in China, 1990–2009, *Atmospheric Environment*, 60, 1-8. doi:10.1016/j.atmosenv.2012.06.025

Li, X., Z. Shen, O. W. H. Wai, and Y. S. Li (2001), Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary, *Marine Pollution Bulletin*, 42(3), 215-223. doi:10.1016/S0025-326X(00)00145-4

Ministry of Land and Resources of the People's Republic of China and China Mining(eds) The distribution of Chinese major Pb-Zn production bases (in Chinese), Retrieved on December 18, 2014, from: http://www.chinamining.com.cn/report/default.asp?v_doc_id=1102.

Mitsuguchi, T., P. X. Dang, H. Kitagawa, T. Uchida, and Y. Shibata (2008), Coral Sr/Ca and Mg/Ca records in Con Dao Island off the Mekong Delta: Assessment of their potential for monitoring ENSO and East Asian monsoon, *Global and Planetary Change*, 63(4), 341-352. doi:10.1016/j.gloplacha.2008.08.002

Mukai, H., N. Furuta, T. Fujii, Y. Ambe, K. Sakamoto, and Y. Hashimoto (1993), Characterization of sources of lead in the urban air of Asia using stable lead isotopes, *Environmental Science and Technology*, 27, 1347-1356. DOI: 10.1021/es00044a009

Nguyen, A. D., J. Zhao, Y. Feng, W. Hu, K. Yu, M. Gasparon, T. B. Pham, and T. R. Clark (2013), Impact of recent coastal development and human activities on Nha Trang Bay, Vietnam: Evidence from a *Porites lutea* geochemical record, *Coral Reefs*, 32(1), 181-193. DOI: 10.1007/s00338-012-0962-4

Niisoe, T., E. Nakamura, K. Harada, H. Ishikawa, T. Hitomi, T. Watanabe, Z. Wang, and A. Koizumi (2010), A global transport model of lead in the atmosphere *Atmospheric Environment*, 44, 1806-1814. doi:10.1016/j.atmosenv.2010.01.001

Nozaki, Y., J. Thomson, and K. K. Turekian (1976), The distribution of ^{210}Pb and ^{210}Po in the surface waters of the Pacific Ocean, *Earth and Planetary Science Letters*, 32(2), 304-312. doi:10.1016/0012-821X(76)90070-4

Patterson, C. C., and D. M. Settle (1987), Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Marine Chemistry*, 22(2-4), 137-162. doi:10.1016/0304-4203(87)90005-3

Qu, T., H. Mitsudera, and T. Yamagata (2000), Intrusion of the North Pacific waters into the South China Sea, *Journal of Geophysical Research: Oceans*, 105(C3), 6415-6424. DOI: 10.1029/1999JC900323

Reuer, M. K. (2002), Continental-scale Elemental and Isotopic Variability in the Tropical and Subtropical North Atlantic Ocean. Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.

Reuer, M. K., E. A. Boyle, and B. C. Grant (2003), Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS, *Chemical Geology*, 200(1-2), 137-153. doi:10.1016/S0009-2541(03)00186-4

Sangster, D. F., P. M. Outridge, and W. J. Davis (2000), Stable lead isotope characteristics of lead ore deposits of environmental significance, *Environmental Reviews*, 8(2), 115-147. doi: 10.1139/a00-008

Schaule, B. K., and C. C. Patterson (1981), Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations, *Earth and Planetary Science Letters*, 54(1), 97-116. doi:10.1016/0012-821X(81)90072-8

Shen, G. T., and E. A. Boyle (1987), Lead in corals: reconstruction of historical industrial fluxes to the surface ocean, *Earth Planetary Science Letters*, 82, 289-304. doi:10.1016/0012-821X(87)90203-2

Storey, I., and C. A. Thayer (2001), Cam Ranh Bay: Past Imperfect, Future Conditional, *Contemporary Southeast Asia*, 23(3), 452-473. DOI: 10.1355/CS23-3D

Suga, T., A. Kato, and K. Hanawa (2000), North Pacific Tropical Water: its climatology and temporal changes associated with the climate regime shift in the 1970s, *Progress in Oceanography*, 47(2-4), 223-256. doi:10.1016/S0079-6611(00)00037-9

UN Data (2014), GDP (current US\$), *World Development Indicators*.

Wang, B. S., N. F. Goodkin, N. Angeline, A. D. Switzer, C.-F. You, and K. Huguen (2011), Temporal distributions of anthropogenic Al, Zn and Pb in Hong Kong Porites coral during the last two centuries, *Marine Pollution Bulletin*, 63(5-12), 508-515. doi:10.1016/j.marpolbul.2011.02.011

Wang, W., X. Liu, L. Zhao, D. Guo, X. Tian, and F. Adams (2006), Effectiveness of leaded petrol phase-out in Tianjin, China based on the aerosol lead concentration and isotope abundance ratio, *Science of the Total Environment*, 364(1-3), 175-187. doi:10.1016/j.scitotenv.2005.07.002

Wei, C. L., S. Y. Lin, D. D. Sheu, W. C. Chou, M. C. Yi, P. H. Santschi, and L. S. Wen (2011), Particle-reactive radionuclides (^{234}Th , ^{210}Pb , ^{210}Po) as tracers for the estimation of export production in the South China Sea, *Biogeosciences*, 8(12), 3793-3808. doi:10.5194/bg-8-3793-2011, 2011

Weiss, D., A. B. Boyle, J. Wu, V. Chavagnac, A. Michel, and M. K. Reuer (2003), Spatial and temporal evolution of lead isotope ratios in the North Atlantic Ocean between 1981 and 1989, *Journal of Geophysical Research: Oceans*, 108(C10), 4-1. DOI: 10.1029/2000JC000762

Wu, J., and E. A. Boyle (1997), Low Blank Preconcentration Technique for the Determination of Lead, Copper, and Cadmium in Small-Volume Seawater Samples by Isotope Dilution ICPMS, *Analytical Chemistry*, 69(13), 2464-2470. doi: 10.1021/ac961204u.

Xie, S.-P., Q. Xie, D. Wang, and W. T. Liu (2003), Summer upwelling in the South China Sea and its role in regional climate variabilities, *Journal of Geophysical Research: Oceans*, 108(C8), 3261. DOI: 10.1029/2003JC001867

Yao, S., B. Xue, and Y. Tao (2013), Sedimentary lead pollution history: Lead isotope ratios and conservative elements at East Taihu Lake, Yangtze Delta, China, *Quaternary International*, 304, 5-12. doi:10.1016/j.quaint.2012.10.058

Zhu, B.-Q., Y.-W. Chen, and X.-Y. Chang (2002), Application of Pb isotopic mapping to environment evaluation in China, *Chemical Speciation and Bioavailability*, 14(1-2), 49-56. DOI:10.3184/095422902782775335

Zhu, L., L. Guo, Z. Gao, G. Yin, B. Lee, F. Wang, and J. Xu (2010), Source and distribution of lead in the surface sediments from the South China Sea as derived from Pb isotopes, *Marine Pollution Bulletin*, 60(11), 2144-2153. doi:10.1016/j.marpolbul.2010.07.026

Chapter 3 : Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities

(published in *Marine Chemistry* [doi:10.1016/j.marchem.2014.10.007](https://doi.org/10.1016/j.marchem.2014.10.007))

Abstract

The spatial and temporal variabilities of Pb were reconstructed from three corals along an east-west transect of the Singapore Strait – in proximity to one of the largest emerging Asian cities and one of the world's busiest ports. In addition to establish the variation in seawater Pb concentration, sources of Pb were also investigated via Pb isotopes in seawater and corals and compared with the isotopes in local aerosols and other potential Pb sources. The annual variation of Pb in corals seems to be related to local annual precipitation while the decadal variation may be related to the long-term development in the region. The decrease of Pb/Ca in coral after 2005 coincided with the regional phasing out of leaded petrol. The Pb isotope ratios in Singapore corals $^{206}\text{Pb}/^{207}\text{Pb}$ rose from as low as ~ 1.166 during the 1960s to ~ 1.189 by the late 1990s, and fluctuated between 1.180-1.198 from the late 1990s to 2010. $^{206}\text{Pb}/^{207}\text{Pb}$ in recent Singapore corals was elevated relative to Singapore atmospheric aerosols (~ 1.140 , which is typical of urban aerosols throughout the southeastern Asian and Indonesian region). The linear distribution of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{207}\text{Pb}$ in triple isotopic plots suggests two end-member mixing of marine Pb between aerosols as the low $^{206}\text{Pb}/^{207}\text{Pb}$ end-member and another source with high $^{206}\text{Pb}/^{207}\text{Pb}$. The proposed high $^{206}\text{Pb}/^{207}\text{Pb}$ sources include: surface runoff from imported south Chinese Pb, crustal materials from riverine inputs or land reclamation, and vessels/dockyard activities.

Keywords: anthropogenic lead, Pb, Pb isotopes, Southeast Asia, South China Sea, Singapore, coral

3.1 Introduction

Lead (Pb) has been an important contaminant in human history, especially since the industrial revolution. The amount of Pb released into the environment increased after the industrial revolution to more than 30 times of global natural emissions in the 1980s, primarily due to the use of leaded petrol (Nriagu 1989, 1979). Prior to the 1980s, the major consumers of leaded petrol were in North America and Western Europe (Kelly et al. 2009; Reuer 1995). As these countries phased out leaded petrol, developing countries (particularly in Asia) continued to use leaded petrol until more recently (e.g: Hirota 2006). Besides leaded petrol consumption, Asian industrialization has also led to an increase in coal burning and high temperature industrial activities, which also contribute to Pb emissions. For example in China, coal consumption has increased 20 times relative to the 1950s (Hao et al. 2008), and in Malaysia, coal consumption has increased nearly 50 times since 1980 (International Energy Statistics). These changes indicate that the relative contributions from different regions and sources to the global Pb flux have certainly changed when compared to the 1980s. Moreover, the recent Asian Pb emissions have received increasing attention, as concentrations of Asian Pb in aerosols were generally an order of magnitude higher than from elsewhere (Bollhöfer and Rosman 2001, 2000). For example, large (~29%) contributions of Asian Pb have been found in aerosols collected in California (Ewing et al. 2010).

Several studies related to Asian anthropogenic Pb in have been undertaken, including the Pb isotope signature in: aerosols and roadside dust from major cities (e.g: Bollhöfer and Rosman 2002, 2001, 2000; Duzgoren-Aydin et al. 2004; Hsu et al. 2006); surface sediments from river mouths and South China Sea basins (e.g: Hao et al. 2008; Ip et al. 2007; Zhu et al. 2010); marine organisms (e.g: Ng et al. 2006); and corals (e.g: Inoue and Tanimizu 2008). Most of these studies have found an anthropogenic Pb signature in the environment, consistent with the recent developments in Asia. But referring to the changing emission inventory of Pb, and the extreme complexity of the transport mechanisms (Church et al. 1990; Flegal 1986; Niisoe et al. 2010), a one-time sample, or even a few years' coverage is not enough to constrain the temporal change of sources and the fluxes of Pb. In this case, a few decades' data coverage would be valuable to resolve the temporal variation of Pb and Pb isotopes in this region.

One approach to study long-term Pb changes is to investigate Pb in natural archives such as corals. During the secretion of coral skeletons, seawater is transported to the calcifying region (Sinclair 2005; Tambutté et al. 2011), and the Pb in seawater can substitute for calcium into the carbonate structure (Shen and Boyle 1987). Although the details of calcification mechanism are still debated, the variation of Pb and Pb isotopes in corals varies closely with that in nearby seawater (Kelly et al. 2009; Shen and Boyle 1987).

The Singapore Strait is an important site to study the anthropogenic impact of Pb to the environment as it was next to one of the most developed/densely populated city in Southeast Asia (Statistics Singapore, 2014). Additionally, the Singapore Strait houses one of the world's busiest ports (American Association of Port Authorities, 2006). The rapid growing city and port is representative of many similarly growing Asian cities. Moreover, the Singapore Strait connects the South China Sea, Java Sea and Northeastern Indian Ocean through Malacca Straits (Figure 3.1). The great connectivity also makes the Singapore Strait an important site to study. In this study, we investigate the historical variabilities of Pb in the Singapore Strait using three coral cores covering the past 40-50 years (Figure 3.1).

3.1.1 Leaded petrol usage in neighboring countries and regions

In general, Pb enters the seawater primarily from atmospheric deposition, which has been largely attributed to leaded petrol emissions in North Atlantic and North Pacific in the previous century (e.g.: Flegal 1986; Weiss et al. 2003). Since leaded petrol is likely to be a major Pb source in the Singapore Strait over the past 50 years, we have estimated the consumption of leaded petrol from the countries adjacent to the Singapore Strait. Major countries surrounding our site include Singapore, Malaysia and Indonesia. Singapore's main island is ~6km north of our coral sites. Malaysia is further north, at the shortest distance of ~25km. Indonesia is to the south of Singapore Strait, and the nearest Indonesian city, Batam, is ~10km from our sites (Figure 3.1). They are all sufficiently close to influence Pb in our corals.

Singapore used petrol with Pb content of 0.8kg/m^3 before 1980. The Pb content was reduced to 0.6 kg/m^3 between 1981 and 1982; and to 0.4 kg/m^3 between 1983 and 1986; and then to 0.15 kg/m^3 from 1987 onwards. Unleaded petrol was introduced to Singapore in 1991, and its market share gradually increased until 1997, when it reached 100% (Ministry of the Environment Singapore, 1987-2000).

Similarly, the Pb content in Malaysian petrol was 0.84 kg/m^3 Pb before 1985; and was reduced to 0.4 kg/m^3 between 1986 and 1989, and to 0.15g/L between 1990 and 1997. Unleaded petrol was first introduced to Malaysia in 1987, and reached 100% market share in 1998 (Afroz et al. 2003).

Indonesia's leaded petrol usage is difficult to estimate as the country phased out leaded petrol city by city. The Pb content of Indonesian petrol was $\sim 0.84\text{ kg/m}^3$ until 1989 (Mukai et al. 1993) and then reduced to 0.3 kg/m^3 by 2001 (Hirota 2006). Leaded petrol was phased out in a few cities beginning in 2001: Jakarta phased out leaded petrol by July 2001; followed by West Java, Cirebon region by October 2001; Bali by November 2001; Batam by June 2003 and Surabaya by September 2004, which together was ~40%

of its national petrol demand at that time (Hirota 2006). The whole country phased out leaded petrol by July 2006. Between 2001 and 2006, the Pb content in petrol in other places in Indonesia was 0.3 kg/m^3 (Hirota 2006; Santosa et al. 2008).

Fortunately when considering Pb in the Singapore Strait, Indonesia should not be considered as a whole. Considering the nature of the narrow strait (~20km) with large cities on each side, the main source of Pb may not be distal transportation, but from the emission from sources that are closer. Batam is the largest city found on the southern margin of the Singapore Strait and is within 20 km of our coral sites. In this case, we think that the prime consideration should be placed on the consumption of Pb in Batam. Estimates of leaded petrol usage from the countries and regions above are shown in Figure 3.2 following the method described in Li et al. (2012).

3.1.2 Pb isotope studies from the Asia-Pacific and Eastern Indian Ocean regions

The isotopic composition of Pb provides clues to investigate the Pb sources. Among the 4 naturally occurring stable isotopes of Pb, ^{204}Pb is the only non-radiogenic isotope and the other 3 isotopes (^{206}Pb , ^{207}Pb and ^{208}Pb) are produced by radioactive decay from ^{238}U , ^{235}U and ^{232}Th (Brown 1962). The relative abundance of Pb isotopes is dependent on the original Pb isotope composition of the ore which depends on the U/Th/Pb composition and age of the source rocks from which the Pb is extracted. Large variabilities in isotopic composition among Pb ores have been observed (Komárek et al. 2008), which allows Pb isotope to be used as a (somewhat smudgy) fingerprint. The Pb isotope in one environment can be compared with a panel of Pb isotopes from different environments in triple- or quadruple- isotope plots, which provide a sense of the similarities and differences of Pb from one environment to another. To provide a framework of Pb isotope for our study, key Pb isotope studies in Asia-Pacific and Eastern Indian Ocean environments are presented here.

The isotopic composition of Pb in aerosols has been studied in major Asian cities from 1994 to 1999, including Kuala Lumpur, Jakarta, Bandung and Ho Chi Minh City (Bollhöfer and Rosman, 2000). The Pb isotopes from these cities were reported as $^{206}\text{Pb}/^{207}\text{Pb} < 1.155$, $^{208}\text{Pb}/^{207}\text{Pb} < 2.430$. Although Singapore was not included in Bollhöfer and Rosman's study, recent aerosol measurements on Pb isotopes performed on samples from the National University of Singapore campus from July 2011 to April 2012, show a consistent isotope ratio as $^{206}\text{Pb}/^{207}\text{Pb} = 1.148 \pm 0.0025$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.425 \pm 0.0030$ (Lee et al. 2014).

Pb isotope data in seawater in this region is extremely sparse, but Pb isotope ratios in corals from Hainan and Jakarta have been reported. A Hainan coral spanning from 1994-

2000 recorded $^{206}\text{Pb}/^{207}\text{Pb} = 1.167 \pm 0.005$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.491 \pm 0.016$; and a Jakarta coral spanning from 1998-2001 recorded $^{206}\text{Pb}/^{207}\text{Pb} = 1.158 \pm 0.007$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.430 \pm 0.010$ (Inoue et al. 2006). Pb isotope ratios in seawater from the central Bay of Bengal were reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.149$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.431$ (Lee et al. 2014).

The Pb isotope ratios of South China Sea sediment have also been surveyed and documented. The general isotopic composition of Pb in South China Sea sediment had $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.199 and $^{208}\text{Pb}/^{207}\text{Pb}$ of ~ 2.491 (Zhu et al. 2010). Low anthropogenic enrichment factors were found in these sediment samples, implying little anthropogenic influence on the sediments, therefore the isotopic composition of Pb in the sediments could reflect natural Pb from the upper crust in this region.

In addition to Pb isotopes in aerosol, seawater, corals and surface sediments, Pb isotopes in coals and Pb ores have been extensively studied and documented. The isotopic composition of Pb from global major coal deposits has been documented by Diaz-Somoano et al. (2009) and the isotopic composition from a number of global major ore deposits have been investigated by Brown in the 1960s (Brown 1962). A more recent review by Flegal et al. summarized Pb isotopic compositions from major ore deposits across China (Flegal et al. 2013). All of these studies provide an important framework for interpreting our Pb data in Singapore corals.

3.2 Sampling and methodology

3.2.1 Site settings of the Singapore Strait

The Singapore Strait is located on the Southwest periphery of the South China Sea and the Northwest side of the Java Sea, and connect to the Eastern Indian Ocean through the Malacca Straits (Figure 3.1). The oceanography of the Singapore Strait is dominated by monsoon-driven currents and closely related to the circulation in the above mentioned seas (Pang and Tkalic, 2003). During the northeast monsoon (November to March), the wind in the South China Sea piles water up to the eastern side of the Malay Peninsula and the strong westward North Equatorial Countercurrent present near Sumatra and western side of Malay Peninsula (Chen et al. 2005), resulting in a westward current in the Singapore Strait. During the southwest monsoon (April to September), the circulation reverses in South China Sea, Java Sea and northeastern Indian Ocean, resulting an eastward current in the Singapore Strait (Chen et al. 2005). In addition to monsoonal currents, tidal currents reverse these prevalent flows twice a day (Chen et al. 2005; Chia et al., 1988).

Three islands along the east-west transect of the Singapore Strait were chosen for our coral sampling: Kusu to the east, Jong in the middle and Hantu to the west. Kusu is 6.4km from Singapore's city center and is minimally developed with a one story tortoise sanctuary and a jetty (Sentosa Development Corporation); Jong, ~9km west from Kusu, remains undeveloped; Hantu is 4.6km west of Jong and 13.4km west of Kusu. Even though Hantu itself is minimally developed, it is surrounded by heavily developed islands, including Bukom/Busing (oil refinery), Jurong (industrial), and Semakau (landfill, Figure 3.1, Sentosa Development Corporation). Sampling information about the corals used in this study is shown in Table 1, including the latitude and the longitude, the depth of the corals and the species of the corals that has been sampled. Seawater samples were also collected at the coral sites to provide a contrast background about the Pb isotope in the environment that corals grew in.

As the Jong coral was the longest record and Jong Island was the only site with no development, the Pb and Pb isotope from Jong coral would be most likely reflecting the variability of Pb in the Singapore Strait. The general variability of Pb in the Singapore Strait using only Jong coral has been discussed elsewhere (in Lee et al. 2014). In contrast this paper focuses on the spatial variability recorded from 3 different coral cores and the isotopic variation of Pb in these corals.

3.2.2 Methodology

Both Pb/Ca and the Pb isotopes were analyzed from our coral samples after careful cleaning. Samples went through a series of treatments using trace metal clean reagents in cleaned plasticware. To ensure the precision, all the samples were cleaned and measured in triplicate. The cleaning method generally followed the methods that were previously described in Shen and Boyle (1988) with slight modification due to the advancement in laboratory techniques. In brief, corals were first crushed into ~700µm pieces for primary cleaning; and further crushed into 270–700µm pieces for secondary cleaning. In each cleaning procedure, alternating alkaline-H₂O₂, dilute (0.1M) HNO₃ and hydrazine-based reductant were applied to selectively dissolve the surface of the coral and to make sure that only the Pb in the carbonate structure remained. The pre-concentration step after the secondary cleaning was skipped as the analysis using quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) allowed samples to be analyzed with lower concentration (10-50nmol/mol) compared to using graphite furnace atomic absorption spectrometer (several µmol/mol, Shen and Boyle 1988) in the 1980s. After secondary cleaning, samples were dissolved in trace metal clean HNO₃ for Pb and Ca measurements. From this dissolved solution, Ca was measured by flame atomic absorption spectroscopy (FAAS) after appropriate dilution, and Pb was measured by Q-ICP-MS with an addition of a known amount of ²⁰⁴Pb enriched spike (Oak Ridge National Laboratory).

For Pb isotope analysis, an Eichrom AG-1X8 (chloride form, 200 – 400 mesh) ion exchange column was employed to purify Pb from the sample matrix. The column procedure typically recovers 99.98% of the Pb from the sample (Reuer et al. 2003). Although we have no data on Pb isotope fractionation during column separation, given the 99.98% recovery rate of Pb, it should be very small compared to the natural variability of the Pb isotope ratios in the environment.

Pb isotope ratios in these coral separates were measured by multi-collector ICP-MS (MC ICP-MS, Micromass/GV IsoProbe) with a Daly ion-counting detector measuring ^{204}Pb . ICPMS mass fractionation was monitored by adding a $^{205}\text{Tl}/^{203}\text{Tl}$ spike into the post-column sample and corrected using the “beta method”; tailing error was corrected by measuring the monoisotopic element ^{209}Bi at half masses. Tl-acid blanks were measured every 10 samples and interpolated values subtracted from the signal assuming an “on peak zero” condition. To ensure the precision, NBS 981 Standard reference Material was measured at the beginning and at the end of the day to calibrate our isotope ratios with the ratios reported in (Baker et al. 2004). Another in house standard was measured at every 5 samples as well as the beginning and the end of the day to constantly monitor the Daly ion counter efficiency. A full description of the mass correction can be found in Reuer et al. (2003) and Boyle et al. (2012).

The Pb isotopes in seawater were prepared using the double $\text{Mg}(\text{OH})_2$ precipitation method by adding small amount of distilled ammonia into the sample to encourage the $\text{Mg}(\text{OH})_2$ precipitation (Reuer et al. 2003). The precipitates were then redissolved using 1.1M HBr and purified using Eichrom ion exchange column as described above.

Common statistical tools were applied in order to interpret the similarities and differences of the data. The statistical tools involved in this study include: calculating mean and standard deviation, T-test, linear regression, and cross-correlation. Such statistical tools will include legends like: standard deviation (SD), correlation coefficient (r), and P-values (P).

3.3 Results

3.3.1 Pb/Ca Variabilities in Singapore corals

The variabilities of Pb relative to Ca (Pb/Ca) in the three Singapore corals are shown in Figure 3.3. Except for the late 1990s to 2010, spatial variabilities among the sites were prominent. Kusu had a generally long term decreasing trend (slope = -0.32, $P = 0.95$) while Jong had a rising trend (slope = 0.24, $P = 0.90$). Despite the difference in long term

trend, the short term variabilities in Jong and Kusu appear to be related to each other ($r = 0.46$, after removing the long-term trends).

Hantu coral had higher Pb/Ca (up to 70nmol/mol) than Jong or Kusu (Figure 3.3), and the temporal variation pattern was less related to Jong ($r = -0.07$) or Kusu ($r = 0.28$). Periods of extremely high Pb/Ca in Hantu coral (one standard deviation higher than the mean) coincided with major industrial developments in Singapore (Figure 3.3). These developments were in Bukom/Busing Island and Jurong Island. Both islands were on the west side of Singapore Strait, close to Hantu (Figure 3.1). To a lesser extent, higher Pb/Ca values during the same period were also observed in other corals.

Temporally, Pb/Ca variability in the Jong and Kusu Singapore corals were positively correlated with the local annual rainfall with a lag time of two years ($r = 0.58$, $P = 0.94$, Figure 3.4). The lag may be due to the comparable residence time of Pb in the oligotrophic surface ocean as estimated by ^{210}Pb studies (~ 4 years estimated from ^{210}Pb data in the eastern Indian Ocean, data from Ostlund et al. 1987; ~ 1.8 years estimated from the northeastern part of the South China Sea, data from Wei et al. 2011).

Seasonal variability of Pb/Ca in Singapore corals was investigated using a few samples from the Hantu coral, where the linear extension rate was nearly 2cm/year. The wet season shows lower Pb/Ca with little variation in isotope ratio (Figure 3.5). Such seasonal variation is not seen in the other two corals as the lower linear extension rate in them prevented us from sampling at seasonal resolution.

It should also be noted that spatial variation of Pb/Ca from all sites converged (in both magnitude and variation pattern) after the late 1990s (see the small figure on the bottom left corner of Figure 3.3). The Pb/Ca in corals all decreased to 20-30nmol/mol after 2005, a value comparable to 1960s and 1970s.

3.3.2 Pb isotope variabilities in Singapore corals

As for Pb/Ca, the temporal Pb isotope variation in Singapore corals also can be categorized into two periods. Before the late 1990s, $^{206}\text{Pb}/^{207}\text{Pb}$ increased from 1.166 to 1.191 and $^{208}\text{Pb}/^{207}\text{Pb}$ increased from 2.442 to 2.484, which generally moved towards higher values. After late 1990s, both temporal and spatial differences between corals were reduced, and coral Pb isotope ratios fluctuated within a narrow range ($^{206}\text{Pb}/^{207}\text{Pb} = 1.185\text{--}1.198$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.464\text{--}2.482$, Figure 3.6). The decrease of the long-term trend in these Pb isotope ratios occurs at the same time as the convergence in Pb/Ca.

The $^{206}\text{Pb}/^{207}\text{Pb}$ in Kusu and Hantu corals generally agree, while the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Jong were slightly higher than Kusu before late 1990s (average difference = 0.01, SD = 0.005, using 1996 as the point of separation). After late 1990s, the difference in

$^{206}\text{Pb}/^{207}\text{Pb}$ between the 2 sites vanished (average difference = 0.004, SD = 0.004). Similarly, $^{208}\text{Pb}/^{207}\text{Pb}$ in Jong was higher than Kusu before late 1990s (average difference = 0.012, SD = 0.006, figure not shown) but was reduced after the late 1990s (average difference = 0.008, SD = 0.006, figure not shown). No clear difference in $^{208}\text{Pb}/^{206}\text{Pb}$ between the Jong and Kusu corals was noted. As these corals were processed by the same method in the same laboratory; the differences cannot be caused by the differences in handling or laboratory environment. There was little possibility for contamination, as the Pb/Ca data triplicates were generally within 5% error with no correlation between Pb isotope ratios and Pb/Ca. Furthermore, the isotopic composition in our corals was clearly different from the laboratory environment where they had been processed, which also indicates little contamination. Therefore we attribute the slight difference between Jong and other sites as true variability. Consequently, the results can be summarized as: the spatial variability in Pb isotope was observed from 1960s to late 1990s, and was diminished after late 1990s.

3.4 Discussion

3.4.1 The Pb/Ca variation in Singapore corals

Pb is released from the combustion of leaded petrol, coal burning, smelting, incineration and high temperature industrial activities in general (Komárek et al. 2008). Also, Pb can be released during the use and disposal of Pb containing materials (such as batteries and lead paint), which can be loosely linked with urbanization. The natural sources of Pb mainly include windblown dusts and volcanogenic particles (Nriagu 1979). Compared to anthropogenic emissions of Pb, natural sources are much smaller (~4% in global Pb flux, Nriagu, 1989), therefore the long term variation of Pb in Singapore corals is likely a result of the urbanization (including leaded petrol consumption) and industrialization of Singapore and the neighboring countries. Although there was no universal long term trend observed before late 1990s, the decrease in Pb/Ca after late 1990s (particularly after 2005) was in parallel with the decline in use of leaded petrol Southeast Asian region (see Figure 3.2).

The short term variabilities of Pb/Ca correlated with local annual rainfall (Figure 3.4, $r=0.58$) with a lag time of ~2 years, suggesting that rainfall might be important in regulating the short term variability of Pb/Ca in corals. This observation could be justified as wet deposition which has been identified as one of the major mechanisms for transporting Pb into the ocean (Duce et al. 1991; Flegal 1986). In addition, rainfall may mobilize the non-atmospheric Pb in the soil and transport it into the sea via surface runoff (Joshi and Balasubramanian 2010).

Besides rainfall, lower or even no correlation was found between Pb/Ca in corals and the leaded petrol from Singapore ($r=0.43$), Malaysia ($r=0.03$) and Batam ($r=0.42$). The low correlation coefficient, together with the deviation of coral Pb isotope from aerosols implies that leaded petrol was not the overwhelming source of Pb to Singapore corals.

Although Pb/Ca in three different coral cores did not show a consistent long term trend, the Pb/Ca from the three corals converged beginning in late 1990s: Pb/Ca in Kusu decreased from $\sim 40\text{nmol/mol}$ in the late 1970s to $\sim 30\text{nmol/mol}$; whilst Pb/Ca in Jong increased from slightly less than 30nmol/mol in the 1970s to $\sim 30\text{nmol/mol}$.

The long-term variation of Pb/Ca between Kusu and Jong may reflect the spatial variation of the local development. In the 1960s and 1970s, the development in Singapore was largely within the area around the Singapore River and Kallang River (Lay 2007, Figure 4.1). The distance of the development area from coral sites may result in higher Pb/Ca in Kusu compare to Jong. As the city progressively expanded, corals from both sites should receive a comparable amount of Pb. In this case, it is reasonable to expect the convergence of Pb/Ca between the two sites.

High Pb/Ca ratios in the Hantu coral were likely related to a series of developments on Singapore's major industrial areas (Figure 3.3). Both industrial islands were close to Hantu and in the shallower region of the Singapore Strait, and the period of development on these two islands coincided with abnormally high Pb/Ca in Hantu coral. It is reasonable to expect that the industrial developments would remobilize some Pb into the water. Concurrently, Hantu was surrounded by other islands (Figure 3.1), the water near Hantu is relatively stagnant, and so the Pb from the industrial islands could not be flushed away easily. Consequently, during these two periods, the Pb/Ca in the Hantu coral was high and the variation pattern deviated from the other two sites.

Seasonal variabilities of Pb/Ca were investigated in the Hantu coral from 1990-1994. The Hantu coral shows a lower Pb/Ca during wet season with little isotope variation. The consistent isotope values seen in both dry and wet seasons indicated that there was little seasonal change in the dominant Pb source. Seasonal variability of Pb/Ca in the Hantu coral was consistent with lower turbidity and a lower downward suspended solid flux in the Hantu during wet seasons (Dikou and van Woesik 2006); this observation implies that rainfall-induced flushing might be an important factor modulating the Pb/Ca in the Hantu coral.

3.4.2 Pb isotopes variation in Singapore corals

Pb isotopes show a high linearity on a triple isotope plot (Figure 3.7), suggesting that Pb in Singapore corals might be a result of mixing between two end members. Therefore a long-term evolution towards higher $^{206}\text{Pb}/^{207}\text{Pb}$ (and $^{208}\text{Pb}/^{207}\text{Pb}$) could be interpreted as

an increasing share of the higher $^{206}\text{Pb}/^{207}\text{Pb}$ source in Singapore corals. In the final period, Singapore coral Pb isotopes fluctuated within a relatively narrow range. This observation could be interpreted as a result of a relatively stable supply of the higher $^{206}\text{Pb}/^{207}\text{Pb}$ source for Singapore corals. The diminished spatial variability in both Pb isotope and Pb/Ca during this phase supports this interpretation.

In the previous decades, there was many sources that potentially contribute Pb to Singapore corals. Leaded petrol was one of the largest sources of Pb and the Pb from vehicle exhausts could enter the surface ocean by atmospheric pathways (Flegal 1986). Monthly aerosol sample measurements in Singapore from June 2011- April 2012, have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.148 ± 0.0025 (Lee et al. 2014), significantly different from the isotope ratios in recent corals ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.185-1.198). Although aerosol sampling was performed in 2011/2012, well after the phasing out the leaded petrol (Singapore in 1997, Malaysia in 1998, Batam in 2003, whole Indonesia in 2006), Pb isotopes in Singapore aerosols was comparable to other Southeast Asian cities between 1994 and 1999 (Kuala Lumpur $^{206}\text{Pb}/^{207}\text{Pb} = 1.141 \pm 0.001$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.410 \pm 0.001$ and Jakarta $^{206}\text{Pb}/^{207}\text{Pb} = 1.131 \pm 0.001$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.395 \pm 0.001$, Bollhöfer and Rosman 2000). Therefore Pb isotopes from aerosols in this region have been consistently too low to determine the isotopic composition of recent Singapore corals.

Despite this the isotope difference between corals and aerosols, the coral isotope ratio can still be remotely linked with the aerosols on the lower side of the triple isotopic plot (Figure 3.7). This implies that atmospheric input was still one of the sources for the Pb in corals, which is normally expected. However, Pb isotope ratios in corals are clearly higher than the ratios in aerosol; this indicates the atmospheric Pb sources may end up as accounting for a small fraction in corals. The higher $^{206}\text{Pb}/^{207}\text{Pb}$ end member in the triple isotope plot is another unidentified Pb source, and the evolution of Pb isotope in Singapore corals implies an increasing share of the as yet unidentified Pb source in Singapore corals, which will be discussed in the following paragraphs.

It would be reasonable to consider that industrial activities and incineration might contribute to Pb in corals. From the incineration ash samples collected in 2010, the Pb isotope in the fly ash was $^{206}\text{Pb}/^{207}\text{Pb} = 1.148 \pm 0.005$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.425 \pm 0.003$, comparable to the Pb isotope in aerosols. Industrial effluent samples are unavailable as of yet, but previously reported aerosol sampling in (Lee et al. 2014) was within 5km of the largest industrial area in Singapore (Jurong Industrial area), therefore the isotopic departure of aerosol and corals may also imply that neither the aerosol emissions from industrial activities nor incineration could be a major contributor to the Pb isotope composition of Singapore corals.

Coal burning emits large amount of Pb to the atmosphere globally; that could also potentially contribute to the Pb in Singapore corals. Indonesia is a large coal consumer, and has also exported more than \$50 billion worth of coal to other countries

(COMTRADE 2012). Since Indonesia is self-sufficient in coal, it is reasonable to expect Indonesian coal is the main source of coal in Indonesia. Between 2002 and 2012, Malaysia imported more than \$10 billion of coal, mainly from Indonesia (66.9%) and Australia (19.6%) (COMTRADE 2012). The consumption of coal in Malaysia and Indonesia is nearly 3 orders of magnitude higher than Singapore. Therefore we expect that the major types of the coals used in this region were from Indonesia and/or Australia. Indonesian coals have a $^{206}\text{Pb}/^{207}\text{Pb} = 1.184 \pm 0.004$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.477 \pm 0.006$; while Australian coals have $^{206}\text{Pb}/^{207}\text{Pb} = 1.121 \pm 0.0002$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.487 \pm 0.0001$ (Díaz-Somoano et al. 2009). Both coal sources have an isotopic composition comparable to the Pb in Singapore corals. However, the Pb isotope composition of Singapore corals deviated from that in aerosols, and the Pb in coal entering the ocean (and then corals) without any footprint in aerosols was unlikely, except possibly from the direct flushing from solid debris released after coal burning. The only coal-based power plant in Singapore was decommissioned in 1962 (Wan and Lau 2009), and the coal used at that time would likely be Australian coals (for which we can cite no official documentation, and have only heard this by word of mouth). As the $^{206}\text{Pb}/^{207}\text{Pb}$ in Australian coal did not agree with that in corals until late 1990s, it is unlikely that the Pb from coal was not seen in the corals while the power plant was operating and has only appeared recently.

Water in the Singapore Strait connects with South China Sea, Java Sea and Northeastern Indian Ocean, and Pb in the Singapore Strait water can be transported from these seas. The seawater sampled in Kusu shown a $^{206}\text{Pb}/^{207}\text{Pb} = 1.197 \pm 0.0003$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.482 \pm 0.0004$, in agreement with the Pb isotopes in corals. In contrast, Pb isotopes in South China Sea water was reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.156 \pm 0.015$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.444 \pm 0.017$ (from eastern part of the South China Sea, Lee et al. 2014) and in Bay of Bengal water was reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.149$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.431$ (Lee et al. 2014). Although no seawater Pb isotope have been reported from the Java Sea, a coral in Jakarta Bay dated between 1998-2001 had $^{206}\text{Pb}/^{207}\text{Pb} = 1.158 \pm 0.007$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.430 \pm 0.010$ (Inoue et al. 2006). Thus Pb isotopes from South China Sea, Bay of Bengal, and Java Sea waters are too low to be a source controlling the Pb isotope composition of Singapore corals.

Scrapings from boat paints and dockyard activities might also be a source of Pb contributing to corals. A recent study reported the Pb content in 6 paints from Asia was higher than 5000mg/kg (Clark et al. 2006). If vessels happen to use these brands of paint, the scrapings from boat paints could contribute Pb into the marine system. Lead paint contamination in corals has also been discussed previously with corals near a dockyard experiencing one standard deviation higher Pb/Ca during the period of dockyard operation (Wang et al. 2011). The Singapore Strait is one of the busiest shipping routes in the world, and all the coral sites are in the vicinity (within ~10km) of the Port of Singapore. High concentrations (420-624 pmol/kg) of Pb were observed in a seawater sample collected near the port of Singapore in January 2010 (Lee et al. 2013). Although it

is difficult to characterize the role of ship paint to Pb in Singapore marine waters, until we have evidence to the contrary we have to consider that vessel paint and dockyard operations may potentially contribute Pb in Singapore Strait. We have no information on the Pb isotopic composition of these paints, so we cannot even speculate whether they contribute to the anomalous Pb isotope composition of Singapore marine waters.

Runoff from various small urban and industrial catchments around the Singapore Strait may also discharge a small amount of water (but concentrated in heavy metals) to the Singapore Strait, potentially contributing Pb to Singapore corals. A recent study of Singapore surface runoff has identified that the runoff from industrial catchments contains more than five times of Pb than residential catchments (Joshi and Balasubramanian 2010). Although no isotope data on surface runoff has been reported, Singapore was one of largest importers of “unwrought Pb” (Harmonized Commodity Description and Coding Systems: HS-96-7801, International Trade Statistics, 2014) from 2000 to 2009 (the 2nd largest trade products containing Pb, comprising 22.8% of total amount of Pb traded in Asia Pacific), and 73% of Singapore’s unwrought Pb was from China (UNEP 2011). The Pb isotope ratios in South Chinese Pb ore was $^{206}\text{Pb}/^{207}\text{Pb} = 1.187 \pm 0.0059$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.475 \pm 0.0038$, (Inoue et al. 2006, Flegal et al. 2013) which is comparable to Singapore coral and seawater. With an isotope agreement between the imported Chinese Pb and the Pb in corals; a relatively clear mechanism delivering the Chinese Pb to Singapore; a reasonable way transporting the Pb to Singapore waters without any footprint in aerosols yet via rainfall, the surface runoff from Industrial catchments could be one of the possible hypothesis explaining the anomalous Pb in Singapore corals.

High $^{206}\text{Pb}/^{207}\text{Pb}$ isotopes in Singapore corals might also be a result of isotope exchange between low-ratio aerosol-derived Pb in seawater and high-ratio crustal material. Although little is known about the potential for isotope exchange of dissolved Pb and crustal particulate Pb, a similar isotope exchange mechanism has been proposed for Sr and Nd isotopes (Oelkers et al. 2012, 2011; Jones et al. 2012). This possible isotope exchange could alter the isotopic ratio of Pb to be more “crustal-like” without requiring an increase in the total Pb concentration. Little was known about the crustal material of Singapore, but the sediment samples in the South China Sea have $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.199 and $^{208}\text{Pb}/^{207}\text{Pb}$ of ~ 2.491 (Zhu et al. 2010), in agreement with the Pb isotopes found in Singapore corals and seawater (Figure 3.7). Based on salinity measurements, the Singapore Strait is within the influence of Johor River (Soeriaatmadja 1956), the crustal materials from Johor River and other rivers in western Malaysia can then be transported just offshore into the Singapore Strait. Furthermore, deforestation, land reclamation and dredging have also increased the sedimentation to the Straits (Thia-Eng et al. 2000). The re-suspension of bottom sediments due to tidal currents has also been noted (Van Maren and Gerritsen 2012). All these mechanisms provide an abundant supply of crustal material with which isotope exchange could happen. In this case, despite lower

$^{206}\text{Pb}/^{207}\text{Pb}$ in local aerosols and in seawater from adjacent seas, the isotopic composition of Pb in these sources may have been modified to higher values due to the isotope exchange with crustal materials as previously hypothesized (Lee et al. 2014). The isotope exchange hypothesis could explain the high $^{206}\text{Pb}/^{207}\text{Pb}$ observed in corals compare to aerosol, it could also explain that the correlation between Pb/Ca and the rainfall without an isotope response. In this case, the isotope exchange hypothesis could be also one of the possible hypotheses and need to be proven by further examine the waters and particles from the river mouths near the Singapore Strait (e.g: Johor River) and the indigenous crustal materials.

3.4.3 Possible attribution of different Pb sources

With the two possible hypothesis (surface runoff, isotope exchange), the attribution of different Pb sources can be estimated by calculating the weightage of isotope ratios from the coral with respect to possible end members. As discussed, the possible end member includes either “aerosol + Chinese Pb” or “aerosol + natural Pb”. Although the attribution of different atmospheric Pb sources to Singapore corals varies largely by the selection of the possible end members (Figure 3.8, the actual data is provided in supplementary material), they both show a decreasing contribution of atmospheric related Pb sources.

The first hypothesis was that the Pb in corals was from the imported Chinese Pb via surface runoff. In this case, the aerosol Pb and South Chinese Pb were chosen as the two end members. The calculation shows that the contribution from Chinese Pb to corals was ~72% in 1970s and 1980s; and rose to more than 98% in 2000s. In contrast, the aerosol Pb contributed ~28% in 1970s and 1980s, and decreased to less than 2% in 2000s. The calculation results agree with the trading statistics as Singapore has imported 1.4×10^{15} kg of Pb containing products during 2000-2009 period (UNEP 2011), 7 orders of magnitude higher than the petrol emissions (in the order of 10^8 kg, Figure 3.2). The amount of imported Pb was so huge that even a small fraction of it entering the Singapore Strait may result in huge change in the Pb isotopes in corals.

The other hypothesis was that the Pb in corals was from natural sources after an isotope exchange. In this case, the aerosol Pb and natural Pb were chosen as the two end members. The calculation shows that the contribution from natural sources was ~43% in 1970s and progressively increased to ~60% in 2000s. On the other hand, the aerosol Pb contributed ~57% in 1970s, and decreased to ~41% in 2000s. The decreasing contribution of atmospheric related Pb was in general agreement of declining of leaded petrol emissions (Figure 3.2).

3.5 Conclusion

Variabilities of Pb in the Singapore Strait were reconstructed from three corals located on an east-west transect of the straits. The temporal and spatial variabilities of Pb/Ca have been discussed, and the Pb isotopes in corals were compared with Pb sources in the region. The following points can be concluded:

1. Large spatial variabilities are observed among corals, yet no clear agreement in the 50-year trend in Pb/Ca is observed. Because the spatial variability of Pb/Ca among sites was associated with only minor variabilities in Pb isotopes, the spatial variation in Pb/Ca may be a reflection of an uneven distribution of Pb sources between the sites. The spatial variation seems to diminish after the late 1990s.
2. Short term variabilities of Pb/Ca in corals positively correlate with local annual precipitation after a two-year lag is considered. Seasonal variability of Pb/Ca in Hantu coral has shown a lower Pb/Ca during wet seasons, while only minor changes in Pb isotopes has been observed. These facts suggest that rainfall is an important factor modulating the Pb/Ca in corals.
3. From the 1970s to the late 1990s, $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore corals increased from 1.166 to 1.191, $^{208}\text{Pb}/^{207}\text{Pb}$ from 2.442 to 2.484. Since the late 1990s, the long-term trend diminished and $^{206}\text{Pb}/^{207}\text{Pb}$ fluctuated between 1.185-1.198, $^{208}\text{Pb}/^{207}\text{Pb}$ fluctuated between 2.464-2.482. Spatial variabilities in Pb isotopes were small between sites, especially after the late 1990s.
4. Recent $^{206}\text{Pb}/^{207}\text{Pb}$ values in Singapore corals are similar to the isotopic composition of Singapore Strait seawater, but deviate in the positive direction from in local aerosol or in seawater from South China Sea, Java Sea or Bay of Bengal. However, Pb isotopes in Singapore corals plot linearly in triple isotopic space, implying a two-source-mixing scenario. The Pb isotope data in Singapore corals in 1960s and 1970s fall on the lower $^{206}\text{Pb}/^{207}\text{Pb}$ side, and can be linked with the Pb isotope in aerosols and incineration ash. Pb isotopes in more recent part of the corals show higher $^{206}\text{Pb}/^{207}\text{Pb}$ and ratios, possibly suggesting a second source of Pb dominating the region. The possible second source is hypothesized as either direct scrap from leaded paint on vessels or dockyard activities or the surface runoff of industrial Pb from various catchments around the Singapore Strait or as a result of isotope exchange of anthropogenic Pb with crustal materials. All of these hypotheses are possible; however the surface runoff and the isotope exchange hypothesis remained the most possible

hypothesis when considering the mechanism transporting the mysterious Pb to Singapore water.

5. The contribution of possible Pb sources varies with respect to different choices of end members, while the decreasing contribution of atmospheric related Pb was prominent.

Figure 3.1: Map of the study site. On the top left corner is a map of Singapore Strait and its relative location in Southeast Asia; on the bottom left corner is a zoomed map of Singapore Strait with respect to the countries and regions in its vicinity, the adjacent countries and ocean basins are denoted. The large map on the right shows a close view of coral sites in this study. The coral sites are highlighted in dots. The figure also shows Singapore's major industrial areas (Jurong and Bukom/Busing); the landfill (Semakau); and the city center (around Singapore River).

Figure 3.2: The estimated Pb emission from petrol in Malaysia (white open rectangles), Singapore (black filled diamonds) and Batam (grey filled triangles). Data are estimated by the product of: road sector petrol emissions; the allowable Pb content in the petrol; the market share of the leaded petrol; and the tailpipe emission factor. Maximum consumption of leaded petrol occurred in 1980 for Singapore; 1984 for Malaysia; and 2003 for Batam.

Figure 3.3: The Pb/Ca in corals from multiple islands in the Singapore Strait. The average error of Pb/Ca in Singapore corals is 2.59 nmol/mol, taken from one standard deviation of triplicate sample measurements. The Pb/Ca are arranged geographically with Kusu on the east, Jong in the middle, and Hantu on the west. Grey open arrows indicate a period of Bukom/Busing development (an industrial Island 400m from Hantu, covering the period of 1984-1989, the location of Bukom/Busing is illustrated in Figure 3.1) and the black filled arrows indicate the period of Jurong island development (the largest industrial island in Singapore, 5km from Hantu, 1991-1998, Figure 3.1). The small figure on the bottom left corner illustrates the Pb/Ca in corals on the same scale.

Figure 3.4: The Pb/Ca from Jong coral (longest record and similar as Kusu, in black filled squares) is correlated with local annual rainfall (in grey open squares) with a lag time of 2 years, possibly due to the residence time of Pb in Surface Ocean. Annual precipitation data retrieved from IRI/LDEO Climate data library.

Figure 3.5: The variation of Pb/Ca (black diamonds) and 206/207 ratio (open squares) in the Hantu coral from 1990 to 1994. Wet seasons (December to March, also called Northeast Monsoon season) are marked in darker color. Such seasonal variation is not clearly seen in other corals.

Figure 3.6: The temporal variation of 206/207 ratio in Singapore corals. From east to west in the Strait, the sites are Kusu (grey filled circles), Jong (black filled squares), and Hantu (white open diamonds). The average two standard error is 0.0001. Note the Singapore aerosol 206/207 ratio is around 1.14 (measured over a year in 2012), the Southeast Asian aerosol 206/207 ratio is around 1.145, taken between 1994 and 1999 (Bollhöfer and Rosman, 2000). The dotted line shows the point of separation between period one and period two. The two periods are differentiated by the magnitude of spatial variability among sites (see text).

Figure 3.7: Triple-isotope plot for Pb isotopes in Singapore coral and selected sources around the region of study, including various Pb ores (Inoue and Tanimizu 2008), aerosols (Bollhöfer and Rosman 2001, Lee et al. 2014), coals (Diaz-Somoano et al. 2009), and the South China Sea sediments (Zhu, et al. 2010). The Kusu water is the seawater sample taken near the coral site in this study.

Figure 3.8: The triple-isotope plot of Pb isotopes in corals (filled squares) compare to the most possible end members suggested in this study, including Singapore aerosol(open circle, Lee et al. 2014); South Chinese Pb ore (open triangle, Inoue et al. 2006); natural regional soil (open diamonds, from central catchment reserve of Singapore, unpublished data). The coral data are divided by every 10 years. The dash line illustrates the linearity of these possible sources to Singapore corals.

Table 3.1: General information about the Singapore coral cores used in this study

Site taken ^a	GPS location ^b	Species	Number of bands ^c	Expected timespan
Kusu	1°13'31.30"N, 103°51'38.98"E	Porites lutea	41	1968-2010
Jong	1°12'55.21"N, 103°47'16.55"E	Porites lutea	48	1962-2010
Hantu	1°13'36.64"N, 103°47'16.55"E	Porites lutea	27	1983-2010

a. the corals were all taken within 5m depth, with a tidal range of ~2m

b. the latitude and longitude shows the location of the reefs where our corals were sampled

c. annual bands are based on the x-ray image with confirmed by fluorescence image

References for Chapter 3

- Afroz, R., Hassan M.N., and Ibrahim N. A., (2003). Review of air pollution and health impacts in Malaysia. *Environmental Research* 92(2): 71-77.
- American Association of Port Authorities (2006), World Port Ranking, retrieved on July 29, from: www.aapa-ports.org.
- Baker, J., Peate, D., Waight, T., and Meyzen, C., (2004). Pb isotopic analysis of standards and samples using a ^{207}Pb - ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical Geology* 211(3-4): 275-303.
- Bollhöfer, A., and Rosman K.J.R., (2002). The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres. *Geochimica et Cosmochimica Acta* 66(8): 1375-1386.
- Bollhöfer, A., and Rosman K.J.R., (2001). Isotopic source signatures for atmospheric lead: the Northern Hemisphere. *Geochimica et Cosmochimica Acta* 65(11): 1727-1740.
- Bollhöfer, A., and Rosman K.J.R., (2000). Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochimica et Cosmochimica Acta* 64(19): 3251-3262.
- Boyle, E. A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkamper, M., Rouxel, O., Sohrin, Y., Stirling C., Thompson, C., Vance, D., Xue, Z., and Zhao, Y., (2012). GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnology and Oceanography: Methods*(10): 653-665.
- Brown, J.S., (1962). Ore leads and isotopes. *Economic Geology* 57(5): 673-720.
- Chen, M., Murali, K., Khoo, B.C., Lou, J., and Kumar, K., (2005). Circulation Modelling in the Strait of Singapore. *Journal of Coastal Research* 21(5): 960-972.
- Chia, L.S., Khan, H., and Chou, L.M., (1988), The coastal environmental profile of Singapore.
- Church, T.M., Véron, A., Patterson, C.C., Settle, D., Erel, Y., Maring, H.R., and Flegal, A.R., (1990). Trace elements in the North Atlantic troposphere: Shipboard results of precipitation and aerosols. *Global Biogeochemical Cycles* 4(4): 431-443.
- Clark, C.S., Rampal, K.G., Thuppil, V., Chen, C.K., Clark, R., and Roda, S., (2006). The lead content of currently available new residential paint in several Asian countries. *Environmental Research* 102(1): 9-12.
- COMTRADE (Commodity Trade Statistics Database). United Nations Statistics Division. retrieved on May 12, 2012 from : <http://comtrade.un.org/db/mr/daCommoditiesResults.aspx?px=H2&cc=2701>
- Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez-Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B., and Weiss, D.J., (2009). Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing. *Environmental Science and Technology* 43(4): 1078-1085.

- Dikou, A., and van Woesik, R., (2006). Survival under chronic stress from sediment load: Spatial patterns of hard coral communities in the southern islands of Singapore. *Marine Pollution Bulletin* 52(1): 7-21.
- Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., and Zhou, M., (1991). The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5(3): 193-259.
- Duzgoren-Aydin, N.S., Li, X.D., and Wong, S.C., (2004). Lead contamination and isotope signatures in the urban environment of Hong Kong. *Environment International* 30(2): 209-217.
- Ewing, S.A., Christensen, J.N., Brown, S.T., Vancuren, R.A., Cliff, S.S., and Depaolo, D.J., (2010). Pb isotopes as an indicator of the Asian contribution to particulate air pollution in urban California. *Environmental Science and Technology* 44(23): 8911-8916.
- Flegal, A.R., Gallon, C., Ganguli, P.M., and Christopher H.C., (2013). All the Lead in China. *Critical Reviews in Environmental Science and Technology* 43(17): 1869-1944.
- Flegal, A.R., (1986). "Lead in tropical marine systems: A review." *Science of the Total Environment* 58(1-2): 1-8.
- Hao, Y., Guo, Z., Yang, Z., Fan, D., Fang, M., and Li, X., (2008). Tracking historical lead pollution in the coastal area adjacent to the Yangtze River Estuary using lead isotopic compositions. *Environmental Pollution* 156(3): 1325-1331.
- Hirota, K. (2006). Review of Lead Phase Out for Air Quality Improvement in the Third World Cities: Lessons from Thailand and Indonesia. *Journal of Studies in Regional Science* 32(2): 527-541.
- Hsu, S.C., Chen Liu, S., Jeng, W.L., Chou, C.C.K., Hsu, R.T., Huang, Y.T., and Chen, Y.W., (2006). Lead isotope ratios in ambient aerosols from Taipei, Taiwan: Identifying long-range transport of airborne Pb from the Yangtze Delta. *Atmospheric Environment* 40(28): 5393-5404.
- Inoue, M., Hata, A., Suzuki, A., Nohara, M., Shikazono, N., Yim W.W., Hantoro, W.S., Donghuai, S., and Kawahata, H., (2006). Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons. *Environmental Pollution* 144(3): 1045-1052.
- Inoue, M. and Tanimizu, M., (2008). Anthropogenic lead inputs to the western Pacific during the 20th century. *Science of the Total Environment* 406(1-2): 123-130.
- International Energy Statistics. Total Coal Consumption by Year. Retrieved on July 1, 2014 from: <http://www.eia.gov/coal/data.cfm>
- International Trade Statistics. Harmonized Commodity Description and Coding Systems (HS), United Nations. Retrieved on August 21, 2014 from: <http://unstats.un.org/unsd/tradekb/Knowledgebase/Harmonized-Commodity-Description-and-Coding-Systems-HS>

- Ip, C.C.M., Li, X.D., Zhang, G., Wai, O.W.H., and Li, Y.S., (2007). Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, *South China. Environmental Pollution* 147(2): 311-323.
- Jones, M.T., Pearce, C.R., and Oelkers, E.H., (2012). An experimental study of the interaction of basaltic riverine particulate material and seawater. *Geochimica et Cosmochimica Acta* 77: 108-120.
- Joshi, U.M., and Balasubramanian, R., (2010). Characteristics and environmental mobility of trace elements in urban runoff. *Chemosphere* 80(3): 310-318.
- Kelly, A.E., Reuer, M.K., Goodkin, N.F., and Boyle E.A., (2009). Lead concentrations and isotopes in corals and water near Bermuda, 1780-2000. *Earth and Planetary Science Letters* 283(1-4): 93-100.
- Komárek, M., Ettler, V., Chrastný, V., and Mihaljevič, M., (2008). Lead isotopes in environmental sciences: A review. *Environment International* 34(4): 562-577.
- Lay, L. T. (2007). Shaping Singapore's Cityscape. *Innovation* 7(2): 32-35.
- Lee, J.M., Boyle, E.A., Nurhati, I.S., Pfeiffer, M., Meltzner, A.J., Suwargadi, B., (2014). Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. *Earth and Planetary Science Letters* 398(0): 37-47.
- Lee, J.M. (2013), Evolution of anthropogenic Pb and Pb isotopes in the deep North Atlantic Ocean and the Indian Ocean, Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.
- Li, Q., Cheng, H., Zhou, T., Lin, C., and S. Guo, (2012), The estimated atmospheric lead emissions in China, 1990–2009, *Atmospheric Environment*, 60(0), 1-8.
- Ministry of the Environment Singapore (1987-2000). Pollution control department: Annual Report.
- Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K., and Hashimoto, Y., (1993). Characterization of sources of lead in the urban air of Asia using stable lead isotopes. *Environmental Science and Technology*. 27(7): 1347-1356.
- Ng, O.-H., Tan, B.C., and Obbard, J.P., (2006). Lichens as bioindicators of atmospheric heavy metal pollution in Singapore. *Environmental Monitoring and Assessment* 123(1-3): 63-74.
- Niisoe, T., Nakamura, E., Harada, K., Ishikawa, H., Hitomi, T., Watanabe, T., Wang, Z., and Koizumi, A., (2010). A global transport model of lead in the atmosphere. *Atmospheric Environment* 44(14): 1806-1814.
- Nriagu, J.O., (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279(5712): 409-411.
- Nriagu, J.O., (1989). A global assessment of natural sources of atmospheric trace metals. *Nature* 338(6210): 47-49.
- Oelkers, E.H., Gislason, S.R., Eiriksdottir, E.S., Jones, M., Pearce, C.R., and Jeandel, C., (2011). The role of riverine particulate material on the global cycles of the elements. *Applied Geochemistry* 26(SUPPL.): S365-S369.

- Oelkers, E.H., Jones, M.T., Pearce, C.R., Jeandel, C., Eiriksdottir, E.S., and Gislason, S.R., (2012). Riverine particulate material dissolution in seawater and its implications for the global cycles of the elements. *Comptes Rendus Geoscience* 344(11-12): 646-651.
- Ostlund, H.G., Craig, H., Broecker, W.S., and Spencer, D., (1987). GEOSECS Atlantic, Pacific and Indian Ocean expeditions. Vol 7 Shorebased data and graphic. Washington, D.C.
- Pang, W.C. and Tkalich P., (2003). Modeling tidal and monsoon driven currents in the Singapore Strait. *Singapore Maritime & Port Journal*: 151-162.
- Reuer, M.K., (1995). Centennial-scale Elemental and Isotopic Variability in the Tropical and Subtropical North Atlantic Ocean. Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.
- Reuer, M.K., Boyle, E.A., and Grant, B.C., (2003). Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS. *Chemical Geology* 200(1-2): 137-153.
- Santosa, S.J., Okuda, T., and Tanaka, S., (2008). Air pollution and urban air quality management in Indonesia. *Clean - Soil, Air, Water* 36(5-6): 466-475.
- Sentosa Development Corporation. Kusu Island. Retrieved on May 13, 2013, from: <http://www.sentosa.com.sg/en/nature/southern-islands/kusu-island/>
- Sentosa Development Corporation. Sisters Islands and Pulau Hantu. Retrieved on May 13, 2013, from: <http://www.sentosa.com.sg/en/nature/southern-islands/sisters-islands-pulau-hantu/>
- Shen, G.T. and Boyle, E.A., (1987). Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. *Earth and Planetary Science Letters* 82(3-4): 289-304.
- Shen, G.T., and Boyle, E.A., (1988). Determination of lead, cadmium and other trace metals in annually-banded corals. *Chemical Geology* 67(1-2): 47-62.
- Sinclair, D.J., (2005). Correlated trace element "vital effects" in tropical corals: A new geochemical tool for probing biomineralization. *Geochimica et Cosmochimica Acta* 69(13): 3265-3284.
- Soeriaatmadja, R.E., (1956). Surface salinities in the Straits of Malacca. *Marine Research in Indonesia*(1-2): 27-41.
- Statistics Singapore (2014), Population & Land Area, edited by Singapore Department of Statistics.
- Tambutté, S., Holcomb, M., Ferrier-Pagès, C., Reynaud, S., Tambutté, É., Zoccola, D., and Allemand, D., (2011). Coral biomineralization: From the gene to the environment. *Journal of Experimental Marine Biology and Ecology* 408(1-2): 58-78.
- Thia-Eng, C., Gorre, I.R.L., Ross, S.A., Bernad, S.R., Gervacio, B., and Ebarvia, M.C., (2000). The Malacca Straits. *Marine Pollution Bulletin* 41(1-6): 160-178.
- UNEP(United Nations Environmental Program) 2011. Study on the possible effects on Human Health and the Environment in Asia and the Pacific of the trade of products containing Lead, Cadmium and Mercury.

van Maren, D.S., and Gerritsen, H., (2012). Residual flow and tidal asymmetry in the Singapore Strait, with implications for resuspension and residual transport of sediment. *Journal of Geophysical Research: Oceans* 117(C4).

Wan, M.H., and Lau, J., (2009). Heritage places of Singapore, Marshall Cavendish Editions.

Wang, B.S., Goodkin, N.F., Angeline, N., Switzer, A.D., You, C.F., and Huguen, K., (2011). Temporal distributions of anthropogenic Al, Zn and Pb in Hong Kong Porites coral during the last two centuries. *Marine Pollution Bulletin* 63(5-12): 508-515.

Wei, C.-L., Lin, S.-Y., Sheu, D.D.-D., Chou, W.-C., Yi, M.-C., Santschi, P.H., and Wen, L.S., (2011). Particle-reactive radionuclides (^{234}Th , ^{210}Pb , ^{210}Po) as tracers for the estimation of export production in the South China Sea. *Biogeosciences* 8(12): 3793-3808.

Weiss, D., Boyle E.A., Wu, J., Chavagnac, V., Michel, A., and Reuer, M.K., (2003). Spatial and temporal evolution of lead isotope ratios in the North Atlantic Ocean between 1981 and 1989. *Journal of Geophysical Research: Oceans* 108(C10): 1978-2012.

Zhu, L., Guo, L., Gao, Z., Yin, G., Lee, B., Wang, F., and Xu, J., (2010). Source and distribution of lead in the surface sediments from the South China Sea as derived from Pb isotopes. *Marine Pollution Bulletin* 60(11): 2144-2153.

Chapter 4 : A century long sedimentary record of anthropogenic lead (Pb), Pb isotopes and other trace metals in Singapore

(manuscript submitted to *Limnology and Oceanography*)

Abstract

Reconstructing the history of metal deposition in Singapore lake sediments can contribute to understanding anthropogenic and natural metal deposition in the data-sparse Southeast Asian region. The 20th century trace metal variability was reconstructed from a ^{210}Pb -dated, 40 cm long sediment freeze-core, collected near the depocenter of MacRitchie Reservoir in central Singapore. The concentration of Pb, Pb isotopes and eleven other metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) were analyzed using an Inductive Coupled Plasma - Mass Spectrometer (ICP-MS) after acid digestion. Based on this sedimentary record, the natural Pb level inferred from sediments deposited prior to the MacRitchie dam wall construction in the 1890s was less than 2 mg/kg for both soil and sediment, with a corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.20 . The concentration of Pb increased between the 1910s and 1950s, peaking at 53 mg/kg in the 1950s. From the 1950s to 1960s, the concentration of Pb decreased to 41 mg/kg and remained at ~ 42 mg/kg until the 1980s. Subsequently, the Pb concentration increased to 55 mg/kg in the 1990s. Correspondingly, the $^{206}\text{Pb}/^{207}\text{Pb}$ in the sediment decreased from ~ 1.20 in 1910s to less than 1.14 in the 1990s. The $^{206}\text{Pb}/^{207}\text{Pb}$ in the top sediment is concordant with the $^{206}\text{Pb}/^{207}\text{Pb}$ signal of aerosols in Singapore and other Southeast Asian cities at that time, suggesting that Pb in the reservoir sediment was mainly from atmospheric deposition. The concentration of Pb in MacRitchie sediments is below the toxic concentrations specified in guidelines around the world. Using the Pb concentration in the topmost layer of sediment, the estimated atmospheric Pb flux in Singapore today is $\sim 1.6 \times 10^{-2}$ g/m²-yr. Eleven other metals preserved in the sediment were determined. A principal component analysis showed that the variabilities of Ag, As, Ba, Cd, and Co all show an increase towards the 1990s, with a local concentration peak in the mid-20th century, while the variabilities of Zn, Ni, Cr, Tl and U were different from the group due to different sources (for U, Tl) or different emission guidelines (for Zn, Ni, Cr).

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

4.1 Introduction

Anthropogenic lead (Pb) has been an important contaminant in human history, especially after the Industrial Revolution. The emission of anthropogenic Pb reached a level greater than 20 times the global natural Pb emission in the 1980s (Nriagu 1989). The anthropogenic Pb sources are mainly atmospheric (Komárek 2008, Nriagu 1979), and among the anthropogenic Pb, the globally overwhelming source in the 1970s-1980s was leaded petrol (Nriagu 1979; 1990). Pb has been recorded in many environments, including the atmosphere (e.g.: Patterson and Settle 1987; Duce et al. 1991; Bollhöfer and Rosman 2000, 2001; Zhu et al. 2002; Flegal et al. 2013); terrestrial (e.g.: Boutron et al 1995; Osterberg et al. 2008; De Deckker et al. 2010; Kylander et al., 2010; Lee et al., 2011); aquatic (e.g.: Arnason and Fletcher 2003, Erel and Patterson, 1994; Graney et al. 1995; Harrington et al. 1998; Kober et al. 1999; Li et al. 2000; Eades et al. 2002;) and oceanic (Turekian, 1977; Schaule and Patterson, 1981; Boyle et al. 1986, 2005; Reuer, 1995; Flegal, 1986; Weiss et al., 2003; Kelly et al., 2009) environments. Since the 1990s, the Asian contribution of Pb has received greater attention as the major Pb contributors in 1970s and 1980s (North America and Western Europe) phased out leaded petrol earlier than many Asian countries. Besides leaded petrol, the increasing emissions of Pb from coal combustion and other industrial sources has also received regional attention in Asia as a consequence of the phasing out of leaded petrol (Díaz-Somoano et al. 2009) and the recent economic boom (e.g.: Hang et al. 2010; Flegal et al. 2013; Zurbrick et al., 2014).

Therefore, the Asian region is increasingly important in assessing the relative contribution of Pb to the global Pb flux. However, Southeast Asia remains data-sparse in terms of environmental data on Pb emissions, despite being the last region in the Asia-Pacific to phase out leaded petrol (Hirota 2006; USAID 2009). In addition to Pb petrol inputs, the rapid economic development in Southeast Asia has also contributed to a dramatic increase in coal burning (International Energy Statistics 2012), exacerbating the Pb emissions (Lee et al. 2014). For example, coal consumption in Malaysia and Indonesia in 2012 was nearly 50 and 30 times of the 1980s average respectively (International Energy Statistics 2012).

The documented Pb content in many Southeast Asian environments has raised concern. For example, the Pb concentrations in recent aerosols in Southeast Asian cities were much higher than Europe, Australia and North America (Bollhöfer and Rosman 2000, 2001); and the Pb/Ca in a coral from southwest of Sumatra records an increasing trend of Pb in the coastal waters during the 1980s (Lee et al. 2014). In addition, the Pb content in lichens from the Singapore Strait was found to be in the upper range of the values recorded (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). It also allows the comparison of different environments with various 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 variation of the isotopes can differentiate various Pb sources, which 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 (Foster and Charlesworth, 1996) and can be used as archives of century-scale Pb variation (Komárek et al. 2008). The reliability of lacustrine records has been demonstrated from studies carried out in Europe, North America and China (e.g: Graney et al. 1995; Eades et al. 2002; Cheng and Hu 2010). For example, the Pb isotopes in Scottish lake sediments reflected the variability in coal burning, smelting the indigenous Pb ores, and the usage of leaded petrol at different periods (Eades et al. 2002). In North America, the temporal change of $^{206}\text{Pb}/^{207}\text{Pb}$ in a sediment core from Lake Erie reflected the release of Pb from various sources, including deforestation, coal combustion, ore smelting and the usage of leaded petrol (Graney et al. 1995). In China, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in recent sediments has a similar ratio to a combination of Chinese Pb ore and Chinese coal, suggesting that the major Pb source in China includes a combination of locally-sourced Pb ore and coal (Cheng and Hu 2010). Lima et al. (2009) analyzed an anoxic estuarine lake for Pb and Pb isotopes and found evidence for industrial and leaded petrol emissions as well as tracing an unusual Pb isotope peak in 1850 to smelting of Upper Mississippi Valley ores.

In order to assess the anthropogenic Pb input in the Southeast Asian region to reconstruct the century-scale variation of Pb in the environment in response to historical emissions, and to evaluate the relative contribution of various Pb sources at different time periods, we analyzed Pb and Pb isotopes from a ^{210}Pb -dated, sediment core recovered from the MacRitchie Reservoir in the central catchment region of Singapore (Figure 4.1). The variabilities of Pb and Pb isotopes are compared with historical Pb emissions from Southeast Asian countries and the isotopic composition of Pb from potential sources. The temporal variation of Pb is also compared with the temporal variabilities of eleven other metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) recovered from the sediment.

4.2 Sampling and methodology

4.2.1 Sediment coring

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. Since no natural lakes occur on the island, a reservoir in the central nature reserve was chosen to investigate the onshore deposition of Pb (Figure 4.1a) and trace metals for comparison with a published marine coral record from the Singapore Strait. 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). Previous studies on the water quality have indicated very low dissolved oxygen near the bottom (Chen et al. 1996), suggesting limited bioturbation of the lake floor sediment.

A sediment freeze core was collected on the 6th August 2012 from the southeastern and deepest (9m deep) section of the MacRitchie Reservoir (Figure 4.1). 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. During sampling, the core was collected by lowering a freeze-corer (filled with slurry of dry ice and ethanol) to the sediment-water interface and pushing into the underlying sediments (Shapiro 1958). The sediment was frozen when collected and the well-preserved stratigraphy was sampled at 2 to 8 cm increments (depending on the sediment density and water content) for ^{210}Pb dating and geochemical analysis. A water sample was also collected to compare the dissolved Pb content in the water with sediments. The water sample was filtered through 0.4 μm Millipore filters, and acidified in a class 100 environment using trace metal clean reagents and labware as laid out in Lee et al. (2011).

4.2.2 Sediment core description 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 supported ^{210}Pb (the ^{210}Pb originally embedded in the sediments) was

subtracted from total ^{210}Pb based on the measured ^{214}Pb at 351.9keV by comparison to ancient pitchblende standard (US-DOE CRM 101).

In order to convert the ^{210}Pb data into estimated dates, the generally accepted Constant flux-constant sedimentation (CF-CS) model was chosen in this study and the unsupported ^{210}Pb activity (C) at depth (z) was expressed by the following equation (Tylmann, 2004):

$$C = C_0 \times \exp(-\lambda \times z / s), \quad (1)$$

Where C_0 was the ^{210}Pb activity at the top of the core in Bq/kg; λ is the decay constant for ^{210}Pb (0.03114 yr^{-1}); and s was the sedimentation rate in cm/yr (Figure 4.3b).

4.2.3 Sample preparation and metal analysis

The sediment samples were leached by a combination of 1.75M HNO_3 -3M HCl for 24 hours following the method described by Graney et al. (1995). This method effectively extracts the metals adsorbed on the particle surface without completely dissolving the mineral grains, therefore, the leachate represents mainly the anthropogenic fraction of the metals. After the leaching, the samples were centrifuged and the supernatant was extracted. The supernatant was then filtered and diluted for metal analysis. The metal concentrations of Pb, Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn were analyzed, and Pb isotope measurements determined using anion column purification by multi-collector plasma mass spectrometry (G/V IsoProbe). The concentrations of the metals were analyzed by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, VG PlasmaQuad 2+).

To determine the Pb concentration 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 concentration 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 (1 ppb) was added to each sample and standard (SPEX CertiPrep), and the Pb concentration in the sample was calculated by comparing the Pb/In in the sample and the standard (Vanhaecke et al. 1992). The results produced by the two analytical methods were compared and differed by less than 1% demonstrating the reproducibility of our results.

The concentrations of Ag, As, Ba, Cd, Co, Cr, Ni, Tl, U and Zn were also analyzed using the internal standard method described above.

Pb isotope ratios (204, 206, 207, and 208) in the samples were measured by a multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, Micromass/GV 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 following the method described in 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 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 concentration of Pb in the water was measured by isotope dilution after a single-batch resin chromatography as laid out in Lee et al. (2011). In brief, an aliquot of cleaned NTA resin was added to the sample (~2400beads/1.3mL water sample) at pH=5.3. After 2 days, the resins beads were rinsed multiple times using distilled deionized water, and then leached in 0.1M HNO_3 . The leachate was analyzed for Pb concentration using Q-ICP-MS.

4.2.4 Regional settings on Pb emission

Pb emitted from leaded petrol and coal combustion from Singapore, Malaysia, Indonesia and Thailand between 1971 and 2000 has been estimated by Lee et al. (2014, Figure 4.2) using a formula proposed by Li et al. (2012). Pb emissions from petrol was estimated as the product of the road-sector petrol consumption, Pb content of the petrol, market share of leaded petrol and the emission factor (the ratio between the amount of Pb in the petrol and the Pb emitted from the tailpipe, Li et al. 2012). 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 1956 (Ramlan 2014). For a better comparison to the historical period recorded in our core, Pb emissions from Singapore were estimated based on the following equation (modified from Li et al., 2012):

$$E_{\text{coal}} = PP \times P_{\text{percap}} \times C \times [\text{Pb}]_{\text{coal}} \times EF \quad (2)$$

Where the E_{coal} is the Pb emitted from coal power plants (t); 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 compare to the amount of the amount of Pb associated with coal burning. The 1920-1959 population data came from Goldewijk et al. (2011) and the 1960 to 1970 population data

came from Statistics Singapore (2014). The P_{percap} since 1970 was adopted from the United Nation database while between 1920s and 1970 the P_{percap} recorded in 1971, as 1154.8 kwh/person was adopted due to lack of data (UN Data 2014). As the electricity consumption should be lower in 1920s-1960s because of a less industrialized society; therefore the P_{percap} used during this period only reflected an upper limit of the Pb emission. The constants used in the coal estimation in this study are 0.472 kg/kWh C (e.g. Lee et al. 2014) study for consistency consideration. 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 by coal burning was plotted in Figure 4.2b, together with the Pb emission estimated using gasoline by Lee et al. (2014).

4.2.5 Principal component analysis on 12 metals in the sediments

In order to determine the potential correlation among the metals, a principal component analysis (PCA) was carried out on the concentration of the metals in the sediment. The concentration data for each metal was centered by subtracting its mean; and standardized by dividing by its standard deviation. The treated data were analyzed by the PCA function in Matlab (Jackson 1991), which returned the eigenvectors, the eigenvalues and the sample scores.

4.3 Results

4.3.1 Sediment core description and ^{210}Pb chronology

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

The ^{210}Pb data was fit with a constant sedimentation model of 0.29 cm/yr (Figure 4.3c). As such, the ^{210}Pb date at 34 cm was ca. 1895. It is likely that the color change at 33 cm marked the damming of the creek valley and the formation of the reservoir in year 1891, which is in good agreement with the ^{210}Pb date. Using the date of sampling (year 2012) and the date of reservoir's formation (year 1891) as the two end-member constraints, the ^{210}Pb dates characterize the chronology of the sediments reasonably well (Figure 4.3c). The deeper portion of the core was classified as a paleo-soil because the construction of the reservoir changed the depositional environment of the basin; the derived ^{210}Pb dates are not likely to be applicable to the paleo-soil. The pale-soils

samples were all considered as “before 1895” without a specific date. Based on the measured ^{210}Pb activity and the CF-CS model, the calculated calendar years are shown in Figure 4.3c and are used in subsequent discussions.

4.3.2 Variation of Pb and Pb isotopes in the sediment

The concentration of the isotope dilution--derived Pb concentration in the sediment core is shown in Figure 4.5(a). The average relative standard deviation (rsd) of the Pb content was 1.57%. 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 (Figure 4.4). Since the sediments were subsampled at 2 to 8 cm increments, the trace metal data should be interpreted as an average concentration over the period the sample represents (ca. 10 years). The period each sample represents is listed in the supplementary material.

Samples from the deeper than 33 cm in the core should be considered as “prior to 1895” and specific dates for this section cannot be accurately determined. The Pb concentrations in these samples were 1.2 ± 0.6 mg/kg (Figure 4.5a). 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 concentration of Pb started to increase in the 1920s and reached a peak of 53 mg/kg in the 1950s, a 27 fold increase from the 1910s. After the 1950s peak, the concentration of Pb decreased to 41 mg/kg in the 1960s, remaining stable over the next two decades (roughly 1960-1984), and then finally increasing to 53 mg/kg in the 1990s. Due to the decadal resolution sampling, events occurring within the past ~10 years are not resolvable.

The temporal variation of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are shown in Figure 4.5b. In the paleosoil samples prior to 1895, the three $^{206}\text{Pb}/^{207}\text{Pb}$ data points were similar and >1.215 . Since 1895, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from >1.215 to ~ 1.140 . The decreasing trend is consistent throughout the core.

4.3.3 Concentration of other metals in the sediments

Besides Pb, the temporal variabilities of the other 11 metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) in the sediments are shown in Figure 4.6. The low rsd for replicates for all the metals (within 3.5%) validates the precision of the measurement methodology. Most metals had their lowest concentrations at the bottom of the core (prior to 1895), and highest concentration in 1990s. The concentrations of the Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn in 1990s were significantly higher than during the 1900s. Other than the high concentrations in the 1990s, the variability of the metals are compared and illustrated using PCA (Figure 4.7). The first and second principal components (PCs) explain ~95% of

the variance (Table 2). Based on the PC scores, the metals can be divided into three different groups (see Figure 4.7a):

1. The first group of elements are positively related to PC1 at similar loadings and weakly correlated to PC2. This group includes Pb, Ba, Cd, Ag, As and Co.
2. The second group positively correlates to PC1 and PC2. This group includes U and Tl.
3. The third group positively correlates to PC1 but negatively correlates to PC2. This group includes Zn, Ni and Cr.

Reconstructing the first PC showed that each metal concentration increased from the 1890s to 1950s, slightly decreased during the 1960s and increased from the 1970s to 1990s (Figure 4.7b). The second PC showed that the concentration increased slightly in the 1910s, plateaued from the 1920s to 1980s and then decreased sharply in the 1990s (Figure 4.7b). This reconstruction of PCs closely matches the measured changes of each metal in Figure 4.6.

The increase of Cu was the largest among all the metals (from less than 1 mg/kg to more than 300 mg/kg). Additionally, the increase in Cu was the most rapid among the metals as almost all the increase happened from 1980s to 1990s. For all these reasons, Cu was treated as a fourth group and is discussed separately. Consequently, Cu was not included in the PCA as the highly skewed variation could potentially overwhelm the variation of other metals.

4.4 Discussion

4.4.1 The Pb content and isotopic composition in the natural background

The natural background Pb level in the catchment provides an important baseline for interpreting the variation of Pb in the sediment, and the natural background Pb isotopic signal was important in assessing the relative contribution of anthropogenic sources. The Pb from natural sources (i.e. weathering of continental rocks) is only dominant in pristine environments (Bindler et al. 1999) or in the deeper sections in the sediment (Graney et al. 1995; Kober et al. 1999, Table 1). Prior to this study, there was no established baseline Pb level from lacustrine sediments in the Singapore region, considering that manufacturing became a prominent industry in Singapore from the 1930s (Kwa et al. 2009; Singapore Manufacturing Federation 2012). The limited industrial development prior to the 1900s suggested that the soil/sediment before the 1900s should not contain much anthropogenic Pb. Therefore we assume the background Pb level was equivalent to ~2 mg/kg that was measured from the lowest sections of the soil and sediment recovered from MacRitchie Reservoir.

The lowest section included three soil samples and one sediment sample deposited prior to the 1900s. The soil samples had a Pb concentrations of 1.9 ± 0.6 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.215 ± 0.001 (Figure 4.5), the sediment sample had a Pb concentration of 1.9 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.199, similar to the soil samples (Figure 4.5). The concentration of Pb in these samples were the lowest across the core, and are also in the lower range of the Pb concentrations found in published pristine/unpolluted soils and sediments from Europe, North America and China (Table 1, compared with Graney et al., 1995; Bindler et al., 1999; Kober et al., 1999; Hansmann and Köppel, 2000; Teutsch et al., 2001; Eades et al., 2002; Wong et al., 2002; Renberg et al. 2002; Watmough and Hutchinson, 2004; Gallon et al., 2005, 2006; Lee et al., 2008; Zhao et al., 2011).

The $^{206}\text{Pb}/^{207}\text{Pb}$ in the soils and sediment samples from the lowest section was 1.211 ± 0.008 , which is in good agreement with the general $^{206}\text{Pb}/^{207}\text{Pb}$ of the upper continental crust across the globe (~ 1.20 for $^{206}\text{Pb}/^{207}\text{Pb}$; Chow and Patterson, 1962; Hamelin et al., 1990), as well as the reported values in the Asian region, including K-feldspar from Asian rivers (Bodet and Schärer 2001) and surface sediments in the deep basin of the South China Sea (1.18 to 1.22 for $^{206}\text{Pb}/^{207}\text{Pb}$; Zhu et al., 2010). The $^{206}\text{Pb}/^{207}\text{Pb}$ in the initial reservoir sediment sample was slightly lower (~ 1.199) than the soil samples. It was difficult to attribute such a difference to anthropogenic Pb since the industrial development in Singapore region in 1900s was minimal (Kwa et al. 2009). The difference in $^{206}\text{Pb}/^{207}\text{Pb}$ of similar scale has been observed previously in a Scottish lake (Eades et al., 2002), implying that even within the same catchment, it was possible to observe Pb isotope differences. Therefore, the limited industrial development in and before 1900s, the low Pb concentration and the crustal $^{206}\text{Pb}/^{207}\text{Pb}$ values suggest that the Pb in the soil and sediment from the lowest section (the lowest 4 values) should be the natural background levels, which has a [Pb] of ~ 1.9 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb} = 1.211 \pm 0.008$ (Figure 4.5).

4.4.2 The variation of Pb content and isotopic composition in 20th century

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 deposition of Pb in the catchment could be mobilized into sediment by weathering of soil particles

which contain some Pb (Eades et al. 2002, Kober et al. 1999). Since the soil particles in the catchment should only contain geogenic Pb and some atmospheric deposited Pb, the catchment input should not introduce additional sources into the system. By excluding the other possibilities, atmospheric deposition was likely the primary cause of Pb variability to the MacRitchie Reservoir sediments.

The Pb content increased higher in the core, and was 55 mg/kg at the top of the core, ~29 times the natural baseline (Figure 4.5). The high Pb content implies that the anthropogenic Pb has been deposited in these sediments. Besides the increasing concentration towards the 1990s, the Pb content in the 1950s was 53 mg/kg, comparable to the 1990s' value. It was reasonable to expect a lower consumption of leaded petrol in the 1950s, therefore the high Pb concentration in the 1950s is probably not be solely caused by leaded petrol. Instead, the high concentration in the 1950s may be attributed to atmospheric emissions from "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 (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). In addition, the coal power plant situated on the south of Singapore was decommissioned in the 1970s (Ramlan 2014). The introduction of the Clean Air Act in 1971 and the closure of the coal power plant coincide with a ~20% decline in Pb and a significant decrease in some other metals (As, Ag, Cd, and Zn) in the sediment from the 1950s to the 1980s (Figure 4.5 and 4.6).

The concentration of Pb 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 4.2). The prevailing winds of Singapore are northerly to northeasterly during northeast monsoon season and are southerly to southwesterly during the southwest monsoon season (National Environmental Agency 2009). Therefore, the tailpipe-emitted Pb could be transported to Singapore from neighboring countries, such as Malaysia or Indonesia. Although the leaded petrol emission from Singapore and Malaysia started to decrease in the mid-1980s (Figure 4.2a), the emission from Indonesia continued to increase until 2006 (Hirota 2006; Lee et al. 2014, Figure 4.2a). The estimated Pb emissions from petrol only extend back to the 1970s, therefore the overlap between the petrol emission time series and our sedimentary record is too short to make a quantitative comparison. However 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 investigate the concentration of Pb in the sediment from a toxicity standpoint, we compared our sediment Pb concentration to the dissolved Pb in MacRitchie water and various sediment quality guidelines from around the world. The dissolved Pb in the MacRitchie water was measured as $7.6 \times 10^{-2} \mu\text{g/L}$, two orders of magnitude lower than the allowable dissolved Pb in the drinking water $10 \mu\text{g/L}$ (Attorney General's Chambers Singapore. 2008). Among the sediment guidelines used around the world, the threshold concentrations (lower than the concentration that would result in rarely observed adverse effects on benthic organisms) of Pb range from 28 to 85 mg/kg dry weight (Burton 2002), and the mid-range concentrations (above the concentration that would likely cause adverse effects on benthic organisms) range from 82 to 530 mg/kg (Burton 2002). Despite the large ranges observed among sediment quality guidelines, the Pb in MacRitchie sediment (peak concentration of $\sim 55 \text{ mg/kg}$) may be higher than some of the threshold concentrations on a consensus base, but still lower than the mid-range concentrations.

In order to gain a better understanding about the variation of Pb in the sediment, the Pb concentration in the sediment was compared with other published records, including a Pb/Ca record from a coral spanning 50 years from the only undeveloped island in the Singapore Strait (Jong Island, Figure 4.5 Chen et al. 2015) and a several sediment cores from the same region (from Nee Soon Swamp and Lower Reservoir; Koh 2014, Ee 2000). Due to the low resolution of the MacRitchie Reservoir sediment data, the overlap between the coral and the sediment only included three data points from the sediment record but 46 points from the coral record. In this case, the comparison could only be made using a 10-year running mean of the coral Pb/Ca data. Despite the low resolution, the Pb/Ca in coral was in agreement with the Pb content in the sediment ($R^2=0.92$). It was noted that the Pb/Ca in the coral started to decrease after 2003, in parallel to the general phasing out the leaded petrol in Southeast Asian region (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. The variation of Pb in the MacRitchie Reservoir sediment was also in general agreement with sedimentary records from Nee Soon Swamp, as the Nee Soon core showed an increase in Pb content from 40 cm upwards (Koh 2014). In parallel to Nee Soon Swamp, the Lower Pierce Reservoir sediment showed enrichment in Pb in the top 10 cm (Ee 2000). The comparison of MacRitchie Reservoir sediment to the Nee Soon Swamp and Lower Peirce Reservoir sediment were limited as ^{210}Pb -dating for the Nee Soon Swamp and Lower Peirce Reservoir sediments were 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.

4.4.3 The variation of Pb isotope ratios in the sediment

Pb isotope ratios from aerosols across Southeast Asian cities in the 1990s showed values of $^{206}\text{Pb}/^{207}\text{Pb}$ of 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 (Bollhöfer and Rosman 2000). Although Singapore was not included in Bollhöfer and Rosman's study, our more recent aerosol measurements show that $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore aerosol was ~ 1.145 (Lee et al. 2014), similar to Pb isotopes in the previously published Southeast Asian aerosols. The range of Pb isotopes in Southeast Asian aerosols compared well with the Pb isotope in the MacRitchie sediment from the 1970s to 1990s (~ 1.137 , Figure 4.5 and 4.8). The agreement in Pb isotope data between the sediments and regional aerosols supports the hypothesis that leaded petrol and atmospheric deposition 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). Industry 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, the Pb from recent industry emissions (after phasing out of leaded petrol) should have been included in the recent aerosol values, but this value was indistinguishable from the aerosols measured in other major Southeast Asian cities when leaded petrol was still in use.

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), comparable to the isotope ratios in the top of the sediment core (1.140 to 1.137). It is difficult to differentiate the relative contribution of Pb from petrol and incineration as they have very similar isotopic composition (Chen et al., 2014). However, the isotopic agreement between incineration fly ash and the sediment suggested that incineration might be a 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). Pb emitted from Malaysia and Indonesia has increased since the 1970s (Figure 4.2b), in conjunction with the increasing Pb concentration in the MacRitchie Reservoir sediments. However, the Pb isotope from the Australian and Indonesian coal (the type of coal most possibly 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 $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.195$ and $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.473$ for Australian coals (Díaz-Somoano et al. 2009), 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 4.5). Therefore the 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 4.5 and 4.8), implying the burning of coal as a possible source of Pb in the 1910 to 1940s period.

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 4.5). Although the hypothesis of mixing not exclude the possible contribution from coal as the Indonesian coals and Australian coals have isotopes 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 4.8), which would likely be a result of mixing between the natural Pb and atmospheric Pb sources.

4.4.4 An estimation of Pb flux into the Singapore region

Since the atmospheric deposition is the main cause of Pb in recent MacRitchie Reservoir sediment, the atmospheric Pb flux into Singapore region could be estimated using the equation modified from Kober et al. (1999):

$$\text{Pb Flux} = S \times \rho \times (C_{\text{measured}} - C_{\text{natural}}) \quad (3),$$

where S is the sedimentation rate, ρ is the dry bulk density of the sediment ($1.05 \times 10^{-3} \text{ g/mm}^3$), and C_{measured} and C_{natural} are the concentrations of Pb in the sediment from measured sample and natural baseline (1.9 mg/kg), respectively. The estimated Pb flux using top core concentration (55 mg/kg) is $1.6 \times 10^{-2} \text{ g/m}^2\text{-yr}$.

Alternatively, the atmospheric Pb deposition could be calculated using the actual aerosol and rainwater data.

$$\text{Pb Flux} = (C_{\text{aerosol}} \times v)_{\text{wet}} + (C_{\text{rain}} \times d)_{\text{dry}} \quad (4),$$

The Pb flux is calculated as a sum of wet deposition and dry deposition as equation 4, where C_{aerosol} is the atmospheric concentration of Pb (10 ng/m³, 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 ppb, measured from 2009 to 2012, pers. comm. Prof. Webster), d is the annual rainfall depth in Singapore (2400 mm/yr; Public Utilities Board 2011). With the aerosol and rainwater data, the calculated Pb flux is $1.4 \times 10^{-2} \text{ g/m}^2\text{-yr}$. The annual atmospheric Pb flux estimated by MacRitchie Reservoir sediment agrees well with the calculations using current atmospheric measurements.

4.4.5 Variation of other metals compared to Pb

The PCA analysis of the metals grouped the metals by their co-variability (Figure 4.7). Each group of metals had very similar loadings on the PCA biplot (Figure 4.7a), and were highly correlated. The first group of metals contains Pb, suggesting that the metals in this group (Pb, Ba, Cd, Ag, As and Co) have behaved similarly. The variabilities 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 was that the production of many metals (i.e. Pb, Cd, Cr, Hg, Zn) has increased over the last two centuries and their use by Singapore industry has increased significantly during the 20th century (e.g. Foster and Charlesworth 1996). Although the rate of increase varies among the metals, on the large scale, the production of the metals all 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 emission control.

The second group discerned by the PCA analysis included Tl and U and record an increase in concentration from the 1890s to 1950s (positively correlated with PC1) and a decrease in concentration from the 1950s to 1990s (positively correlated with PC2). The decreasing concentration from the 1950s to 1990s differs from the behavior of other metals. 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). Similarly, U concentrations in MacRitchie Reservoir sediments (0.4 to 2.4 mg/kg) are within the concentration range of sedimentary rocks (0.45 to 3.7 mg/kg; Turekian and Wedpohl 1961). Therefore, based on this evidence, U and Tl cannot be attributed clearly to anthropogenic activities.

The third group recognized in the PCA includes Zn, Ni and Cr. These elements recorded a sharp increase from the 1980s to 1990s. The decrease in concentration in the 1970s was not clearly observed in Ni or Cr, possibly because these metals were not included in the emission control guidelines (Singapore Anti-Pollution Unit 1970-1972). Zn, Ni and Cr 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.

Copper had the largest magnitude and most rapid increase of all of the metals measured from MacRitchie Reservoir (Figure 4.6). Such increases could only be caused by anthropogenic activities. Copper sulfate (CuSO_4) had been used as an algicide in reservoirs around the globe for decades (e.g. Hawkins et al. 1987). Such application has remained the most common method for controlling the 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 sediments as the same order of increase has been observed in other reservoirs that have employed CuSO_4 treatment (e.g. AWWA 1995, Haughey et al. 2000). Other terrestrial sources of and pumping activities via copper pipes could also be possible explaining the Cu in MacRitchie sediments, but at present these sources remain elusive.

4.5 Conclusion

The temporal variation of Pb and Pb isotopes were reconstructed from a sediment freeze core retrieved from MacRitchie Reservoir, located in the central nature reserve of Singapore. The core spans the period 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 in potential sources, and the variation of eleven other metals (Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Tl, U and Zn) in the sediment. This study signifies the importance of identifying Pb and other metal concentrations and Pb isotopes from high-resolution archives in terrestrial environments to reconstruct the history of Pb and trace metals, and the following conclusions can be drawn:

1. The baseline (before any human intervention) Pb content in the Singapore soil is ~ 2 mg/kg and ~ 1.215 in $^{206}\text{Pb}/^{207}\text{Pb}$, and the Pb content in the MacRitchie Reservoir sediments is ~ 2 mg/kg and ~ 1.199 in $^{206}\text{Pb}/^{207}\text{Pb}$.
2. The Pb content in the sediment increases almost linearly 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 temporal variation of Pb content in the sediment was in agreement with the variation

of Pb/Ca measured from a coral retrieved from the Singapore Strait. The estimated atmospheric Pb flux in Singapore region is $\sim 1.6 \times 10^{-2} \text{ g/m}^2\text{-yr}$.

3. The dissolved Pb concentration in MacRitchie water was $7.6 \times 10^{-2} \text{ }\mu\text{g/L}$, 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.
4. 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.
5. The Ag, As, Ba, Cd, Co, Cr, Ni and Zn content in the sediment have all increased greatly, and range from 3 to 78 fold increase from the 1910s to 1990s. The increase in metal content parallels trends in the urbanization and industrialization of the Singapore region. 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 Tl 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.

Figure 4.1: A map of the sampling site in this study. (a) Map of Macritchie Reservoir with the major inlet and the dam. The black star denotes the coring location. The relative location of Macritchie Reservoir in Singapore is shown on the rectangular map on the bottom left corner. The black area in the rectangular map on the bottom left corner indicates the Macritchie Reservoir. Singapore's relative location within Southeast Asia is shown by the latitude and longitude beside the map. (b) 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, including the direct discharge, the atmospheric deposition, and the natural/anthropogenic Pb from the catchment. The coring site in this study is highlight as a black star.

4.2: Estimated historical Pb emissions from petrol usage and coal combustion in the countries around Singapore. Including Singapore (white open diamonds), Malaysia (grey filled triangles), Thailand (black filled squares) and Indonesia (white open circles). Dotted lines are for the years there data are unavailable. (a) the estimated Pb emissions in tons from petroleum Pb usage (Lee et al. 2014). (b) the estimated Pb emission from coal burning for electricity production (Lee et al. 2014).

Figure 4.3: The illustration of: (a) The picture of the sediment core. The top, bottom of the core and the change in color during reservoir's construction were all marked. (b) Unsupported ^{210}Pb activities (black diamonds) in Bq/kg of dry sample. The blue dotted line is the 0.29cm/yr fit using a constant sedimentation rate model (see section 2.2). The vertical axis on the left shows the depth of the sediment and the axis on the right shows the converted calendar years from the ^{210}Pb data. (c) the sediment composition change throughout the core, includes clay (light grey); silt (dark grey) and sand (white). The red horizontal bar across (b) and (c) highlights the time when the reservoir was constructed.

Figure 4.4: The comparison between the Pb concentrations measured by 2 methods. The horizontal axis is the concentration measured by isotope dilution method and the vertical axis is by Indium spike method. The dashed line is the least square regression from the method comparison, which records a significant positive relationship between the two methods.

Figure 4.5: (a) The Pb concentration in the sediments (grey filled diamonds) compare to the Pb/Ca in the Jong island coral (open diamonds, Lee et al. 2014). The GPS location for the coral is $1^{\circ}12'54.25''\text{N}$, $103^{\circ}47'11.17''\text{E}$. (b) the 206/207 ratio (grey filled circles) and 208/207 (open triangles) in the sediment. Note that the 206/207 ratios for natural Pb is ~ 1.20 and for local aerosol is ~ 1.14 .

Figure 4.6: The concentrations of all the metals (As, Pb, Cu, Ag, Cd, Zn, Cr, Co, Ni, U, Tl, and Ba) measured in the sediment are plotted. The horizontal axes are all in mg/kg and the vertical axes are the corresponding years of each sample.

Figure 4.7: The plots show the results from principal component analysis. The first and second principal components could explain around 95% of the total variabilities in the core. (a) The PCA bi-plot showing PC1 versus PC2. The directions and expressing powers of each metal in the PC space are expressed in vectors. (b) The first 2 eigenvectors (PCs) from the principal component analysis (PCA). The horizontal axis is a dimensionless unit to express the variation of the principal component; and the vertical axis is the calendar year.

Figure 4.8: The plot of 206/207 ratios against 208/207 ratios in Singapore sediments (white open triangles) together with a panel of possible end-members. The Singapore aerosols (Lee et al. 2014) and incineration fly ashes are shown in grey filled circles; the Indonesian coals (Diaz-Somoano et al. 2009) are shown in grey filled squares; the Australian coals (Diaz-Somoano et al. 2009) are shown grey filled triangles; the South China Sea sediments (Zhu et al. 2010) are shown in small grey filled crosses; the south Chinese Pb ore are shown in grey open crosses; the Singapore corals are shown in dark grey dots; and the Chinese aerosol, Thailand aerosol, Indonesian aerosols are shown in black open squares; grey open diamonds; black open circles correspondingly. The dashed line illustrates the binary mixing scenario between natural and atmospheric Pb sources.

Table 4.1: Lead concentrations and isotope ratios of the natural soils and sediments

Soil

Location	Methodology	[Pb] (mg/kg)	206/207	208/207	Source
Macritchie reservoir (Singapore)	HNO ₃ -HCl leach	1.451-2.560	1.214-1.215	2.506-2.507	this study
Rural south central Ontario (Canada)	HNO ₃ leach	~6-7	1.31-1.32		Watmough and Hutchinson (2004)
Pearl River Delta (China)	HNO ₃ + HClO ₄ leach	7.7-54.7	1.195	2.499	Wong et al. (2002)
Jerusalem (Israel)	HNO ₃ + HClO ₄ + HF leach	17.0-19.0	1.206-1.219		Teutsch et al. (2001)
pristine forest soil (Sweden)	HNO ₃ + HClO ₄ leach	<0.1			Bindler et al. (1999)
Swedish pre-industrialization forest soil (Sweden)	HNO ₃ + HClO ₄ leach	2.4-6.7	1.372-1.455		Bindler et al. (1999)
Swiss unpolluted soil (Switzerland)	HNO ₃ leach	5.4-17.5	1.209	2.472	Hansmann and Koppel (2000)

Sediments

Location	Methodology	[Pb] (mg/kg)	206/207	208/207	Source
Macritchie reservoir (Singapore)	HNO ₃ -HCl leach	1.911	1.199	2.488	this study
Lake Constance (Central Europe)	HNO ₃ -HCl leach	20.5-21.7	1.197	2.472	Kober et al. (1999)
Lake Erie and other lakes (Northeastern US)	HNO ₃ -HCl leach	11.3-13.3	1.252	2.492	Graney et al. (1995)
Loch Lomond north (Scotland)	HNO ₃ -HCl leach	23-29	1.160		Eades et al. (2002)
Loch Lomond south (Scotland)	HNO ₃ -HCl leach	11.0-19.0	1.174		Eades et al. (2002)
Loch Ness (Scotland)	HNO ₃ -HCl leach	10.4-13.4	1.215		Eades et al. (2002)
Swedish lakes (Sweden)	HNO ₃ + HClO ₄ leach	~2-17	1.28-2.01		Renberg et al. (2002)
Lake Tantaré (Canada)	HNO ₃ + HClO ₄ + HF leach	4.14-9.12	1.161	2.444	Gallon et al. (2006)
Lake Despériers and other lakes (Canada)	HNO ₃ +HF leach	~5-8	1.221		Gallon et al. (2005)
Hongfeng Lake (southwest China)	HNO ₃ leach	29.04	1.233	2.478	Zhao et al. (2011)
Liangzhi Lake (central China)	HNO ₃ + HClO ₄ leach	15.5	1.193	2.495	Lee et al. (2008)

Table 4.2: Eigenvalues and variance contribution in principal component analysis

Principal component	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%

References for Chapter 4

- Agency for Toxic Substances and Disease Registry (ATSDR), (2007). Toxicological Profile for Barium and compounds (Update), edited, Atlanta, GA: U.S. Department of Public Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR), (2012). Toxicological Profile for Chromium. U.S. Department of Health and Human Services, U.S. Public Health Service, Agency for Toxic Substances and Disease Registry.
- Alleman, L. Y., Véron, A. J., Church, T. M., Flegal, A. R., and Hamelin B., (1999). Invasion of the abyssal North Atlantic by modern anthropogenic lead, *Geophysical Research Letters*: 26(10), 1477-1480.
- American Association of Port Authorities, World Port Ranking (2008). Retrieved from: <http://aapa.files.cms-plus.com/PDFs/061410TABLE%20B%20WORLD%20PORT%20RANKING%202008.pdf>.
- Arnason, J.G., and Fletcher, B.A., (2003). A 40+ year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA, *Environmental Pollution*: 123(3), 383-391.
- Attorney General's Chambers Singapore, (2008). Environmental Public Health (Quality of Piped Drinking Water) Regulations 2008. ENVIRONMENTAL PUBLIC HEALTH ACT. Chapter 95.. Retrieved from: <http://statutes.agc.gov.sg/aol/search/display/view.w3p;page=0;query=Id%3A%223e48e1ef-867a-4d80-819a-0a48b7ddff0a%22%20Status%3Ainforce;rec=0#Sc->.
- AWWA (American Water Works Association), (1995). Request for Proposals: Alternative (i.e., non-copper) Algae Control Strategies. American Water Works Association Research Foundation, (RFP 267).
- Baker, J., Peate, D., Waight, T., and Meyzen, C., (2004). Pb isotopic analysis of standards and samples using a ^{207}Pb - ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS, *Chemical Geology*, 211(3-4), 275-303.
- Bindler, R., Brännvall, M-L., Renberg, I., Emteryd, O., and Grip, H., (1999). Natural lead concentrations in pristine boreal forest soils and past pollution trends: A reference for critical load models, *Environmental Science and Technology*: 33(19), 3362-3367.
- Bodet, F., and Schärer, U., (2001). Pb isotope systematics and time-integrated Th/U of SE-Asian continental crust recorded by single K-feldspar grains in large rivers, *Chemical Geology*: 177(3-4), 265-285.
- Bollhöfer, A., and Rosman, K.J.R., (2001). Isotopic source signatures for atmospheric lead: The Northern Hemisphere, *Geochimica et Cosmochimica Acta*: 65(11), 1727-1740.
- Bollhöfer, A., and Rosman, K.J.R., (2000). Isotopic source signatures for atmospheric lead: The Southern Hemisphere, *Geochimica et Cosmochimica Acta*: 64(19), 3251-3262.

- Boutron, C.F., Candelone, J-P., and Hong, S., (1995). Greenland snow and ice cores: Unique archives of large-scale pollution of the troposphere of the Northern Hemisphere by lead and other heavy metals, *Science of the Total Environment*: 160-161, 233-241.
- Boyle, E.A., Chapnick, S.D., Shen, G.T., and Bacon, M.P., (1986). Temporal variability of lead in the western North Atlantic. *Journal of Geophysical Research: Oceans*: 91(C7), 8573-8593.
- Boyle, E.A., Bergquist, B.A., Kayser, R.A., and Mahowald N., (2005). Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA: Temporal variability and an intermediate water hydrothermal plume. *Geochimica et Cosmochimica Acta*: 69(4), 933-952.
- Boyle, E.A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkamper, M., Rouxel, O., Sohrin, Y., Stirling, Y., Thompson, C., Vance, D., Xue, Z., Zhao, Y.. (2012). GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnology and Oceanography: Methods*: (10), 653-665.
- Burton, J. G. A. (2002) Sediment quality criteria in use around the world. *Limnology*, 3, 65-76.
- Chen, M., Lee, J-M., Nurhati, I, Switzer, A.D., and Boyle E.A., (2015). Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities, *Marine Chemistry*: 168, 49-59.
- Chen, W., Tan, S.K., and Tay, J.H., (1996). Distribution, fractional composition and release of sediment-bound heavy metals in tropical reservoirs. *Water, Air, and Soil Pollution*: 92(3-4), 273-287.
- Cempel, M.; Nikel, G., (2006). Nickel: A Review of Its Sources and Environmental Toxicology, *Polish Journal of Environmental Studies*: 15(3), 375-382.
- Cheng, H., and Hu, Y., (2010). Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review, *Environmental Pollution*: 158(5), 1134-1146.
- Chorus, I., Bartram, J. (Eds.), (1999). Toxic cyanobacteria in water. A guide to their public health consequences, monitoring and management, Routledge, London: pp. 275–312.
- Chow, T.J., and Patterson C.C., (1962). The occurrence and significance of lead isotopes in pelagic sediments. *Geochimica et Cosmochimica Acta*: 26, 263-308.
- COMTRADE (Commodity Trade Statistics Database), (2012). United Nations Statistics Division, edited 2012.
- De Deckker, P., Norman, M., Goodwin, I.D., Wain, A., and Gingele, F.X., (2010). Lead isotopic evidence for an Australian source of aeolian dust to Antarctica at times over the last 170,000 years, *Palaeogeography, Palaeoclimatology, Palaeoecology*: 285(3-4), 205-223.
- Devi, G.U., (2002). Singapore's 100 Historical Places, Archipelago Press in association with National Heritage Board.
- Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez – Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B., and Weiss, D.J., (2009). Stable lead isotope

compositions in selected coals from around the world and implications for present day aerosol source tracing, *Environmental Science and Technology*: 43(4), 1078-1085.

Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M. (1991), The atmospheric input of trace species to the world ocean, *Global Biogeochemical Cycles*: 5(3), 193-259.

Eades, L.J., Farmer, J.G., MacKenzie, A.B., Kirika, A., and Bailey-Watts A.E., (2002). Stable lead isotopic characterisation of the historical record of environmental lead contamination in dated freshwater lake sediment cores from northern and central Scotland, *Science of the Total Environment*, 292(1-2), 55-67.

Ee, K.L.R. (2000). Variabilities of heavy metal concentrations in reservoir sediments. Honors thesis. National University of Singapore.

Erel, Y., and Patterson C.C., (1994). Leakage of industrial lead into the hydrocycle, *Geochimica et Cosmochimica Acta*: 58(15), 3289-3296.

EPA, (2005). Toxicological review of zinc and compounds - in support of summary information on the integrated risk information system. U.S. Environmental Protection Agency, Washington D.C..

Flegal, A.R., (1986). Lead in tropical marine systems: A review, *Science of the Total Environment*: 58(1-2), 1-8.

Flegal, A.R., Gallon, C., Ganguli, P.M., and Conaway, C.H., (2013). All the Lead in China, *Critical Reviews in Environmental Science and Technology*: 43(17), 1869-1944.

Foster, I.D.L., and Charlesworth, S.M., (1996). Heavy metals in the hydrological cycle: Trends and explanation, *Hydrological Processes*: 10(2), 227-261.

Gäggeler, H., von Gunten, H.R., and Nyffeler, U., (1976). Determination of ^{210}Pb in lake sediments and in air samples by direct gamma-ray measurement, *Earth and Planetary Science Letters*: 33(1), 119-121.

Gallon, C., Tessier, A., Gobeil, C., and Beaudin, L., (2005). Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: Inferences from Pb isotopes and PAH profiles, *Geochimica et Cosmochimica Acta*: 69(13), 3199-3210.

Gallon, C., Tessier, A., Gobeil, C., and Carignan, R., (2006). Historical perspective of industrial lead emissions to the atmosphere from a Canadian smelter, *Environmental Science and Technology*: 40(3), 741-747.

Goldewijk, K.K., Beusen, A., van Drecht, G., and de Vos, M., (2011). The HYDE 3.1 spatially explicit database of human-induced global land-use change over the past 12,000 years, *Global Ecology and Biogeography*: 20(1), 73-86.

Graney, J.R., Halliday, A.N., Keeler, G.J., Nriagu, J.O., Robbins, J.A., and Norton, S.A., (1995). Isotopic record of lead pollution in lake sediments from the northeastern United States, *Geochimica et Cosmochimica Acta*: 59(9), 1715-1728.

- Grönholm, T., Aalto, P.P., Hiltunen, V., Rannik, Ü., Rinne, J., Laakso, L., Hyvönen, S., Vesala, T., and Kulmala, M., (2007). Measurements of aerosol particle dry deposition velocity using the relaxed eddy accumulation technique. *Tellus*: B, 59.
- Hamelin, B., Grousset, F., and Sholkovitz, E.R., (1990). Pb isotopes in surficial pelagic sediments from the North Atlantic, *Geochimica et Cosmochimica Acta*: 54, 37-47.
- Hamelin, B., Ferrand, J.L., Alleman, L., Nicolas, E., and Véron, A., (1997). Isotopic evidence of pollutant lead transport from North America to the subtropical North Atlantic gyre, *Geochimica et Cosmochimica Acta*: 61, 4423.
- Hansmann, W., and Köppel, V., (2000). Lead-isotopes as tracers of pollutants in soils, *Chemical Geology*: 171(1–2), 123-144.
- Hargraves, A.J., (1993). History of coal mining in Australia, Australian Institute of Mining and Metallurgy, Parkville.
- Harrington, J.M., LaForce, M.J., Rember, W.C., Fendorf, S.E., and Rosenzweig, R.F., (1998). Phase associations and mobilization of iron and trace elements in Coeur d'Alene Lake, Idaho, *Environmental Science and Technology*: 32(5), 650-656.
- Haughey, M.A., Anderson, M. A., Whitney, R. D., Taylor, W. D., and Losee, R. F., (2000). Forms and fate of Cu in a source drinking water reservoir following CuSO₄ treatment. *Water Research*. 34(13): p. 3440-3452.
- Hawkins, P.R. and Griffiths, D.J., (1987). Copper as an algicide in a tropical reservoir. *Water Research*. 21(4): p. 475-480.
- Hirota, K., (2006). Review of Lead Phase Out for Air Quality Improvement in the Third World Cities Lessons from Thailand and Indonesia. *Journal of Studies in Regional Science*: 32(2), 527-541.
- International Energy Statistics (2012), Total Coal Consumption by Year.
- Jackson, B.P., Winger, P.V., and Lasier, P.J., (2004). Atmospheric lead deposition to Okefenokee Swamp, Georgia, USA. *Environtal Pollution*: 130(14), 445–451.
- Jackson, J. E., (1991). A User's Guide to Principal Components, John Wiley and Sons, INC.: 592.
- Kelly, A.E., Reuer M.K., Goodkin, N.F., and Boyle E.A., (2009). Lead concentrations and isotopes in corals and water near Bermuda, 1780-2000, *Earth and Planetary Science Letters*: 283(1-4), 93-100.
- Kersten, M., Garbe-Schönberg, C-D., Thomsen, S., Anagnostou, C., and Sioulas, A., (1997). Source apportionment of Pb pollution in the coastal waters of Elefsis Bay, Greece, *Environmental Science and Technology*: 31(5), 1295-1301.
- Kober, B., Wessels, M., A. Bollhöfer, A., and Mangini, A., (1999). Pb isotopes in sediments of Lake Constance, Central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere, *Geochimica et Cosmochimica Acta*: 63(9), 1293-1303.
- Koh, Y.T.R. (2014). A sedimentary record of land use change and heavy metal deposition in Nee Soon Swamp Forest, Singapore. Honors thesis. Nantional University of Singapore.

- Komárek, M., Ettler, V., Chrastný, V., and Mihaljevič, M., (2008). Lead isotopes in environmental sciences: A review, *Environment International*: 34(4), 562-577.
- Krishnaswamy, S., Lal, D., Martin, J.M., and Meybeck, M., (1971). Geochronology of lake sediments, *Earth and Planetary Science Letters*: 11, 407-414.
- Kwa, C.G., Heng, D., Tan, T.Y., (2009). Singapore: A 700-year history from early emporium to world city. National Archives of Singapore.
- Kylander, M. E., Klaminder, J., Bindler, R., and Weiss, D.J., (2010). Natural lead isotope variabilities in the atmosphere, *Earth and Planetary Science Letters*: 290(1-2), 44-53.
- Lee, C.S.L., Qi, S.H., Zhang, G., Luo, C.L., Zhao, L.Y.L., and Li, X.D., (2008). Seven thousand years of records on the mining and utilization of metals from lake sediments in central China, *Environmental Science and Technology*: 42(13), 4732-4738.
- Lee, J-M., Boyle, E.A., Nurhati, I.S., Pfeiffer, M., Meltzner, A.J., and Suwargadi, B., (2014). Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century, *Earth and Planetary Science Letters*: 398, 37-47.
- Lee, K., Hur, S.D., Hou, S., Burn-Nunes, L.J., Hong, S., Barbante, C., Boutron, C.F., and Rosman, K.J.R., (2011). Isotopic signatures for natural versus anthropogenic Pb in high-altitude Mt. Everest ice cores during the past 800 years, *Science of the Total Environment*: 412-413, 194-202.
- Li, Q., Cheng, H., Zhou, T., Lin, C., and Guo, S., (2012). The estimated atmospheric lead emissions in China, 1990–2009, *Atmospheric Environment*: 60(0), 1-8.
- Li, X., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, M.H., and Thornton, I., (2000). Heavy metal distribution in sediment profiles of the Pearl River estuary, South China, *Applied Geochemistry*: 15(5), 567-581.
- Lima, A., Bergquist, B.A., Boyle, E.A., Reuer, M.K., Dudas, F.O., Reddy, C.M., and T.I. Eglinton, (2005). High-resolution historical records from Pettaquamscutt River basin sediments: Pb isotopes reveal a potential new stratigraphic marker, *Geochimica et Cosmochimica Acta*: 69(7), 1813-1824.
- Lucarelli, B., (2000). The history and future of Indonesia's coal industry: impact of politics and regulatory framework on industry structure and performance, Freeman Spogli Institute for International Studies.
- National Environmental Agency, (2009). Weatherwise Singapore. National Environmental Agency.
- Ng, O.H., Tan, B.C., and Obbard, J.P., (2006). Lichens as bioindicators of atmospheric heavy metal pollution in Singapore, *Environmental Monitoring and Assessment*: 123(1-3), 63-74.
- Nriagu, J.O., (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, *Nature*: 279(5712), 409-411.
- Nriagu, J.O., (1989). A global assessment of natural sources of atmospheric trace metals, *Nature*: 338(6210), 47-49.
- Nriagu, J.O., (1990). The rise and fall of leaded petrol, *Science of the Total Environment*: 92, 13-28.

- Osterberg, E., Mayewski, P., Kreutz, K., Fisher, D., Handley, M., Sneed, S., Zdanowicz, C., Zheng, J., Demuth, M., Waskiewicz, M., and Bourgeois, J., (2008). Ice core record of rising lead pollution in the North Pacific atmosphere, *Geophysical Research Letters*: 35(5).
- Patterson, C.C., and Settle, D.M., (1987). Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Marine Chemistry*, 22(2-4), 137-162.
- Peter, A.L. and Viraraghavan, T., (2005). Thallium: a review of public health and environmental concerns. *Environment International*. 31(4): p. 493-501.
- Public Utilities Board, (2011), Code of practice on surface water drainage. Sixth Edition.
- Public Utilities Board, (2010). Collecting Every Drop of Rain, Public Utilities Board.
- Ragaini, R.C., Ralston, H.R., and Roberts, N., (1977). Environmental Trace Metal Contamination in Kellogg, Idaho, near a Lead Smelting Complex, *Environmental Science and Technology*: 11, 773-781.
- Ramlan, N., (ed) (2014). St James Power Station, in Singapore Infopedia, National Library Board Singapore.
- Renberg, I., Brännvall, M-L., Bindler, R., and Emteryd, O., (2002). Stable lead isotopes and lake sediments - A useful combination for the study of atmospheric lead pollution history, *Science of the Total Environment*: 292(1-2), 45-54.
- Reuer, M.K., (2002). Centennial-scale Elemental and Isotopic Variability in the Tropical and Subtropical North Atlantic Ocean, Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.
- Reuer, M.K., Boyle, E.A., and Grant, B.C., (2003). Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS, *Chemical Geology*: 200(1-2), 137-153.
- Salomons, W., and Förstner, U., (1984). Metals in the Hydrocycle, Springer Berlin Heidelberg.
- Schaule, B.K., and Patterson, C.C., (1981). Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations, *Earth and Planetary Science Letters*, 54(1), 97-116.
- Shapiro, J., (1958). The core freezer - a new sampler for lake sediments, *Ecology*: 39(758).
- Shi, G. T., Chen, Z. L., Xu, S. Y., Zhang, J., Wang, L., Bi, C. J., and Teng, J. Y., (2008). Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environmental Pollution*: 156, 251-260.
- Singapore Anti-Pollution Unit (1970-1972). Annual Report.
- Singapore Manufacturing Federation, (2012). Achievements. Retrieved on September 4, 2014, from the website: <http://www.smfederation.org.sg/index.php/profile/achievements>.
- Statistics Singapore, (2014). Population & Land Area, edited by Singapore Department of Statistics.

- Switzer, A.D.,. Measuring and analyzing particle size in a geomorphic context. In: Shroder, J. (Editor in Chief), Switzer, A.D., Kennedy, D.M. (Eds.), (2013). *Treatise on Geomorphology*. Academic Press, San Diego, CA. *Methods in Geomorphology*: 14 pp. 224-242.
- Teutsch, N., Erel, Y., Halicz, L., and Banin, A., (2001). Distribution of natural and anthropogenic lead in Mediterranean soils, *Geochimica et Cosmochimica Acta*: 65(17), 2853-2864.
- Turekian, K.K., (1977). The fate of metals in the oceans, *Geochimica et Cosmochimica Acta*: 41(8), 1139-1144.
- Turekian, K.K. and Wedepohl, K.H., (1961). Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*: 72, 175-192.
- Tylmann, W., (2004). Estimating recent sedimentation rates using ^{210}Pb on the example of morphologically complex lake (Upper Lake Raduńskie, N Poland), *Geochronometria*: 23, 21-26.
- UN Data, (2014). Electric power consumption (kWh per capita).
- USAID, (2009). A phase-out of leaded petrol makes Indonesian cities healthier places to live.
- Vanhaecke, F., Vanhoe, H., Dams, R., and Vandecasteele, C., (1992). The use of internal standards in ICP-MS, *Talanta*: 39(7), 737-742.
- Wan, M. H., and Lau, J., (2009). *Heritage places of Singapore*, Marshall Cavendish Editions.
- Watmough, S.A., and Hutchinson, T.C., (2004). The quantification and distribution of pollution Pb at a woodland in rural south central Ontario, Canada, *Environmental Pollution*: 128(3), 419-428.
- Weiss, D., Boyle, A.B., Wu, J., Chavagnac, V., Michel, A., and Reuer, M.K., (2003). Spatial and temporal evolution of lead isotope ratios in the North Atlantic Ocean between 1981 and 1989, *Journal of Geophysical Research C: Oceans*, 108(10), 4-1.
- Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., and Min, Y.S., (2002). Heavy metals in agricultural soils of the Pearl River Delta, *South China Environmental Pollution*: 119(1), 33-44.
- Wu, J., and Boyle, E.A., (1997). Low Blank Preconcentration Technique for the Determination of Lead, Copper, and Cadmium in Small-Volume Seawater Samples by Isotope Dilution ICPMS, *Analytical Chemistry*: 69(13), 2464-2470.
- Zayed, A. and Terry, N., (2003). Chromium in the environment: factors affecting biological remediation. *Plant and Soil*. 249(1): p. 139-156.
- Zhang, J., Mauzerall, D.L., Zhu, T., Liang, S., Ezzati, M., and Remais, J.V., (2010). Environmental health in China: progress towards clean air and safe water, *The Lancet*: 375(9720), 1110-1119.
- Zhao, Z-Q., Liu, C-Q., Zhang, W., and Wang, Q-L., (2011). Historical lead pollution in the central region of Guizhou Province, China: A record of lead stable isotopes of lake sediments, *Applied Geochemistry*: 26, Supplement(0), S267-S270.

Zhu, B-Q., Chen, Y-W., and Chang, X-Y., (2002). Application of Pb isotopic mapping to environment evaluation in China, *Chemical Speciation and Bioavailability*: 14(1-4), 49-56.

Zhu, L., Guo, L., Gao, Z., Yin, G., Lee, B., Wang, F., and Xu, J., (2010). Source and distribution of lead in the surface sediments from the South China Sea as derived from Pb isotopes, *Marine Pollution Bulletin*: 60(11), 2144-2153.

Zurbrick, C., Gallon, C., Flegal, A.R., in press. Asian industrial lead within the northwest Pacific Ocean evidenced by lead isotopes in seawater, *Environmental Science and Technology*.

Chapter 5 : Isotope exchange of Pb by riverine input of particulate matters: a preliminary study on the Johor River mouth

Abstract

A few independent studies on anthropogenic Pb and Pb isotopes in coastal corals from the Singapore Straits and other places have shown an isotopic excursion where the main Pb sources discharging to the water move to more crustal-like values, indicating that the Pb in coastal waters might exchange isotopically with crustal particulates without much change in concentration. To investigate this issue, Pb isotope exchange is assessed through a closed-system exchange experiment using estuarine waters collected at the Johor River mouth (discharging to the Singapore Straits). During the experiment, a known amount of NBS-981 ($^{206}\text{Pb}/^{207}\text{Pb}=1.093$) was spiked into the unfiltered Johor water (dissolved $^{206}\text{Pb}/^{207}\text{Pb} = 1.199$) and the changing isotopic composition of the dissolved Pb was monitored. Shortly after the spike addition, dissolved Pb exhibited $^{206}\text{Pb}/^{207}\text{Pb}=1.178$, reflecting the influence of the spike. Within the following few days, the $^{206}\text{Pb}/^{207}\text{Pb}$ in the water increased to >1.190 with unpropotional changes of the dissolved Pb concentration. The observations in closed-system experiment agree with the isotope difference between Singapore aerosol and seawater in our ~2-year-long field observations. The kinetics of isotope exchange were assessed using a simple model, which reproduced $>70\%$ of the observed Pb isotope variance. Both the close-system experiment and field measurements imply that isotope exchange can be an important mechanism for regulating the Pb and Pb isotopes in coastal waters. Investigations on the distribution of Pb and Pb isotope in estuaries and coastal waters should further assess the role of isotope exchange in ocean Pb chemistry.

5.1 Introduction

Fluvial transport has long been noted as an important source for metals in the ocean [e.g.: *Salomons and Förstner*, 1984; *Turekian*, 1977, and references therein]. Transport of metals involves both direct injection of dissolved metals and particulate matter that can release or exchange elements when it contacts seawater [*Dupré et al.*, 2003; *Jeandel and Oelkers*, 2015; *Viers et al.*, 2009, *Shiller and Boyle*, 1991]. Through their interaction with seawater, crustally-derived particulates can increase the concentration of some metals in estuarine waters (e.g.: Cd, Fe, Ba, *Duce et al.* 1991, *Shiller and Boyle*, 1991). More recently, it has been found that the interaction of crustal particulates could also affect the isotope composition of some elements in seawater without much change in concentration [*Jones et al.*, 2014]. Such isotope exchange has been noted for Sr and Nd in both closed system experiments [*Jones et al.*, 2012a; *Pearce et al.*, 2013] and in field observations [*Jones et al.*, 2014; *Lacan and Jeandel*, 2005, 2001]. Yet, there is little information on whether such isotope exchange influences Pb isotope data in coastal and estuarine waters.

Pb is commonly used to trace pollution, as its isotopic composition can distinguish the sources from different reservoirs [*Komárek et al.*, 2008]. Understanding the processes that affecting Pb isotopes in different environments is of critical importance in interpreting the Pb data in a dynamic environment (i.e. oceans). In the modern open ocean, aeolian input is the major source of Pb [*Patterson and Settle*, 1987], and the Pb isotope ratios of the surface ocean are the same as that of the atmospheric aerosols that are deposited in the sea surface [e.g.: *Church et al.*, 1990; *Duce et al.*, 1991; *Flegal*, 1986;]. While in estuarine and coastal environments, the fluvial contribution of elemental Pb and its isotopes into the ocean has not been clearly assessed because of the extensive global contamination of anthropogenic Pb into the atmosphere and natural waters.

As an alternative, the fluvial contribution to the Pb cycle has been investigated extensively using the dissolved and particulate ^{210}Pb activity in estuaries. It has been found that the majority ($\geq 79\%$) of ^{210}Pb in an estuary were associated with suspended particulate matter [e.g.: *Baskaran and Santschi*, 1993; *Benninger*, 1978; *Benninger et al.*, 1975; *Rama et al.*, 1961; *Windom et al.*, 1988], although some exceptions have been found in rivers with high concentrations of dissolved organic matter [e.g.: *Baskaran et al.*, 1997]. These studies have concluded that ^{210}Pb is scavenged within the estuaries and by analogy it was suggested that stable Pb should be scavenged as well. However, there are significant differences between the pathways that natural Pb and ^{210}Pb move through the environment. Much of the elemental Pb is originally contained within mineral crystals (although dissolution during weathering can release dissolved elemental Pb which can adsorb onto mineral surfaces, e.g. *Erel et al.*, 1991), whereas ^{210}Pb is released from the ^{238}U decay series with its immediate precursor the inert gas ^{222}Rn . So there may

be some differences in the elemental Pb budget compared to the ^{210}Pb budget, although this subject has never been explored in the field.

Despite few observations on the stable Pb isotopes in estuarine and coastal water, there are a few studies implied that isotope exchange may influence Pb in coastal and estuarine regions. One example comes from coral Pb studies in the Singapore Strait. Three corals were investigated on an east-west transect of the straits, and Pb isotopes in these corals all shown $^{206}\text{Pb}/^{207}\text{Pb} \Rightarrow 1.190$ [Chen *et al.*, 2015; Lee *et al.* 2014], which was distinctly different from regional aerosols ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.097\text{--}1.167$ in Southeast Asia, Bollhöfer and Rosman, 2000). No high $^{206}\text{Pb}/^{207}\text{Pb}$ sources in the region have been found except regional natural soil. In this case, isotope exchange between seawater and crustal particulates may possibly explain why $^{206}\text{Pb}/^{207}\text{Pb}$ was higher in marine systems compared to the atmospheric aerosols.

Another example is a coral Pb study by [Zhao *et al.*, submitted] in the northern Persian/Arabian Gulf (Kuwait Bay). In Zhao *et al.*'s study, a box model was employed to quantify the relative contribution of atmospheric (mostly anthropogenic) and fluvial (mostly natural) Pb to the Kuwait Bay. The Pb concentration history of the seawater (inferred from the coral) was clearly dominated by anthropogenic inputs yet the natural contribution of Pb (inferred from the Pb isotope budget) appeared to be $\sim 50\%$. The misfit between Pb concentration and Pb isotope budget in the model implied that Pb isotopes in the water might have been altered by isotope exchanged with the natural crustal particulates transported from the Euphrates and Tigris rivers.

A third example is the Japanese GEOTRACES data on dissolved Pb and Pb isotopes in Indian Ocean seawater (KH09-5, November to December 2010; Lee, 2013). 13 stations were covered including the Arabian Sea and Bay of Bengal. The $^{206}\text{Pb}/^{207}\text{Pb}$ in one profile obtained from the Bay of Bengal was 0.005–0.01 higher than another profile obtained from the Arabian Sea despite a concentration profile depth distribution that was almost identical. The isotopic offset could not be fully explained by different anthropogenic sources as the offset was observable throughout the water column whereas the anthropogenic Pb contamination was confined to the upper ocean. From these observations, Lee proposed that isotope exchange in the Arabian Sea and Bay of Bengal might have also contributed the isotopic offset between the two profiles.

These examples imply that isotope exchange might be an important mechanism modulating Pb isotope ratios in the ocean. The objective of this study is to experimentally illustrate the isotope exchange of Pb between the dissolved phase and coastal particulate matter, and investigate the kinetics of exchange using simple quantitative models. Pb isotopes in coastal environments will then be re-evaluated using our improved understanding of the mechanism of isotopic exchange.

5.2 Sampling and methodology

5.2.1 Closed system isotope exchange experiment

A closed system isotope exchange experiment was carried out using estuarine water from Johor River mouth (Figure 5.1). The Johor River is located at the southern end of the Malaysian Peninsula and discharges a large quantity of freshwater from Malaysian Peninsula to the Singapore Strait [Thia-Eng *et al.*, 2000; Wood *et al.*, 1997]. The mean annual discharge rate for Johor River is $37.7 \text{ m}^3/\text{s}$ [or $\sim 1200 \text{ km}^3/\text{year}$, Kia *et al.* 2012]. At the same time, a large quantity of fluvial particulate matter is delivered to the Singapore Strait due to the mountainous terrain, intense chemical weathering, and heavy rainfall in the maritime continent [Milliman and Farnsworth, 2011]. The upstream of the Johor River basin is mainly forest while the downstream is agriculture land (oil palm, and rubber, Tan *et al.*, 2015). On November 2013, $\sim 8\text{L}$ of water samples were collected at Johor River mouth ($1^\circ 25' 22''\text{N}$ $104^\circ 00' 05''\text{E}$, Figure 5.1) using the pole sampling method. After the water was collected, the samples were transferred to the laboratory in a dark cooler icebox.

In the lab, 250mL of unfiltered water and 250mL of $0.4\mu\text{m}$ filtered water were sub-sampled to provide a baseline state of Pb and Pb isotope in the water before the isotope exchange experiment. The remaining samples were divided into 2 groups (A and B) with different protocols during the isotope exchange experiment. For group A, $\sim 3.5\text{L}$ unfiltered sample were put into a 4L trace metal clean narrow mouth bottle (Bottle A). For group B, $\sim 3.5\text{L}$ of samples was filtered through a $0.4\mu\text{m}$ Nuclepore® filter, and then kept in another identical narrow mouth bottle (Bottle B) to serve as a control on the potential isotope exchange on organic collides and particles less than $0.4\mu\text{m}$. At time $t=0$, both bottles were spiked with a Pb isotope spike (1.75mL of 21nmol/L NBS-981 $^{206}\text{Pb}/^{207}\text{Pb}=1.093$, Baker *et al.*, 2004). The amount of spike added should result in 10.5 pmol/L concentration increase in the sample if no adsorption occurs. Vigorous shaking was applied on the bottle during spike addition to minimize the influence of acidic spike on the water chemistry. After the spike addition, a 250mL sample was separated and filtered from each 4L “B” bottle at different time points up to 60 days. A schematic illustration about the isotope exchange experiment is shown in Figure 5.2.

5.2.2 Aerosol sampling

Aerosol samples for Pb isotopes were collected on the roof of buildings building S16 of National University of Singapore (NUS) from July 2011 through November 2012. The aerosol samples were collected by pumping air through a pre-cleaned 0.45µm PTFE filter using a diaphragm pump (similar to that employed by Bollhöfer et al. 1999). Most aerosol samples were collected over about a week although had longer collection periods (multiple weeks) due to the travel schedule of the sampling personnel. From November 2012 to April 2013, the aerosol sampling station was moved to NUS CREATE building but the two buildings were within 1 km distance.

5.2.3 Seawater sampling

Seawater samples were collected seasonally in both Hantu and Kusu since September 2011 through November 2013. The samples were collected by lowering a plastic coated pole sampler near the front of the boat while the boat was slowly moving forward. A trace-metal-clean bottle was attached in the front of the pole to collect the water sample. The samples were filtered (0.4µm) and eventually acidified to pH~2 with ultrapure 6N HCl. The time between sample collection and filtration varies from within 1 day to 6 months due to the limitations on accessing to clean laboratory facilities. Due to the limitations in filtration, only Pb isotopes are reported (the Pb concentration should change due to the ambiguous time between sample collection and filtration while Pb isotope shouldn't). The samples were stored acidified for at least 2 months before analysis to ensure the release of Pb adsorbed onto the surface of the container.

5.2.4 Methods for analyzing Pb and Pb isotopes

The filtered samples were analyzed for both Pb concentration and Pb isotope. The Pb concentrations were measured using isotope dilution after single batch nitrilotriacetate (NTA) resin extraction [Lee et al., 2011]. In brief, 1.3mL of seawater samples were spiked with a known amount of ^{204}Pb enriched spike (Oak Ridge National Laboratories) and then adjusted to pH=5.3 by adding an ammonium acetate buffer. ~2400 NTA superflow resin beads were added to each sample. After 4 days on a shaker table to allow the resin beads to bind Pb, the sample and resins were rinsed several times with ultrapure water and then eluted using 0.1M high purity nitric acid. The eluted samples were then analyzed on a Quadruple ICP-MS (VG PlasmaQuad 2+). All samples were run in triplicate and accepted only if at least two out of three replicates agreed.

The Pb isotope in the seawater was measured using an IsoProbe multi-collector ICP-MS after $\text{Mg}(\text{OH})_2$ co-precipitation and HCl-HBr ion exchange chromatography as described in Boyle *et al.* [2012] and Reuer *et al.* [2003]. The seawater sample was spiked with a minimum dose of ammonia solution to induce $\text{Mg}(\text{OH})_2$ precipitation, which scavenges the Pb from the seawater. The precipitates were redissolved by a minimum amount of high purity HCl and the $\text{Mg}(\text{OH})_2$ precipitation repeated for a second time to further concentrate and separate the Pb from the Mg. The final precipitates were redissolved in 200 μL of ultrapure 1.1M HBr and loaded onto an Eichrom AG-1X8 (chloride form, 200 – 400 mesh) anion exchange resin column to separate the Pb from the sample matrices. After ion exchange, the samples were dried in a class 100 clean environment and then redissolved in ultrapure 0.2M HNO_3 for ICP-MS analysis. Standardization and corrections were handled as discussed in Boyle *et al.* [2012]. Although the expected precision and accuracy of the measurement depends on the concentration of the sample (limited by Johnson resistor noise), in general this $^{206}\text{Pb}/^{207}\text{Pb}$ data should be good to at least ± 0.001 (2σ).

The aerosol Pb isotope ratios were measured using the MC-ICP-MS in the same way as seawater samples after leaching the filter in 6M high purity HCl and passing the leachates through the HCl-HBr ion exchange columns.

5.3 Results

The Pb isotope ratios in aerosols and seawater samples are shown in Figure 5.3. $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore seawater was consistently ~ 1.195 with no evident seasonal cycle. Additionally, no spatial difference for Pb isotopes was observed. The $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore aerosols was ~ 1.147 , with the $^{206}\text{Pb}/^{207}\text{Pb}$ in the northeast monsoon season (November to March) ~ 0.005 higher than in southwest monsoon season (April to September). Pb isotope ratios in Singapore aerosols are clearly different from Singapore Strait' seawater.

The Pb concentration variability during the batch isotope exchange experiment is shown in Figure 5.4. The dissolved Pb concentration in the filtered sample at the beginning of the experiment was 18.3 pmol/kg; the unfiltered and acidified sample concentration was 371 pmol/kg ('total dissolvable Pb'), indicating a large reservoir of particulate Pb pmol/kg. After the spike addition, the Pb concentration in Bottle A filtered increased to 25.4 pmol/kg. The Pb concentration increased to 32.7 pmol/kg within 3 hours of spike addition, reflecting some release of the original particulate Pb. From 3 hours to 1 day, the Pb concentration decreased from 32.7 pmol/kg to 21.1 pmol/kg, indicating some uptake of Pb onto the particles. Afterwards, the Pb concentration increased from ~ 21

pmol/kg to ~35 pmol/kg within 7 days and remained there after 2 months ~35 pmol onwards.

The Pb concentration in the filtered Bottle B was fairly stable at ~46.3 pmol/kg within 7 days and gradually decreased to ~36.4 pmol/kg over 2 months. It was surprising to see the Pb concentration increased 28 pmol/kg (from 18.3 pmol/kg to ~46.3 pmol/kg) by the amount of spike added, which should only cause 10.5 pmol/kg increase in Pb concentration. We suspect that the higher Pb concentration in Bottle B was introduced during the large-volume filtration process involved in filling up Bottle B (this filtration took up to 3 hours and some Pb from the particles might have been released into the water during the filtration process. The high Pb concentration could also be caused by contamination during the filtration process. However, neither cause of the high Pb concentration affects the interpretation of Pb variability due to adsorption. It was reasonable to see the Pb concentration in Bottle B change only ~20% from 2 days to 2 month suggesting that the effect of bottle wall uptake should be minimal in the particle-buffered unfiltered experiment.

During the 2 months of the experiment, the Pb isotope composition of the filtered and spiked bottle “B” was $1.168 \pm .002$ (2σ), indicating no addition of Pb by leaching from the bottle. On the other hand, the Pb isotopic variability during the unfiltered “A” batch isotope exchange experiment is shown in Figure 5.5. Before spiking, $^{206}\text{Pb}/^{207}\text{Pb}$ in both filtered and acidified unfiltered samples was 1.199, showing that both the dissolved and acid-soluble particulate lead have the same isotopic composition. Assuming that the filtered (dissolved) concentration of this water was 18.3 pmol/kg, the spike addition (1.75mL of 21nmol/L) should have lowered the dissolved $^{206}\text{Pb}/^{207}\text{Pb}$ in the bottle to 1.161 (calculated $T=0$, Figure 5.5). About a half hour after spike addition, the $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A was 1.178 and further increased to 1.189 by 3 hours. From 3 hours to 1 day, the $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A decreased from 1.189 to 1.181. Following that brief drop, $^{206}\text{Pb}/^{207}\text{Pb}$ increased steadily from 1.181 to 1.197 at 2 months (Figure 5.5).

5.4 Discussion

5.4.1 Pb isotopes in Singapore seawater and aerosol

Pb isotope ratios in Singapore seawaters were generally stable over our sampling period, with $^{206}\text{Pb}/^{207}\text{Pb} = 1.195 \pm 0.004$ (2σ) and $^{208}\text{Pb}/^{207}\text{Pb} = 2.479 \pm 0.006$ (2σ). The steady Pb isotope ratios in Singapore seawater indicates that the Straits’ Pb was dominated by a consistent Pb reservoir with high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. This consistency is at odds with the oceanographic setting of the Singapore Strait. Singapore Strait waters are dominated by

seasonal monsoon-driven currents [Pang and Tkalic, 2003]. The Singapore Strait is ventilated mainly by South China Sea water during the Northeast Monsoon (November to March) and mainly by the Malacca Straits and Java Sea water during Southwest Monsoon (April to September) [Chen et al., 2005]. The two water sources should have Pb isotope ratios that are lower than the Pb seen in the Singapore Strait. There is almost no Pb isotope data in either of these regions, but we have one analysis of a surface water in the South China Sea near Taiwan [Lee et al., 2014], but neither South China Sea water (one surface sample collected near Taiwan in 2000 had $^{206}\text{Pb}/^{207}\text{Pb} = 1.156 \pm 0.015, 2\sigma$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.444 \pm 0.017, 2\sigma$, Lee et al. 2014) nor Indian Ocean water (eight samples of Central Indian Ocean surface water had $^{206}\text{Pb}/^{207}\text{Pb} = 1.144 \pm 0.006, 2\sigma$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.426 \pm 0.009, 2\sigma$ Lee et al., submitted) seem to determine the isotope ratios of Pb in Singapore seawater.

The high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Singapore seawater is clearly distinct from Pb isotope ratios of Singapore aerosols. Singapore aerosol $^{206}\text{Pb}/^{207}\text{Pb}$ averaged 1.150 in northeast monsoon season and 1.145 in southwest monsoon season (Figure 5.3). The atmospheric deposition appears to be the main source of Pb to the Singapore region as suggested by the sedimentary record from the central catchment reserve (Chen et al., submitted, also seen in Chapter 4). However, neither of these ratios in aerosol accounts for the 1.195 ± 0.004 (2σ) that in the Singapore Strait seawater. Instead of the aerosol Pb isotope value, the high $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore water is similar to the 100-year old natural soil we observe in this region (Chen et al., submitted, also seen in Chapter 4). In this case, the isotope differences between Singapore seawater and aerosols, together with the consistency of Pb isotopes in the seawater all suggest the Pb isotopes in Singapore seawater might have been altered into more 'crustal-like' values by exchanging with crustal particulates despite the deposition of aerosols with much lower $^{206}\text{Pb}/^{207}\text{Pb}$.

5.4.2 Mechanisms inferred from the closed-system isotope exchange experiment

The total dissolvable Pb concentration in the Johor River mouth sample was 371 pmol/kg, but only 18.3 pmol/kg was dissolved at natural pH. This data indicates that less than 5% of Pb was in the dissolved form. The fraction of dissolved Pb is similar to that observed for ^{210}Pb in many estuaries (e.g.: Baskaran and Santschi, 1993; Benninger, 1978; Benninger et al., 1975; Rama et al., 1961; Windom et al., 1988). Soon after spike addition, the Pb concentration in Bottle A increased to 25.4 ± 1.4 pmol/kg, which was nearly consistent compare to the amount of spike added to the water. Within the first 3 hours, the Pb concentration increased from 25.4 pmol/kg to 32.7 pmol/kg, and then decreased steadily to 20.9 pmol/kg from 3 hours to 2 days. It is hard to be certain whether the high Pb concentration at T= 3hr is a real signal as it was only a single sample that must be

considered in view of Pb's contamination-prone character. The decreased Pb concentration from 3 hours to 2 days was more prominent as the decreasing trend was visible at T = 5hr, 24hr and 47.5hr. The decrease in Pb concentration implied that Pb was scavenged from the water from 3 hours to 2 days. In the following 2 days to 2 months, the Pb concentration increased to 33.9 pmol/kg at T=7days and remained at ~33 pmol/kg. The increase in Pb concentration from 2 days to 2 months suggested that processes other than scavenging removal can release Pb from particulate matter into the water. The release of Pb from particles has been suggested in some estuaries [e.g.: *Guieu et al.*, 1998]. The dissolution and scavenging of Pb might function at different rates that result in the observed fluctuations of Pb concentration in Bottle A. We cannot specify which processes account for these Pb removal/addition observations, but some possibilities are ion exchange with particle surfaces (+ or -), biological uptake (-), biological decomposition (+), scavenging onto mineral or biological surfaces (-), mineral dissolution (+), mineral precipitation (-). The time dependence of these processes may differ substantially, i.e., some may occur quickly and others slowly.

Pb isotope ratios in the unfiltered Bottle A show large change over the experiment. Soon after the spike addition, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from 1.199 to 1.178, reflecting the low $^{206}\text{Pb}/^{207}\text{Pb}$ isotope from the NBS-981 spike (1.093). It should be noted that by simply adding 1.75mL of 21nmol/L NBS-981 into the 18.3 pmol/kg of sample, the resulting $^{206}\text{Pb}/^{207}\text{Pb}$ should be 1.160 (calculated from mass balance assuming simple mixing), which was lower than the observed $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.178). The higher observed $^{206}\text{Pb}/^{207}\text{Pb}$ from simple mixing indicated that some isotope exchange could have happened within seconds to minutes so that the $^{206}\text{Pb}/^{207}\text{Pb}$ in the bottle has already been altered to higher value within a few minutes (our filtration would generally take ~3 minutes). The $^{206}\text{Pb}/^{207}\text{Pb}$ increased to 1.190 within 7 days while the Pb concentration only increased by 9.8 pmol/kg. If the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ was purely due to release from particulate Pb (1.199), the resulting $^{206}\text{Pb}/^{207}\text{Pb}$ at T = 7 days should be 1.184 by mass balance, which was again lower than the observed 1.190. The disproportional increase in $^{206}\text{Pb}/^{207}\text{Pb}$ also indicates that the particulates have been exchanging Pb isotopically and altered the $^{206}\text{Pb}/^{207}\text{Pb}$ to higher values. From 7 days to 2 months, the $^{206}\text{Pb}/^{207}\text{Pb}$ further increased to 1.197 without obvious change in Pb concentration, which further supports an isotope exchange mechanism. It is difficult to explain the $^{206}\text{Pb}/^{207}\text{Pb}$ data for T = 3 hr and T = 1 day (Figure 5.5) given the coarse temporal resolution we have in this study. However, despite these uncertainties our closed-system experiment clearly demonstrates a rapid Pb isotope exchange process (hours to days to months, Figure 5.5).

5.4.3 A model for Pb isotope exchange

It has been previously suggested that isotope exchange without net element transfer occurs for Sr and Nd isotopes. The mechanism for this isotope exchange was proposed as contemporaneous dissolution and precipitation into secondary minerals [Jeandel and Oelkers, 2015; Jones *et al.*, 2014; Jones *et al.*, 2012a, 2012b]. That suggested mechanism for Sr isotopes might not be plausible for Pb as the concentration for Pb in seawater was generally in the pico-molar region [e.g.: Boyle *et al.* 2014]. In the pico-molar concentration region, the formation of secondary minerals by precipitation is not likely.

One way to mathematically express the Pb isotope exchange happens in various exchangeable reservoirs, where each reservoir has its own rate of exchange:

where k is the rate constant for each particular reservoir. As the release of Pb from minerals could be related to the strength of the bond binding Pb onto each particular mineral type and the surface area of the particulate matter in contact with the seawater [e.g.: Noyes and Whitney, 1897 as a general reference]; while the scavenging of Pb from the water column might be dependent on the Pb concentration in the water and the amount of particulates presented in the water column [e.g.: Bacon *et al.* 1976], different exchangeable reservoirs of Pb might operate at different rates. As discussed in section 5.4.1, there might be at least a fast exchange reservoir that operates from seconds to minutes and a slow exchange reservoir that operates from days to months.

In terms of changing Pb isotope, the release of Pb from each exchangeable reservoir contains the isotope ratios within that reservoir, while the Pb scavenged from the water should contain the isotope ratios in the water column. As time proceeds, both reservoirs should have more homogeneous Pb isotope values. Therefore in the model, we assume Pb ions move in and out from each reservoir to the dissolved pool regardless of its isotope (note – it is known that small stable isotope ratio fractionations can occur during ion exchange – e.g. Anbar *et al.*, 2000 – but these fractionations are generally small (a few permil) compared to the very large radiogenic Pb isotope signature differences in nature and in this experiment). By assuming first order kinetics (generally assumed because of the highly unknown nature of kinetics happening in natural environments), the amount of Pb that is exchanging in each reservoir is assumed to be related to the size of the exchangeable reservoir and a rate constant:

$$[Pb]_{ex-Ri,t} \times V = [Pb]_{Ri,t} \times k_i \times V \times \Delta t \quad (2)$$

where the k_i is the isotope exchange constant that determines the amount of Pb that can participate in isotope exchange in that reservoir; $[Pb]_{ex-Ri}$ is the concentration of Pb that has exchanged; $[Pb]_{Ri}$ is the concentration of Pb in the reservoir, V is the volume of the water in the system, and Δt is the time step. It should be noted that by assuming the volume of water in the closed system experiment was conservative, the equation (2) can be simplified into concentration of Pb only as equation (3), which is also more straightforward illustrate the first-order kinetics.

$$[Pb]_{ex-Ri,t} = [Pb]_{Ri,t} \times k_i \times \Delta t \quad (3)$$

As Pb that moves from each reservoir to dissolved pool should carry the isotopic composition in the reservoir; and the Pb that moves from the dissolved pool to the reservoir should carry the isotopic composition in the dissolved pool; the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for each reservoir and seawater at time t can be calculated as:

$$\left(\frac{^{206}}{^{207}}\right)_{Ri,t} = \frac{1}{[Pb]_{Ri,t}} \times \left\{ [Pb]_{Ri,t} \times \left(\frac{^{206}}{^{207}}\right)_{Ri,t-1} + [Pb]_{ex-Ri,t} \times \left(\frac{^{206}}{^{207}}\right)_{sw,t-1} - [Pb]_{ex-Ri,t} \times \left(\frac{^{206}}{^{207}}\right)_{Ri,t-1} \right\} \quad (4)$$

$$\left(\frac{^{206}}{^{207}}\right)_{sw,t} = \frac{1}{[Pb]_{sw,t}} \times \left\{ [Pb]_{sw,t} \times \left(\frac{^{206}}{^{207}}\right)_{sw,t-1} + \left[\sum_{i=1}^n ([Pb]_{ex-Ri,t} \times \left(\frac{^{206}}{^{207}}\right)_{Ri,t-1}) \right] - \left[\sum_{i=1}^n [Pb]_{ex-Ri,t} \times \left(\frac{^{206}}{^{207}}\right)_{sw,t-1} \right] \right\} \quad (5)$$

In terms of changing Pb concentration, as more Pb added into the closed-system via spike addition, the Pb in each reservoir should be redistributed. In the model, the redistributed of Pb concentration (Pb_{∞}) in each reservoir was calculated by a particulate-seawater partition coefficient K_d . The K_d value in the model is obtained by the ratio of unfiltered and filtered sample that measured before spike (2×10^6 , assuming particulate concentration is 10mg/kg). Using this K_d value, the redistributed of Pb concentration (Pb_{∞}) in the water is calculated as 19.0 pmol/kg, which is very similar to our measured concentration at $T = 1$ day, 2 day, and 1 month (21.1 pmol/kg, 20.9 pmol/kg, and 21.0 pmol/kg) respectively. The rate of the redistribution was calculated by assuming first-order kinetics with a reservoir-specific rate constant k_i , which has been discussed calculating the isotope exchange. Therefore the concentration of Pb in each reservoir and water can be expressed as:

$$[Pb]_{Ri,t} = [Pb]_{Ri,t-1} + [Pb]_{Ri,\infty} \times (1 - e^{-k_i t}) \quad (6)$$

$$[Pb]_{sw,t} = [Pb]_{sw,t-1} - \sum_{i=1}^n [[Pb]_{Ri,\infty} \times (1 - e^{-k_i t})] \quad (7)$$

With the mathematical equations 4 and 7, the model was constructed to access the possibility of quantitatively achieving the observed concentrations and isotopes. The time step was set as 1 hour as it clearly resolves our 2-month-long experiment. The Pb

isotope exchange constant k_i , and the size of each exchangeable Pb reservoir were adjusted to achieve the least deviation between the observations and the model. The modeled $^{206}\text{Pb}/^{207}\text{Pb}$ and dissolved Pb together with observed values are shown in Figure 5.6 and Figure 5.7. The model could not reproduce the fluctuation in $^{206}\text{Pb}/^{207}\text{Pb}$ variation in the first 48 hours (particularly $T = 3$ & 24 hr). However, it is difficult to determine whether the observed variation was caused by complex seawater-particulate dynamics or simply by scattering. Increasing the sampling resolution could further address the fluctuation of Pb and Pb isotopes within the first 48 hours. Despite the uncertainty, our simple isotope exchange model could reproduce the fast increase in $^{206}\text{Pb}/^{207}\text{Pb}$ as we observed in the close-system experiment at $R^2=0.58$ (by excluding the odd isotope numbers at $T = 3$ & 24 hr, the $R^2=0.92$).

5.4.4 Comparison between batch experiment and field measurements in Singapore Strait water

The change in $^{206}\text{Pb}/^{207}\text{Pb}$ during the experiment provides a direct evidence for the existence of Pb isotope exchange; and supports the field observations in Singapore seawater. Investigations in Singapore seawater indicated the $^{206}\text{Pb}/^{207}\text{Pb}$ in the seawater was >1.190 (Figure 5.3), different from either regional aerosols ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.140$) or the open-ocean seawater feeding the Singapore Strait ($^{206}\text{Pb}/^{207}\text{Pb} = 1.144\text{--}1.156$, *Inoue et al.*, 2006; *Lee et al.*, 2014). In the isotope exchange experiment, $^{206}\text{Pb}/^{207}\text{Pb}$ increased from 1.178 to >1.190 . The magnitude of the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ during the experiment was comparable to the difference between Singapore seawater and aerosols.

Besides the magnitude of increase, the timescale of the isotope exchange in the close-system experiment also supports the consistent isotopic departure between Singapore seawater and aerosols. In the experiment, major change in Pb isotopes happened between hours to days, suggesting the timescale of isotope exchange should likely be within hours to days. If the timescale of isotope exchange is shorter than the residence time of Pb in Singapore water, the isotope exchange could maintain the observed isotopic difference between Singapore seawater and aerosol (Figure 5.3). The residence time of Pb in the Singapore Strait has not been directly investigated but the temporal variation of Pb in Singapore corals seem to correlate with the local rainfall with a lag of 2 years [*Chen et al.*, 2015]. The 2-year-lag agreed with the ^{210}Pb -derived residence time in the surface oceans feeding water to the Singapore Strait (1.8 year in South China Sea, *Wei et al.*, 2011, 4 year in eastern Indian Ocean, *Cochran et al.*, 1983) and could be an estimation of the residence time of Pb in Singapore water. In this case, the timescale of isotope exchange (hours to days) should be significantly shorter than the residence time

of Pb in Singapore water and the isotope exchange could maintain the observed isotopic difference in Singapore water.

5.4.5 The potential role of Pb isotope exchange for ocean chemistry

Crustal particulates transported by rivers have been proposed as an important factor regulating the chemistry of marine trace elements [Jeandel and Oelkers, 2015]. The global suspended riverine flux has been estimated as 15-20 Gt/year [Meybeck *et al.*, 2003; Walling, 2006]; among which, rivers in South Asia and maritime continent transport disproportionately high amount of particulates to the Pacific and Indian Ocean (~2/3 of the global suspended particle flux, Milliman and Farnsworth, 2011). These fluvial particulates provide abundant materials for isotope exchange happening in these regions, changing the Pb isotope in the water to more 'crustal-like' ratios. The influence of isotope exchange on the geochemistry of Pb, and the extent of this influence is still poorly understood due to sparse seawater Pb isotope data in estuaries, coastal areas and near continental margins. Despite sparse observational data, the observations from the laboratory batch experiment imply that isotope exchange could significantly influence the isotopic composition of Pb in coastal environments, and illuminate the fate of particulate material upon its arrival to oceans. Further investigations, including sterilized systems that will not have biological uptake or decay, targeted exchange experiments using waters from other rivers (especially in regions where the geological Pb source is extreme); some simple single well-characterized phase experiments to illuminate the exchange process in a simple system, and better establishing the spatial distribution of Pb isotope in estuaries and coastal environments could provide important insights on the extent of Pb isotope exchange and its influence to the ocean Pb geochemistry.

5.5 Conclusion

The isotope exchange of Pb in coastal waters has been investigated through a closed-system exchange experiment using estuarine waters sampled from the Johor River mouth. During the experiment, the $^{206}\text{Pb}/^{207}\text{Pb}$ in the sample changed from 1.178 to >1.190 within 7 days with disproportional changes in Pb concentration. The change in Pb isotope ratios in the batch experiment was significantly larger than the measurement error. With a timescale of isotope exchange much shorter than the residence time of Pb in a water environment, isotope exchange could maintain a consistent isotope departure from the Pb source feeding the water, which has been observed in the Singapore Strait.

In addition to our closed-system experiment and field observations, a simple mathematical model was employed to simulate the kinetics of isotope exchange. Using a simple exchange model, >70% of the observed $^{206}\text{Pb}/^{207}\text{Pb}$ variance can be simulated. The observations in both batch experiment and field measurement provides a compelling evidence for rapid (days-months) Pb isotope exchange between seawater and suspended particulate materials. Further investigation of the distributions of Pb and Pb isotopes around estuaries and coastal areas could enhance our understanding on the role of isotope exchange in marine Pb geochemistry.

Figure 5.1: Map of the Singapore Strait and the Johor River. The sampling sites are denoted as red boxes. The sampling sites include: 1. Johor River mouth for isotope exchange water samples; 2. National University of Singapore for aerosol samples; 3. Kusu for seasonal seawater samples; 4. Hantu for seasonal seawater samples.

Figure 5.2: Schematics of the isotope exchange experiments

Figure 5.3: The Pb isotope time series in Singapore aerosols (grey filled diamonds) and seawater (squares). The seawater samples were taken from the Singapore Strait near either Hantu (black filled squares) or Kusu (open squares). The dashed line illustrates an average 206/207 ratio in Singapore Strait water. The aerosol samples were taken on top of the S16 building and CREATE building (courtesy to Dr. Lee J.M.).

Figure 5.4: The measured Pb concentration in seawater after spiking with NBS-981 standard reference material. Bottle A (filled triangles) is the unfiltered seawater; Bottle B (open triangles) is the 0.4 μ m filtered seawater; and the unspiked sample is shown in a blue open triangle. The main figure shows the detail change in Pb concentration in Bottle A within first 200 hours and the inset figure shows the 2-month-long variation of Pb concentration in both Bottle A and B.

Figure 5.5: The measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of seawater after spiking with NBS-981 standard reference material (red open triangle). The main figure shows the detailed change in $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A (filled squares) after spike addition. The inset figure shows the overview of the $^{206}\text{Pb}/^{207}\text{Pb}$ in unfiltered sample (blue open triangle); spike (red open triangle); the calculated T = 0 (green open triangle, calculated 18.3 pM initial dissolved + 10.5 pM NBS-981 point) and change in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Bottle A and Bottle B (filtered at t=0, open squares).

Figure 5.6: The modelled $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (dashed grey line) compared to measured values from the close-system experiment (filled squares).

Figure 5.7: The modelled dissolved Pb concentration (dashed grey line) compared to measured values from the close-system experiment (filled squares).

References for Chapter 5

- Anbar, A. D., J. E. Roe, J. Barling, and K. H. Nealson, (2000). Non-biological fractionation of iron isotopes, *Science*, 288, 126–128.
- Bacon, M. P., D. W. Spencer, and P. G. Brewer (1976), ^{210}Pb – ^{226}Ra and ^{210}Po – ^{210}Pb disequilibria in seawater and suspended particulate matter, *Earth and Planetary Science Letters*, 32(2), 277–296.
- Baker, J., D. Peate, T. Waight, and C. Meyzena (2004), Pb isotopic analysis of standards and samples using a ^{207}Pb – ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS *Chem. Geol.*, 211, 275–303.
- Baskaran, M., and P. H. Santschi (1993), The role of particles and colloids in the transport of radionuclides in coastal environments of Texas, *Marine Chemistry*, 43(1–4), 95–114.
- Baskaran, M., M. Ravichandran, and T. S. Bianchi (1997), Cycling of ^7Be and ^{210}Pb in a High DOC, Shallow, Turbid Estuary of South-east Texas, *Estuarine, Coastal and Shelf Science*, 45(2), 165–176.
- Benninger, L. K. (1978), ^{210}Pb balance in Long Island Sound, *Geochimica et Cosmochimica Acta*, 42(8), 1165–1174.
- Benninger, L. K., D. M. Lewis, and K. K. Turekian (1975), Use of natural lead-210 as a heavy metal tracer in the river–estuarine system, in *Marine chemistry in the coastal environment*, edited.
- Bollhöfer, A., W. Chisholm, and K. J. R. Rosman (1999), Sampling aerosols for lead isotopes on a global scale, *Analytica Chimica Acta*, 390(1–3), 227–235.
- Bollhöfer, A., and Rosman K.J.R., (2000). Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochimica et Cosmochimica Acta* 64(19): 3251–3262.
- Bollhöfer, A., and Rosman K. J. R., (2001), Isotopic source signatures for atmospheric lead: The Northern Hemisphere, *Geochimica et Cosmochimica Acta*, 65(11), 1727–1740.
- Boyle, E. A., J. M. Lee, Y. Echegoyen, A. Noble, S. Moos, G. Carrasco, N. Zhao, R. Kayser, J. Zhang, T. Gamo, H. Obata and K. Norisuye (2014) Anthropogenic lead emissions in the ocean: The evolving global experiment. *Oceanography*, 27, 69–75.
- Boyle, E. A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkamper, M., Rouxel, O., Sohrin, Y., Stirling C., Thompson, C., Vance, D., Xue, Z., and Zhao, Y., (2012), GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration, *Limnology and Oceanography: Methods*(10), 653–665.
- Chen, M., E. A. Boyle, A. D. Switzer, and C. Gouramanis (submitted), A century long sedimentary record of anthropogenic lead (Pb), Pb isotopes and other trace metals in Singapore. Submitted to *Limnology and Oceanography*.

- Chen, M., J. M. Lee, I. S. Nurhati, A. D. Switzer, and E. A. Boyle (2015), Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities, *Marine Chemistry*, 168, 49-59.
- Chen, M., Murali, K., Khoo, B.C., Lou, J., and Kumar, K., (2005). Circulation Modelling in the Strait of Singapore. *Journal of Coastal Research* 21(5): 960-972.
- Church, T. M., A. Véron, C. C. Patterson, D. Settle, Y. Erel, H. R. Maring, and A. R. Flegal (1990), Trace elements in the North Atlantic troposphere: Shipboard results of precipitation and aerosols, *Global Biogeochem. Cycles*, 4(4), 431-443.
- Cochran, J. K., M. P. Bacon, S. Krishnaswami, and K. K. Turekian (1983), ²¹⁰Po and ²¹⁰Pb distributions in the central and eastern Indian Ocean, *Earth and Planetary Science Letters*, 65(2), 433-452.
- Duce, R. A., P. S. Liss, J. T. Merrill, E. L. Atlas, P. Buat-Menard, B. B. Hicks, J. M. Miller, J. M. Prospero, R. Arimoto, T. M. Church, W. Ellis, J. N. Galloway, L. Hansen, T. D. Jickells, A. H. Knap, K. H. Reinhardt, B. Schneider, A. Soudine, J. J. Tokos, S. Tsunogai, R. Wollast & M. Zhou. (1991), The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cycles*, 5(3), 193-259. Dupré, B., C. Dessert, P. Oliva, Y. Goddérís, J. Viers, L. François, R. Millot, and J. Gaillardet (2003), Rivers, chemical weathering and Earth's climate, *Comptes Rendus Geoscience*, 335(16), 1141-1160.
- Dupré, B., C. Dessert, P. Oliva, Y. Goddérís, J. Viers, L. François, R. Millot, and J. Gaillardet (2003), Rivers, chemical weathering and Earth's climate, *Comptes Rendus Geoscience*, 335(16), 1141-1160.
- Erel, Y., J. J. Morgan and C. C. Patterson (1991). Natural levels of lead and cadmium in a remote mountain stream. *Geochimica et Cosmochimica Acta* 55: 707-719.
- Flegal, A. R. (1986), Lead in tropical marine systems: A review, *Science of the Total Environment*, 58(1-2), 1-8.
- Guieu, C., J. M. Martin, S. P. C. Tankéré, F. Mousty, P. Trincherini, M. Bazot, and M. H. Dai (1998), On Trace Metal Geochemistry in the Danube River and Western Black Sea, Estuarine, *Coastal and Shelf Science*, 47(4), 471-485.
- Inoue, M., A. Hata, A. Suzuki, M. Nohara, N. Shikazono, W. W. S. Yim, W. S. Hantoro, S. Donghuai, and H. Kawahata (2006), Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons, *Environmental Pollution*, 144(3), 1045-1052.
- Jeandel, C., and E. H. Oelkers (2015), The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles, *Chemical Geology*, 395(0), 50-66.
- Jones, M. T., C. R. Pearce, and E. H. Oelkers (2012a), An experimental study of the interaction of basaltic riverine particulate material and seawater, *Geochimica et Cosmochimica Acta*, 77, 108-120.
- Jones, M. T., C. R. Pearce, C. Jeandel, S. R. Gislason, E. S. Eiriksdottir, V. Mavromatis, and E. H. Oelkers (2012b), Riverine particulate material dissolution as a significant flux of strontium to the oceans, *Earth and Planetary Science Letters*, 355-356, 51-59.

- Jones, M. T., S. R. Gislason, K. W. Burton, C. R. Pearce, V. Mavromatis, P. A. E. Pogge von Strandmann, and E. H. Oelkers (2014), Quantifying the impact of riverine particulate dissolution in seawater on ocean chemistry, *Earth and Planetary Science Letters*, 395(0), 91-100.
- Kia, M., S. Pirasteh, B. Pradhan, A. Mahmud, W. Sulaiman, and A. Moradi (2012), An artificial neural network model for flood simulation using GIS: Johor River Basin, Malaysia, *Environmental Earth Sciences*, 67(1), 251-264.
- Komárek, M., V. Ettler, V. Chrastný, and M. Mihaljevič (2008), Lead isotopes in environmental sciences: A review, *Environment International*, 34(4), 562-577.
- Lacan, F., and C. Jeandel (2001), Tracing Papua New Guinea imprint on the central Equatorial Pacific Ocean using neodymium isotopic compositions and Rare Earth Element patterns, *Earth and Planetary Science Letters*, 186(3-4), 497-512.
- Lacan, F., and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent-ocean interface, *Earth and Planetary Science Letters*, 232(3-4), 245-257.
- Lee, J.-M., E. A. Boyle, Y. Echegoyen-Sanz, J. N. Fitzsimmons, R. Zhang, and R. A. Kayser (2011), Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry, *Analytica Chimica Acta*, 686(1), 93-101.
- Lee, J.-M., E. A. Boyle, I. Suci Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014), Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century, *Earth and Planetary Science Letters*, 398(0), 37-47.
- Lee, J. M. (2013), Evolution of anthropogenic Pb and Pb isotopes in the deep North Atlantic Ocean and the Indian Ocean, Honors thesis, Degree of Arts, Geology, Massachusetts Institute of Technology.
- Meybeck, M., L. Laroche, H. H. Dürr, and J. P. M. Syvitski (2003), Global variability of daily total suspended solids and their fluxes in rivers, *Global and Planetary Change*, 39(1-2), 65-93.
- Milliman, J. D., and K. L. Farnsworth (2011), River Discharge to the Coastal Ocean: A Global Synthesis, *Cambridge University Press*.
- Noyes, A. A., and W. R. Whitney (1897), The rate of solution of solid substances in their own solutions, *Journal of the American Chemical Society*, 19(12), 930-934.
- Pang, W. C., and P. Tkalich (2003), Modeling tidal and monsoon driven currents in the Singapore Strait, *Singapore Maritime & Port Journal*, 151-162.
- Patterson, C. C., and D. M. Settle (1987), Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Marine Chemistry*, 22(2-4), 137-162.
- Pearce, C. R., M. T. Jones, E. H. Oelkers, C. Pradoux, and C. Jeandel (2013), The effect of particulate dissolution on the neodymium (Nd) isotope and Rare Earth Element (REE) composition of seawater, *Earth and Planetary Science Letters*, 369-370(0), 138-147.
- Rama, M. Koide, and E. D. Goldberg (1961), Lead-210 in natural waters, *Science*, 134, 98.

- Reuer, M. K., E. A. Boyle, and B. C. Grant (2003), Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS, *Chemical Geology*, 200(1-2), 137-153.
- Salomons, W., and U. Förstner (1984), Metals in the Hydrocycle, *Metals in the hydrocycle*.
- Shiller, A.M. and E.A. Boyle (1991) Trace elements in the Mississippi River Delta outflow region: behavior at high discharge, *Geochimica et Cosmochimica Acta*. 55:3241-3251
- Tan, M. L., A. L. Ibrahim, Z. Yusop, Z. Duan, and L. Ling (2014), Impacts of land-use and climate variability on hydrological components in the Johor River basin, Malaysia, *Hydrological Sciences Journal*, 60(5), 873-889.
- Thia-Eng, C., I. R. L. Gorre, S. Adrian Ross, S. R. Bernad, B. Gervacio, and M. Corazon Ebarvia (2000), The Malacca Straits, *Marine Pollution Bulletin*, 41(1-6), 160-178.
- Turekian, K. K. (1977), The fate of metals in the oceans, *Geochimica et Cosmochimica Acta*, 41(8), 1139-1144.
- Viers, J., B. Dupré, and J. Gaillardet (2009), Chemical composition of suspended sediments in World Rivers: New insights from a new database, *Science of The Total Environment*, 407(2), 853-868.
- Walling, D. E. (2006), Human impact on land-ocean sediment transfer by the world's rivers, *Geomorphology*, 79(3-4), 192-216.
- Wei, C. L., S. Y. Lin, D. D. Sheu, W. C. Chou, M. C. Yi, P. H. Santschi, and L. S. Wen (2011), Particle-reactive radionuclides (^{234}Th , ^{210}Pb , ^{210}Po) as tracers for the estimation of export production in the South China Sea, *Biogeosciences*, 8(12), 3793-3808.
- Windom, H., R. Smith Jr, C. Rawlinson, M. Hungspreugs, S. Dharmvanij, and G. Wattayakorn (1988), Trace metal transport in a tropical estuary, *Marine Chemistry*, 24(3-4), 293-305.
- Wood, A. K. H., Z. Ahmad, N. A. M. Shazili, R. Yaakob, and R. Carpenter (1997), Geochemistry of sediments in Johor Strait between Malaysia and Singapore, *Continental Shelf Research*, 17(10), 1207-1228.
- Zhao, N., Boyle, E.,A., Nurhati, I., Carrasco, G., Gevao, B., Ghadban, A.,N., Ali, L., (submitted) Pb, Pb isotopes and Cd history in the northern Arabian Gulf seawater over the past 60 years: Anthropogenic and natural processes. Submitted to *Geochimica et Cosmochimica Acta*.

Chapter 6 : Conclusion

6.1 Summary of the works

The general understanding of Asian Pb fluxes was limited by the sparse data and thus many questions remain underexplored. In order to address these questions, this study set out to investigate the temporal and spatial variabilities of Pb in South China Sea, an important marginal ocean basin bounded by many emerging Asian countries. The scope of this study involves the following aspects:

- Investigating the Pb and Pb isotope variability over the past two centuries using a coral from off the Nha Trang Bay, central Vietnam (Chapter 2). This chapter provides an overall picture on how the Pb varies in the western South China Sea.
- Investigating the spatial and temporal variation of Pb and Pb isotopes in the Singapore Strait using three corals located on an east-west transect of the strait (Chapter 3). This chapter provides a detail picture on how the Pb varies next to one of the largest Asian cities and one of the world's busiest ports.
- Investigating the century-scale variation of Pb, Pb isotopes and other eleven metals in Singapore region using a sediment core collected from MacRitchie Reservoir (Chapter 4). This chapter is a parallel study in comparison to the coral study as the near-pristine catchment provides the possibility to reconstruct the atmospherically deposited metals in Singapore region.
- Investigating the isotope exchange of Pb between seawater and crustal particulates through a laboratory batch isotope exchange experiment (Chapter 5).

The results shown in these four chapters provide new perspectives on the Asian contribution of Pb through records at various timescales and resolutions. Major conclusions include:

- Anthropogenic Pb in the South China Sea region started to appear in significant amounts beginning in the 1950s. This is observable in both the Vietnam coral and in Singapore reservoir sediments (not determined in Singapore corals because of their short timespan). Pb in the Vietnam coral increased by ~4x from the pre-1950s' level over the last 50 years; and has started to decrease since 2004.
- The temporal variation of Pb in Singapore is resolved from the MacRitchie sediment core. The Pb in the sediment had increased ~30x from the natural level over the last century. The start of the increase was earlier than the Vietnam coral probably because the urbanization in Singapore started earlier than most of the countries in this region. The Pb in Singapore corals show significant spatial variability, however the temporal variability of Pb in the Jong coral (longest, most pristine, coral record) seem to be similar to the changes in the MacRitchie

sediment core over the last 50 years. The Pb content in Singapore corals started to decrease since 2003, but such a decrease was not resolvable in the MacRitchie sediments due to the coarse resolution of the core.

- Pb isotopes in the Vietnam coral indicate a contribution of Chinese emitted Pb to the South China Sea; while the Pb isotopes in MacRitchie sediments show contribution of Pb from typical Southeast Asian sources. Despite difference in Pb sources, the Pb isotopes in both records exhibit increasing contribution of anthropogenic Pb over the last century. The increasing contribution of anthropogenic Pb agrees with the extensive industrialization in Asian regions.
- The Pb isotopes in Singapore corals deviate from both the aerosols in the region and the adjacent seas. No other Pb source with similar isotope ratios was found in the region except the crustal particulates. In this case, isotope exchange with natural crustal materials is the most probable mechanism explaining the anomalous isotope ratios observed in Singapore corals.

6.2 Discussions on the environmental perspective of the records

Anthropogenic Pb has left a major imprint in the environment in the area of study, previously mainly from leaded petrol and later from other industrial sources. From our reconstruction in both Nha Trang and Singapore, it is clear to see that the anthropogenic Pb imprint in Singapore started earlier than Nha Trang (Figure 6.1), which can be explained by the earlier developments in Singapore. Another interesting finding in both Singapore and Nha Trang records is that lower Pb content would always be found in the record after new emission control policies were introduced (Figure 6.1). For example, the introduction of “Clean Air Act” in Singapore coincided with ~20% lower Pb content in the MacRitchie sediment record. Also, in the 1980s, major countries surrounding SCS decreased the lead content in their petrol. These series of reducing lead content in petrol results in a decrease in Pb/Ca in the Vietnam coral. To summarize in an environmental perspective, environment is clearly responding to the anthropogenic Pb emissions in both Nha Trang and Singapore, and in both coral and sediment. In order to reduce these anthropogenic Pb imprint to the environment, stricter pollution control measures has proven effectiveness and necessity.

6.3 Implications to the ocean Pb cycle

Besides exploring the Asian Pb sources and variability, this study also opens new perspectives on the fate and transport of Pb in the ocean. The major two aspects are: 1)

transport of Pb to the Vietnam upwelling regions through advection of North Pacific Tropical Water, and 2) isotope exchange between dissolved Pb and crustal particulates.

The transport of North Pacific Tropical Water to the Vietnam upwelling regions has modulated the Pb variability in the Vietnam coral. The peak Pb/Ca in the coral lags the peak petroleum Pb emission for 4-7 years. The lag is longer than the residence time of Pb in the surface South China Sea and therefore should better be explained as the transport of historically emitted Pb deposited in tropical Pacific waters. The variabilities of Pb in the Vietnam coral provide evidence on the oceanic transport of Pb in the South China Sea region. It also implies the potential of using the transient of Pb in the coral to illustrate the ocean circulation in this region.

The isotope exchange of Pb is the second aspect in this study that provides new perspectives on the fate and transport of Pb. Fast isotope exchange between crustal particulates and spiked seawater has been demonstrated through the batch experiment. While the batch experiment provides a direct observation on the isotope exchange process, the observations (including corals, waters, sediments, aerosols, and incineration ash) in Singapore provide a model for observing isotope exchange in the field. The isotope exchange further constrains our understanding on the influence of crustal particulates to Pb in coastal waters and enhances our ability to interpret Pb isotopes in coastal environments.

6.4 Limitations and recommendations to future research

There are several limitations in this study. Firstly, the study is limited by the small sample size compare to a dynamic environment. The sources and fluxes of anthropogenic Pb have been constantly changing; while the small sample size could potentially limit the amount of information that can be extracted from such a constant-changing environment. The number of water samples one can obtain is limited by the number of cruises one can participate and the extensive effort needed for each cruise (i.e.: sampling permit, logistics, bottles, sampling devices, boat, shipping permit); the number of samples one can extract from a coral is limited by the coral growth rate; and the number of samples one can extract from a sediment core is limited by the sediment accumulation rate. More samples could further constrain the variation of Pb in the environment and further resolve the unanswered questions left in this study.

Besides the sample size, the potential for contamination could be another limiting factor for this trace metal study. Trace amount of Pb can be introduced during sample collection, processing or during measurement. However, even in trace amount, it might result in major change in the concentration or isotopic composition in a sample. The contaminated samples could potentially mislead in the interpretation on the data.

Contamination issues have been minimized by a number of control measures during sampling and processing, but it is difficult to verify that contamination never occurs. Besides the contamination-control measures, the reproducibility of the sample and variation pattern of the time series have been examined to minimize the potential misinterpretation due to contamination.

The third major limitation is the identification of the region one archive should represent. For example, spatial variability has been found in the three coral cores collected in different areas of the Singapore Strait. It is difficult to determine the exact area that each coral represents, however, information including the circulation patterns, salinity distribution, topography, and developments near the coral was all considered, to a reasonable and representative area for each coral.

Nevertheless, this dissertation provides new perspectives on both the emerging Asian Pb sources and ocean Pb cycling based on the immediate accessible resources we had over the last four years. The results in this dissertation lead to a number of directions that worth exploring in the future. In terms of the temporal Pb variability, the Vietnamese coral may evidence an upwelling-modulated Pb signal in the western South China Sea, while the Pb variability in the general South China Sea remain unexplored. Investigating the Pb variability in the general South China Sea requires exploration of pristine corals located at non-upwelling areas (i.e. Xisha Islands). The variation of Pb in general South China Sea could be a worthwhile comparison with the Vietnamese coral in this study.

Also, investigating the temporal and spatial variability of Pb in the northern part of South China Sea could further constrain the contribution of Chinese Pb to the region. China has become a major Pb source within the last few decades [Flegal *et al.*, 2013]. The intrusion of Chinese Pb has been noted in the remote western Pacific [Inoue and Tanimizu, 2008] and even in California [Ewing *et al.*, 2010]. Also, one of the conclusions in this dissertation is that a large amount (~46%) of Chinese Pb has contributed to the western South China Sea. Assessing the contribution of Chinese Pb in the South China Sea could be achieved by investigating the spatial distribution of Pb and Pb isotopes in the South China Sea water or quantitatively assessing the surface transient of Pb in corals northern part of South China Sea compared to the emission inventory.

The modulation of Pb by ocean circulation is another aspect that is worth exploring in the future. In this dissertation, the temporal variability of Pb in the Vietnam coral seems to be modulated by the summer upwelling. However, the circulation of Pb in South China Sea remains poorly understood. Investigating on other proxies in the Vietnam coral (i.e.: ^{14}C) could improve on the understanding of the upwelling water mass. While investigating other transient tracers across the South China Sea (i.e.: CFC, CCl_4) could better constrain the water masses and the flow pattern and timescale of the intrusions of Pacific water into the South China Sea.

Pb isotope exchange is the fourth aspect that leads to further investigation. Despite a clear isotope exchange observed in our batch experiment, the extent of Pb isotope exchange; the materials involved in isotope exchange; the environment in which isotope exchange takes place and the influence of Pb isotope exchange on the ocean Pb cycle still remains undeveloped. Many directions can be explored but investigating exchange kinetics in major rivers around the world; exploring the spatial Pb isotope distribution in various river mouths could be most productive way to further assess the importance of isotope exchange in the ocean Pb cycle.

Figure 6.1: A comparison of the Pb content in MacRitchie sediment record (grey filled diamonds) with Pb/Ca in Vietnam coral (blue filled squares). The y-axes are not in the same scale. The three arrows indicate major emission control measures for Pb in the history, including: introducing of “Clean Air Act” (for Singapore), reducing the Pb content in leaded petrol (all major countries in Southeast Asia and China), and phasing out of leaded petrol.

References for Chapter 6

Ewing, S. A., J. N. Christensen, S. T. Brown, R. A. Vancuren, S. S. Cliff, and D. J. Depaolo (2010), Pb isotopes as an indicator of the Asian contribution to particulate air pollution in urban California, *Environmental Science and Technology*, 44(23), 8911-8916.

Flegal, A. R., C. Gallon, P. M. Ganguli, and H. C. Christopher (2013), All the Lead in China, *Critical Reviews in Environmental Science and Technology*, 43(17), 1869-1944.

Inoue, M., and M. Tanimizu (2008), Anthropogenic lead inputs to the western Pacific during the 20th century, *Science of the Total Environment*, 406(1-2), 123-130.

Appendix

Appendix A: Measured data involved in this thesis

Appendix A-1: Vietnam coral Pb/Ca measurements

Year	Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)	Year	Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1841.5	12.1	1.3	1888	13.3	2.6
1842.5	12.2	1.5	1890	15.2	2.7
1845.5	13.1	1.6	1892	17.3	0.4
1846	9.5	3.7	1893.75	13.7	1.3
1847.5	10.4	3.4	1895.25	13.8	0.9
1856.5	12.7	0.8	1896.75	16.5	1.1
1857.75	14.6	1.7	1897.5	12.7	1.3
1861.25	15.7	2.7	1898.5	14.0	0.6
1862.25	11.9	4.2	1900.25	12.7	0.3
1863.5	11.0	1.3	1901	12.3	0.8
1864.5	10.8	2.8	1902.25	14.0	2.3
1865.75	14.1	0.7	1903	13.2	1.0
1867.25	15.5	3.0	1904.75	14.4	2.0
1868	12.9	1.9	1906.25	16.0	1.1
1869.5	11.6	2.6	1908	15.4	1.1
1870.5	13.2	2.7	1910	15.6	0.9
1872	14.1		1912	14.9	4.4
1873.5	12.3	2.6	1914	14.1	3.3
1874.5	15.6	2.6	1916	14.1	0.4
1878.25	13.7	1.5	1918	13.1	0.7
1880	15.2	0.3	1920	13.7	0.8
1881.5	16.2	0.9	1922	16.8	2.1
1882.75	13.8	1.8	1924	15.2	0.8
1884	13.0	1.5	1926	17.4	4.1
1885.25	12.2	2.4	1928	16.7	0.8
1885.5	14.5	0.6	1929.75	18.5	0.5

Appendix A-1: Vietnam coral Pb/Ca measurements (continued)

Year	Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1931	13.7	0.6
1932.25	15.1	1.0
1935	16.8	2.3
1936.75	14.5	0.9
1938.25	17.5	1.7
1940	15.6	0.5
1941.75	14.5	0.6
1943.25	15.7	0.5
1945	17.6	1.5
1947	18.0	1.0
1949	17.2	0.9
1951	17.7	0.9
1953	16.6	0.4
1954.75	14.7	1.4
1956.25	13.9	0.6
1958	14.5	0.5
1958.85	22.0	0.3
1960.85	19.2	1.4
1962.35	19.0	0.9
1964	18.2	1.3
1965.5	20.6	1.0
1966.25	19.9	2.8
1967.75	19.8	0.5
1969.5	22.1	0.3
1971.25	18.4	0.8
1973.25	18.0	0.7

Year	Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1974.75	18.9	4.7
1976.25	17.6	1.4
1978	20.6	0.8
1982.5	24.6	0.8
1985	31.5	0.5
1987	26.4	1.8
1989	21.0	0.5
1991	24.6	1.25
1993	22.8	1.0
1995	26.5	1.2
1996.85	23.3	0.6
1998.85	24.0	2.3
2001	31.0	1.1
2003	32.3	1.2
2004.5	44.2	2.3
2006	37.8	0.7
2008	37.8	1.4
2010	33.9	2.1

* the standard deviation was the standard deviation observed in triplicated measurements

Appendix A-2: Singapore corals Pb/Ca measurements

Kusu coral

Year	Average Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1969	46.0	3.3
1970	42.0	6.5
1971	38.6	4.3
1972	44.4	**
1973	44.2	7.4
1974	46.8	2.7
1975	46.7	6.2
1976	35.8	6.3
1977	38.0	7.0
1978	37.6	1.7
1979	37.2	1.0
1980	41.2	0.2
1981	36.0	4.3
1982	39.6	1.8
1983	52.0	11.3
1984	52.5	3.0
1985	58.2	5.2
1986	51.8	6.4
1987	45.7	5.0
1988	38.0	2.1
1989	36.5	13.8
1990	35.7	1.8
1991	35.0	2.2
1992	34.7	5.7
1993	30.6	3.5

Year	Average Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1994	32.12	5.5
1995	28.70	5.7
1996	41.19	1.0
1997	44.59	1.1
1998	48.44	3.2
1999	38.20	3.7
2000	37.61	4.9
2001	30.62	1.9
2002	33.83	1.1
2003	45.73	2.5
2004	39.66	7.8
2005	30.71	8.1
2006	23.55	2.4
2007	28.40	2.3
2008	30.20	*
2009	35.42	2.0
2010	31.46	1.4

**sample loss due to various reasons (e.g.: boring organism, instrumental issues, contamination, etc)

Appendix A-2: Singapore corals Pb/Ca measurements (continued)

Hantu coral

Year	Average Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
1983	37.4	5.1
1984	30.9	4.0
1985	37.5	2.0
1986	29.3	5.0
1987	55.3	**
1988	58.0	3.4
1989.96	36.1	5.1
1990.7	41.9	0.1
1991.17	37.6	2.1
1991.67	46.6	1.0
1992.17	40.0	2.6
1992.67	53.6	3.9
1993.125	36.3	4.3
1993.75	56.3	4.7
1994	48.5	6.2
1995	70.7	6.5
1996	43.5	2.8
1997	37.0	1.1
1998	36.4	3.1
1999	53.2	3.6
2000	33.2	2.1
2001	34.6	0.2
2002	49.8	1.5
2004	37.4	3.5
2005	42.7	3.0

Year	Average Pb/Ca (nmol/mol)	Standard deviation (nmol/mol)
2006	31.7	4.0
2007	23.1	1.1
2008	26.0	4.8
2009	34.4	2.7
2010	24.2	0.9

Jong coral was measured by Dr. Lee Jong-Mi, and can be found in Lee et al. 2014 EPSL

Appendix A-3: MacRitchie sediment trace metal measurements

²¹⁰ Pb Year	Representing period	[Pb] mg/kg	[Cu] mg/kg	[Zn] mg/kg
1998	2012-1984	55.1	309.3	122.5
1979	1984-1974	43.0	9.5	41.8
1967	1974-1960	41.3	10.9	37.0
1955	1960-1950	52.9	9.7	48.4
1945	1950-1940	35.8	9.7	55.0
1931	1940-1922	27.1	35.9	34.2
1915	1915-1909	11.4	4.3	13.2
1903	1909-1901	1.9	1.0	2.5
1895	before 1895	1.7	1.2	4.3
1888		1.5	1.0	3.7
1879		2.6	1.9	70.1

²¹⁰ Pb Year	Representing period	[As] mg/kg	[Ag] mg/kg	[Cd] mg/kg
1998	2012-1984	13.6	0.238	0.399
1979	1984-1974	8.9	0.113	0.214
1967	1974-1960	5.9	0.126	0.249
1955	1960-1950	7.5	0.157	0.284
1945	1950-1940	10.0	0.137	0.273
1931	1940-1922	6.1	0.121	0.239
1915	1915-1909	3.2	0.046	0.067
1903	1909-1901	2.6	0.008	0.015
1895	before 1895	2.0	0.004	0.003
1888		1.8	0.007	0.001
1879		2.5	0.008	0.006

²¹⁰ Pb Year	Representing period	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
1998	2012-1984	1.137	2.122	2.413
1979	1984-1974	1.138	2.121	2.415
1967	1974-1960	1.151	2.111	2.431
1955	1960-1950	1.152	2.111	2.432
1945	1950-1940	1.180	2.086	2.461
1931	1940-1922	1.189	2.078	2.471
1915	1915-1909	1.185	2.083	2.469
1903	1909-1901	1.199	2.076	2.488
1895	before 1895	1.215	2.064	2.507
1888		1.214	2.065	2.506
1879		1.215	2.063	2.507

Appendix A-3: MacRitchie sediment trace metal measurements (continued)

²¹⁰ Pb Year	Representing period	[Ba] mg/kg	[Tl] mg/kg	[U] mg/kg
1998	2012-1984	21.1	0.110	1.55
1979	1984-1974	21.3	0.134	1.80
1967	1974-1960	17.6	0.160	1.88
1955	1960-1950	17.8	0.177	2.18
1945	1950-1940	18.8	0.225	2.36
1931	1940-1922	15.8	0.223	2.05
1915	1915-1909	8.2	0.126	0.82
1903	1909-1901	5.2	0.025	0.44
1895	before 1895	3.2	0.011	0.54
1888		4.1	0.015	0.46
1879		4.3	0.016	0.79

²¹⁰ Pb Year	Representing period	[Cr] mg/kg	[Co] mg/kg	[Ni] mg/kg
1998	2012-1984	19.1	1.19	7.76
1979	1984-1974	7.9	0.66	1.53
1967	1974-1960	6.5	0.57	0.93
1955	1960-1950	7.1	0.59	0.81
1945	1950-1940	7.6	0.63	0.79
1931	1940-1922	9.4	0.46	0.80
1915	1915-1909	5.1	0.21	0.33
1903	1909-1901	7.0	0.11	0.10
1895	before 1895	6.6	0.07	0.17
1888		7.0	0.07	0.08
1879		9.6	0.12	0.10

²¹⁰ Pb Year	Representing period	Clay %	Silt %	Sand %
1998	2012-1984	44.7	53.2	2.1
1979	1984-1974	47.4	34.2	18.5
1967	1974-1960	57.6	40.8	1.8
1955	1960-1950	34.1	40.3	25.6
1945	1950-1940	44.2	46.0	9.8
1931	1940-1922	37.7	49.4	12.9
1915	1915-1909	31.9	55.2	12.9
1903	1909-1901	29.4	60.2	10.4
1895	before 1895	18.4	41.8	39.9
1888		23.3	38.5	38.2
1879		31.2	52.5	16.2

Appendix A-4: Vietnam coral Pb isotope measurements

Year	$^{206}\text{Pb}/^{207}\text{Pb}$	2SE^{***}	$^{206}\text{Pb}/^{207}\text{Pb}$	2SE
1857.75	1.1919	0.0007	2.4802	0.0013
1862.25	1.1956	0.0009	2.4828	0.0017
1865.75	1.1963	0.0006	2.4834	0.0007
1869.5	1.1917	0.0005	2.4793	0.0007
1873.5	1.1932	0.0003	2.4836	0.0007
1878.25	1.1923	0.0005	2.4812	0.0005
1882.75	1.1943	0.0004	2.4831	0.0007
1885.5	1.1952	0.0003	2.4851	0.0008
1892	1.1929	0.0005	2.4794	0.0009
1896.75	1.1954	0.0005	2.4846	0.0009
1900.25	1.1931	0.0004	2.4817	0.0005
1903	1.1905	0.0009	2.4765	0.0017
1908	1.1907	0.0010	2.4784	0.0008
1914	1.1945	0.0005	2.4842	0.0006
1916	1.1898	0.0005	2.4776	0.0012
1918	1.1923	0.0004	2.4820	0.0005
1920	1.1913	0.0005	2.4796	0.0010
1922	1.1927	0.0004	2.4832	0.0004
1924	1.1915	0.0005	2.4827	0.0006
1926	1.1921	0.0003	2.4821	0.0005
1928	1.1911	0.0002	2.4797	0.0003
1929.75	1.1935	0.0002	2.4854	0.0004
1931	1.1944	0.0004	2.4855	0.0006
1931	1.1920	0.0003	2.4829	0.0006
1932.25	1.1943	0.0001	2.4846	0.0002
1935	1.1934	0.0001	2.4833	0.0002
1936.25	1.1930	0.0002	2.4835	0.0004
1938.25	1.1925	0.0002	2.4791	0.0004
1940	1.1934	0.0002	2.4827	0.0004
1941.75	1.1918	0.0002	2.4804	0.0003
1943.25	1.1938	0.0002	2.4830	0.0004
1945	1.1932	0.0002	2.4838	0.0004

*** the 2 S.E. was twice of the normalized standard deviation associated with the internal counting statistics of the ICP-MS during the run

Vietnam coral Pb isotope measurements (continued)

Year	$^{206}\text{Pb}/^{207}\text{Pb}$	$\pm\text{SE}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$\pm\text{SE}$
1947	1.1929	0.0002	2.4828	0.0003
1949	1.1919	0.0002	2.4819	0.0003
1951	1.1921	0.0002	2.4810	0.0003
1953	1.1904	0.0002	2.4802	0.0004
1954.75	1.1910	0.0002	2.4807	0.0004
1956.25	1.1903	0.0011	2.4785	0.0017
1958.85	1.1776	0.0002	2.4618	0.0003
1965.5	1.1829	0.0002	2.4658	0.0003
1965.5	1.1840	0.0002	2.4661	0.0003
1966.25	1.1828	0.0013	2.4656	0.0021
1967.75	1.1825	0.0002	2.4675	0.0005
1969.5	1.1844	0.0002	2.4697	0.0005
1971.25	1.1860	0.0003	2.4682	0.0005
1973.25	1.1854	0.0002	2.4699	0.0003
1974.75	1.1846	0.0004	2.4689	0.0008
1976.25	1.1851	0.0003	2.4681	0.0004
1980	1.1870	0.0003	2.4688	0.0004
1982.5	1.1853	0.0003	2.4708	0.0005
1985	1.1852	0.0001	2.4721	0.0004
1987	1.1836	0.0002	2.4721	0.0004
1989	1.1822	0.0001	2.4646	0.0005
1991	1.1823	0.0001	2.4626	0.0003
1993	1.1783	0.0001	2.4624	0.0003
1995	1.1793	0.0002	2.4636	0.0003
1996.85	1.1835	0.0002	2.4672	0.0005
1998.85	1.1782	0.0001	2.4668	0.0002
2001	1.1767	0.0001	2.4630	0.0001
2003	1.1737	0.0001	2.4614	0.0002
2006	1.1744	0.0001	2.4581	0.0002
2008	1.1762	0.0001	2.4627	0.0002
2010	1.1766	0.0001	2.4628	0.0002

Appendix A-5: Singapore corals Pb isotope measurements

Kusu coral

<u>Year</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>	$^{208}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>
1969	1.1715	0.0002	2.4562	0.0004
1970	1.1704	0.0002	2.4543	0.0005
1971	1.1615	0.0003	2.4457	0.0003
1972	1.1709	0.0006	2.4545	0.0012
1973	1.1668	0.0002	2.4490	0.0004
1974	1.1658	0.0002	2.4456	0.0005
1975	1.1688	0.0002	2.4504	0.0005
1976	1.1681	0.0001	2.4504	0.0003
1977	1.1669	0.0004	2.4483	0.0005
1978	1.1725	0.0001	2.4563	0.0003
1979	1.1797	0.0004	2.4636	0.0004
1980	1.1730	0.0003	2.4562	0.0005
1981	1.1755	0.0003	2.4575	0.0005
1982	1.1747	0.0003	2.4575	0.0004
1983	1.1739	0.0001	2.4548	0.0003
1984	1.1750	0.0002	2.4571	0.0004
1985	1.1706	0.0002	2.4544	0.0003
1986	1.1749	0.0003	2.4590	0.0004
1987	**			
1988	1.1722	0.0002	2.4549	0.0005
1989	1.1791	0.0002	2.4636	0.0004
1990	1.1779	0.0006	2.4561	0.0007
1991	1.1725	0.0004	2.4549	0.0007
1992	**			
1993	1.1783	0.0002	2.4641	0.0004

<u>Year</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>	$^{208}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>
1994	1.1775	0.0001	2.4612	0.0002
1995	1.1760	0.0002	2.4600	0.0003
1996	1.2017	0.0001	2.4659	0.0001
1997	1.1930	0.0001	2.4730	0.0002
1998	1.1859	0.0002	2.4694	0.0005
1999	1.1849	0.0001	2.4687	0.0002
2000	1.1869	0.0002	2.4641	0.0003
2001	1.1860	0.0001	2.4723	0.0003
2002	1.1846	0.0002	2.4669	0.0003
2003	1.1954	0.0001	2.4781	0.0002
2004	1.1917	0.0001	2.4757	0.0003
2005	1.1870	0.0001	2.4707	0.0002
2006	1.1851	0.0001	2.4685	0.0003
2007	1.1871	0.0001	2.4647	0.0002
2008	1.1841	0.0001	2.4646	0.0002
2009	1.1849	0.0001	2.4664	0.0003
2010	1.1910	0.0002	2.4727	0.0004

** sample loss due to various reasons (e.g.: boring organism, instrumental issues, contamination, etc)

Singapore corals Pb isotope measurements (continued)

Hantu coral

<u>Year</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>	$^{208}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>
1983	1.1821	0.0001	2.4666	0.0002
1984	1.1808	0.0001	2.4663	0.0002
1985	1.1783	0.0001	2.4612	0.0002
1986	1.1769	0.0001	2.4589	0.0003
1988	1.1666	0.0001	2.4464	0.0001
1989.96	1.1774	0.0003	2.4601	0.0006
1990.7	1.1771	0.0001	2.4603	0.0002
1991.17	1.1747	0.0001	2.4573	0.0002
1991.67	1.1768	0.0001	2.4580	0.0001
1992.17	1.1719	0.0001	2.4531	0.0002
1992.67	**			
1993.125	1.1726	0.0001	2.4550	0.0001
1993.75	1.1758	0.0001	2.4584	0.0001
1994	1.1717	0.0001	2.4544	0.0001
1995	1.1752	0.0001	2.4554	0.0001
1996	1.1862	0.0001	2.4693	0.0001
1997	1.1801	0.0001	2.4641	0.0002
1998	1.1873	0.0001	2.4694	0.0001
1999	1.1907	0.0001	2.4697	0.0002
2000	1.1901	0.0003	2.4736	0.0005
2001	1.1887	0.0001	2.4738	0.0002
2002	1.1885	0.0001	2.4742	0.0002
2004	1.1898	0.0001	2.4765	0.0002
2005	1.1843	0.0001	2.4669	0.0002
2006	1.1874	0.0002	2.4700	0.0003
2007	1.1857	0.0002	2.4692	0.0003
2008	1.1815	0.0001	2.4666	0.0002
2009	1.1766	0.0001	2.4609	0.0002
2010	1.1810	0.0003	2.4645	0.0004

** sample loss due to various reasons (e.g.: boring organism, instrumental issues, contamination, etc)

Appendix A-6: MacRitchie sediment Pb isotope measurements

²¹⁰ Pb Year	<i>Representing period</i>	²⁰⁶ Pb/ ²⁰⁷ Pb	<u>2SE</u>	²⁰⁸ Pb/ ²⁰⁷ Pb	<u>2SE</u>
1998	2012-1984	1.1372	0.0001	2.4130	0.0001
1979	1984-1974	1.1384	0.0000	2.4145	0.0001
1967	1974-1960	1.1513	0.0000	2.4309	0.0001
1955	1960-1950	1.1523	0.0000	2.4322	0.0001
1945	1950-1940	1.1797	0.0000	2.4612	0.0001
1931	1940-1922	1.1888	0.0001	2.4708	0.0002
1915	1915-1909	1.1853	0.0000	2.4691	0.0001
1903	1909-1901	1.1987	0.0001	2.4884	0.0001
1895	before 1895	1.2148	0.0001	2.5069	0.0002
1888		1.2138	0.0000	2.5058	0.0001
1879		1.2151	0.0001	2.5066	0.0001

Appendix A-7: Singapore Strait water Pb isotope measurements

<u>Name & Year</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>	$^{208}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>
Kusu Nov 2011	1.1975	0.0003	2.4829	0.0004
Hantu Dec 2011	1.1962	0.0005	2.4807	0.0008
Kusu July 2012	1.1939	0.0001	2.4778	0.0003
Hantu July 2012	1.1978	0.0004	2.4838	0.0005
Kusu Dec 2012	1.1955	0.0004	2.4792	0.0006
Hantu Dec 2012	1.1908	0.0003	2.4736	0.0004
Kusu July 2013	1.1920	0.0001	2.4776	0.0002
Hantu July 2013	1.1937	0.0002	2.4790	0.0002
Kusu Nov 2013	1.1935	0.0002	2.4782	0.0004
Hantu Nov 2013	1.1942	0.0001	2.4791	0.0002

Appendix A-8: Singapore incineration ash Pb isotope measurements

<u>Name</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>	$^{208}\text{Pb}/^{207}\text{Pb}$	<u>2SE</u>
Tuas South	1.1414	0.0011	2.4198	0.0024
Senoko	1.1496	0.0008	2.4265	0.0016
Keppel Seglers	1.1535	0.0008	2.4246	0.0011
Tuas	1.1474	0.0015	2.4253	0.0020

Appendix A-9: Observed Pb concentration and Pb isotopes in isotope exchange experiment

<u>Name & Timestep</u>	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	[Pb] ($\mu\text{mol/L}$)	SD ($\mu\text{mol/L}$)
Johor A unfiltered	1.1987	2.5438	373.4	5.4
Johor A T0 no spike	1.1998	2.5239	18.3	2.0
Johor A T0	1.1781	2.5085	25.4	1.4
Johor A T 3 hrs	1.1893	2.5283	32.7	0.5
Johor A T 5 hrs	1.1841	2.5364	27.1	2.4
Johor A T 24 hrs	1.1811	2.5317	21.1	1.5
Johor A T 47.5 hrs	1.1869	2.5400	20.9	1.0
Johor A T 7 days	1.1900	2.5456	35.2	0.5
Johor A T 23 days	1.1938	2.4788	22.0	2.0
Johor A T 2 months	1.1967	2.5368	33.0	3.7
Johor B T 0	1.1668	2.5210	47.8	1.9
Johor B T 2 hrs	1.1671	2.5253	45.9	1.6
Johor B T 21 hrs	1.1675	2.5255	43.9	1.1
Johor B T 44.5 hrs	1.1678	2.5206	47.4	1.3
Johor B T 7 days	1.1667	2.5234	***	
Johor B T 23 days	1.1711	2.4553	36.0	1.8
Johor B T 2 months	1.1673	2.5849	36.8	2.3

*** Not enough sample for a sensible measurement
The Pb isotope in Singapore aerosols was measured by Dr. Lee Jong-Mi

Appendix B: Estimated data involved in this thesis

Appendix B-1: The isotopic composition in average Chinese Pb ores as of 1996

Province	Pb production as of 1996 (10 ⁴ ton) *	% total	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
Liaoning	6.36	16.82%	1.057	2.378	2.252
Hunan	14.23	37.63%	1.181	2.474	2.095
Guangdong	5.02	13.27%	1.172	2.473	2.110
Guangxi	2.34	6.19%	1.059	2.387	2.253
Yunnan	9.87	26.10%	1.179	2.397	2.096
Total	37.82				
Average Chinese Pb ore			1.151	2.432	2.133

* The isotope data was estimated by the major Pb mines in the province, source Sangster et al. (2000) and Mukai et al. (1993). The production of Pb from these provinces accounts >85% of total national production. Production data from Ministry of Land and Resources of the People's Republic of China and China Mining (eds). The distribution of Chinese major Pb-Zn production bases (in Chinese).

Appendix B-2: The estimated isotopic composition of Chinese emitted Pb as of 2000 (peak petrol emission) and 2008 (more recent, leaded petrol phased out)

The isotopic composition of Chinese Pb (as of 2000)

Emission type	Emission (ton)	% total	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Pb ore smelting	903.105	4.67%	1.151	2.432	2.133
Coal emission	6013	31.08%	1.166	2.464	2.113
Petrol	12430	64.25%	1.134	2.429	2.143
total emission	19346.105				
Average emitted Chinese Pb 2000			1.145	2.440	2.133

The isotopic composition of Chinese Pb (as of 2008)

Emission type	Emission (ton)	%	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Pb ore smelting	13414	45.79%	1.151	2.432	2.133
Coal emission	15473	52.82%	1.166	2.464	2.113
Petrol	407	1.39%	1.134	2.429	2.143
total emission	29293.7316				
Average emitted Chinese Pb 2008			1.159	2.449	2.123

Appendix C: Methods for making mini-columns

Mini-columns are used to house the HCl-HBr ion exchange chromatography which is essential Pb isotope measurement. The materials and method making these columns is presented here.

Materials need for column

3/8" shrinkable Teflon tube (purchased at: http://www.texloc.com/hs_fep_1_3_1.html)
Frit for columns (thin sheets made in polypropylene materials obtained from Interstate Speciality Products medium HDPE sheet, 1/16 inch thickness, pre size: 45-90 micro and cat# 4903.)

Tools need for column

A ceramic stick with outer diameter of ~3/8". (I used the pestle for our mini mortar)
Glass beaker with water
Heat gun
Circle puncher (I used small pipette tips)
2 thin stick (I used 2 tooth sticks)

Steps in making a column

1. Cut the shrinkable Teflon tubings to 4-5cm length, put the ceramic stick ~2cm into the Teflon tube and leave 2-3cm of the tube hollow.
2. Prepare a beaker filled with water for cooling purpose.
3. Turn on the heat gun. Start from the lowest power and gradually increase the heating. Adjust to a suitable temperature by testing the shrink speed of the Teflon tubing. The suitable temperature should shrink the Teflon tubing smoothly and in a workable speed.
4. Put the cooling water beside the heat gun. Hold the ceramic stick (with Teflon tubing on one end) on one hand and the heat gun on the other hand. Place the open end of the Teflon tubing in front of the heat gun. Rotate the ceramic stick a bit to help unify the heating. The open end of the Teflon tubing should shrink while the side with the ceramic stick should stay at its original diameter.
5. Quench the heated Teflon tubing in the cooling water and then remove it from the ceramic stick.
6. Trim the sharp side of a thin pipette tip to an adequate diameter (the inner diameter of the trimmed side comparable to the inner diameter of the shrinked side of the Teflon tube).
7. Use the trimmed pipette tip as a circle puncher and punch it onto the frit material. A small circular piece of frit should be made.
8. Squeeze the frit into the shrinked side of the Teflon tubing. Adjust the orientation of the frit using 2 thin sticks.

Now the column should be ready for cleaning. New columns should be cleaned by boiling aqua regia for a few days and then followed by conventional leach before use.

Appendix D: X-ray and luminescence images of the coral slabs used in this thesis

Appendix D-1: X-ray image of the Vietnam coral with annual bands identified

Appendix D-2: X-ray image of the Kusu coral

KU-B

Appendix D-3: X-ray image of the Hantu coral

Appendix D-4: Luminescence image of the Hantu coral

Appendix E: Formatted version of the published Marine Chemistry paper (chapter 3)

Marine Chemistry 188 (2015) 49–58

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

ELSEVIER

WILEY-BOSCH

Isotopic record of lead in Singapore Straits during the last 50 years: Spatial and temporal variations

Mengli Chen^{a,b,c,*}, Jong-Mi Lee^d, Intan S. Nurhati^c, Adam D. Switzer^{a,b,c}, Edward A. Boyle^{c,d}

^a Division of Earth Sciences, Nanyang Technological University, 50 Nanyang Avenue, 636798, Singapore
^b Earth Observatory of Singapore, Nanyang Technological University, 50 Nanyang Avenue, 636798, Singapore
^c Singapore-MIT Alliance on Research and Technology, Center of Environmental Sensing and Modelling, 1 CREATE Way, #09-03 CREATE Tower, 138602, Singapore
^d Department of Earth, Atmospheric, and Planetary Sciences, 225, Massachusetts Institute of Technology, Cambridge MA 02142, USA

ARTICLE INFO

Article history:
Received 10 July 2014
Received in revised form 23 September 2014
Accepted 16 October 2014
Available online 24 October 2014

Keywords:
Anthropogenic lead
Pb
Pb isotopes
Southeast Asia
South China Sea
Singapore
Coral

ABSTRACT

The spatial and temporal variations of Pb were reconstructed from three corals along an east–west transect of the Singapore Straits – in proximity to one of the largest emerging Asian cities and one of the world's busiest ports. In addition to establish the variation in seawater Pb concentration, sources of Pb were also investigated via Pb isotopes in seawater and corals and compared with the isotopes in local aerosols and other potential Pb sources. The annual variation of Pb in Singapore corals seems to be related to local annual precipitation while the decadal-scale variation may be related to the long-term development of the region. The decrease of Pb/Ca in coral after 2005 coincided with the regional phasing out of leaded gasoline. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Singapore corals rose from as low as -1.166 during the 1960s to -1.189 by the late 1990s, and fluctuated between -1.180 – -1.198 from the late 1990s to 2010. $^{206}\text{Pb}/^{207}\text{Pb}$ in recent Singapore corals was elevated relative to Singapore atmospheric aerosols (-1.147 , which is typical of urban aerosols throughout the southeastern Asian and Indonesian region). The linear distribution of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{207}\text{Pb}$ in triple isotope plots suggests two end-member mixing between the aerosol–Pb as a low- $^{206}\text{Pb}/^{207}\text{Pb}$ end-member and an unidentified source with higher $^{206}\text{Pb}/^{207}\text{Pb}$. Possible high $^{206}\text{Pb}/^{207}\text{Pb}$ sources include: surface runoff from imported south Chinese Pb, crustal materials from riverine inputs (sediments and suspended matter) or land reclamation, and vessels/dockyard activities.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lead (Pb) has been an important contaminant in human history, especially since the industrial revolution. The amount of Pb released into the environment was more than 25 times of global natural emissions in the 1980s, primarily due to the use of leaded gasoline (Nriagu, 1979, 1989). Prior to the 1980s, the major consumers of leaded gasoline were in North America and Western Europe (e.g.: Hilton, 2006). As these countries phased out leaded gasoline, developing countries (particularly in Asia) continued to use leaded gasoline until quite recently (e.g.: Hirota, 2006). Besides leaded gasoline consumption, Asian industrialization has also led to an increase in coal burning and high temperature industrial activities, which also contribute to Pb emissions. For example in China, coal consumption has increased 20 times relative to the 1950s (Hao et al., 2008), and in Malaysia, coal consumption has increased nearly 50 times since 1980 (International Energy Statistics). These changes indicate that the relative contributions from different regions and sources to the global Pb flux have certainly changed when compared to the 1980s. Moreover, the recent Asian Pb emissions have received increasing

attention, as concentrations of Asian Pb in aerosols were generally an order of magnitude higher than from elsewhere (Bollhöfer and Rosman, 2000, 2001). For example, large (~29%) contributions of Asian Pb have been found in aerosols collected in California (Ewing et al., 2010).

Several studies have investigated anthropogenic Pb in Asia by looking at the Pb isotope signature in: aerosols and roadside dust from Asian cities (e.g.: Bollhöfer and Rosman, 2000, 2001, 2002; Duzgören-Aydin et al., 2004; Hsu et al., 2006); surface sediments from major river mouths and South China Sea basin (e.g.: Hao et al., 2008; Ip et al., 2007; Zhu et al., 2010); marine organisms in Singapore seaways (e.g.: Ng et al., 2006); and corals from the western Pacific (e.g.: Inose and Tanimizu, 2008). Most of these studies have found an anthropogenic Pb signature in the environment, reflecting the recent developments in Asia. But referring to the changing emission inventory of Pb, and the extreme complexity of the transport mechanisms (Church et al., 1990; Flegal, 1986; Nilsson et al., 2010), a one-time sample, or even a few years' coverage is not enough to constrain the temporal change of sources and the fluxes of Pb. In this case, a few decades' data coverage would be valuable to establish the temporal variations of Pb and Pb isotopes in this region. One approach to study long-term Pb changes is to investigate Pb in natural archives such as corals. During the secretion of coral skeletons, seawater is transported to the calcifying region (Sinclair, 2005; Tambutté et al., 2011), and the Pb in seawater can be substituted for calcium into the

* Corresponding author at: Division of Earth Sciences, Nanyang Technological University, 50 Nanyang Avenue, 636798, Singapore.
E-mail address: chenm27@nus.edu.sg (M. Chen).

carbonate structure (Shen and Boyle, 1987). Although the details of calcification mechanism are still debated, the variation of Pb and Pb isotopes in corals closely follows that in nearby seawater (Kelly et al., 2009; Shen and Boyle, 1987).

The Singapore Straits is an important site to study the environmental impact of anthropogenic Pb emitted from Asian countries as its shores with the rapidly growing countries of Singapore, Malaysia and Indonesia. Singapore, one of the most developed/densely populated cities in Southeast Asia (Statistics Singapore, 2014) lies in its close proximity. The strait also houses one of the world's busiest ports (American Association of Port Authorities, 2006), representative of that in many similarly growing Asian cities. The Singapore Straits connects the South China Sea, Java Sea and Northeastern Indian Ocean through Malacca Straits (Fig. 1), and strong monsoonal winds over the region can also deliver aerosols from distant countries such as China and Thailand. Thus, the temporal evolution of Pb in the Singapore Straits is representative of that of many similarly developing Asian cities. In this study, we investigate the historical variations of Pb in the Singapore Straits using three coral cores covering the past 40–50 years (Fig. 1).

1.1. Leaded gasoline usage in neighboring countries and regions

Pb in the North Atlantic and North Pacific has been largely attributed to leaded gasoline emissions that were introduced to the ocean by atmospheric deposition (e.g.: Flegal, 1986; Weiss et al., 2003). Since leaded gasoline is also likely to be a major Pb source in the Singapore Straits over the past 50 years, we have estimated the consumption of leaded gasoline from the countries adjacent to the Singapore Straits. Major countries surrounding our site include Singapore, Malaysia and Indonesia. Singapore's main island is ~6 km north of our coral sites. Malaysia is further north, at the shortest distance of ~25 km. Indonesia is to the south of Singapore Straits, and the nearest Indonesian city, Batam, is ~10 km from our sites (Fig. 1). They are all sufficiently close to influence Pb in our corals.

Singapore used gasoline with Pb content of 0.8 kg/m³ before 1980. The Pb content was reduced to 0.6 kg/m³ between 1981 and 1982; and to 0.4 kg/m³ between 1983 and 1986; and then to 0.15 kg/m³ from 1987 onwards. Unleaded gasoline was introduced to Singapore in 1991, and its market share gradually increased until 1997, when it reached 100% (Ministry of the Environment Singapore, 1987–2000).

Similarly, the Pb content in Malaysian gasoline was 0.84 kg/m³ Pb before 1985; and was reduced to 0.4 kg/m³ between 1986 and 1989, and to 0.15 kg/m³ between 1990 and 1997. Unleaded gasoline was first introduced to Malaysia in 1987, and reached 100% market share in 1998 (Afroz et al., 2003).

Indonesia's leaded gasoline usage is difficult to estimate as the country phased out leaded gasoline city by city. The Pb content of Indonesian gasoline was ~0.84 kg/m³ until 1989 (Mukai et al., 1993) and then reduced to 0.3 kg/m³ by 2001 (Hirota, 2006). Leaded gasoline was phased out in a few cities beginning in 2001: Jakarta phased out leaded gasoline by July 2001; followed by West Java, Cirebon region by October 2001; Bali by November 2001; Batam by June 2003 and Surabaya by September 2004, which together was ~40% of its national gasoline demand at that time (Hirota, 2006). The whole country phased out leaded gasoline by July 2006. Between 2001 and 2006, the Pb content in gasoline in other places in Indonesia was 0.3 kg/m³ (Hirota, 2006; Santosa et al., 2008).

Fortunately when considering Pb in the Singapore Straits, Indonesia should not be considered as a whole because only a small part of the country neighbors the Singapore Straits. Batam is the largest Indonesian city that is proximal to the study site. It is within 20 km of our coral sites. In this case, we primarily consider the consumption of Pb in Batam as the Pb in the Singapore Straits is likely to have come mainly from proximal sources. Estimates of leaded gasoline usage from the countries and regions above are shown in Fig. 2 following the method described in Li et al. (2012).

1.2. Pb isotope studies from the Asia-Pacific and Eastern Indian Ocean regions

The isotopic composition of Pb provides clues to investigate Pb sources. Among the four naturally occurring stable isotopes of Pb, ²⁰⁴Pb is the only non-radiogenic isotope and the other 3 isotopes (²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) are produced by radioactive decay from ²³⁸U, ²³⁵U and ²³²Th (Brown, 1962). The relative abundance of Pb isotopes is dependent on the original Pb isotope composition of the ore which depends on the U/Th/Pb composition and age of the source rocks from which the Pb is extracted. Large variations in isotopic composition among Pb ores have been observed (Komárek et al., 2008), which allows Pb isotope to be used as a (somewhat smudgy) fingerprint. Pb isotopes in one environment can be compared with an array of Pb isotopes from different environments in triple- or quadruple-isotope plots, which provide a sense of the similarities and differences of Pb from one environment to

Fig. 1. Map of the study site. On the top left corner is a map of Singapore Straits and its relative location in Southeast Asia; on the bottom left corner is a zoomed map of Singapore Straits with respect to the countries and regions in its vicinity, the adjacent countries and ocean basins are denoted. The large map on the right shows a close view of coral sites in this study. The coral sites are highlighted in dots. The figure also shows Singapore's major industrial areas (Jorong and Hantu/Jorong); the landfill (Senakau); and the city center (around Singapore River).

Fig. 2. The estimated Pb emission from gasoline in Malaysia (white open rectangles), Singapore (black filled diamonds) and Batam (gray filled triangles). Data are estimated by the product of: road sector gasoline emissions; the allowable Pb content in the gasoline; the market share of the loaded gasoline; and the tailpipe emission factor. Maximum consumption of loaded gasoline occurred in 1980 for Singapore; 1984 for Malaysia; and 2003 for Batam.

another. To provide a framework of Pb isotope for our study, key Pb isotope studies in Asia-Pacific and Eastern Indian Ocean environments are presented here.

The isotopic composition of Pb in aerosols has been studied in major Asian cities from 1994 to 1999, including Kuala Lumpur, Jakarta, Bandung and Ho Chi Minh City (Bollhöfer and Rosman, 2000). The Pb isotopes from these cities were reported as $^{206}\text{Pb}/^{207}\text{Pb} < 1.155$, $^{206}\text{Pb}/^{207}\text{Pb} < 2.430$. Although Singapore was not included in Bollhöfer and Rosman's study, recent aerosol measurements on Pb isotopes performed on samples from the National University of Singapore campus from July 2011 to April 2012, show a consistent isotope ratio as $^{206}\text{Pb}/^{207}\text{Pb} = 1.147 \pm 0.003$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.425 \pm 0.003$ (Lee et al., 2014).

Pb isotope data in seawater in this region is extremely sparse, but Pb isotope ratios in corals from Hainan and Jakarta have been reported. A Hainan coral spanning from 1994–2000 recorded $^{206}\text{Pb}/^{207}\text{Pb} = 1.167 \pm 0.005$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.491 \pm 0.016$; and a Jakarta coral spanning from 1998–2001 recorded $^{206}\text{Pb}/^{207}\text{Pb} = 1.158 \pm 0.007$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.430 \pm 0.010$ (Inoue et al., 2006). Pb isotope ratios in seawater from the central Bay of Bengal were reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.149$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.431$ (Lee et al., 2014).

Pb isotope ratios of South China Sea sediments have also been surveyed and documented. The general isotopic composition of Pb in South China Sea sediment had $^{206}\text{Pb}/^{207}\text{Pb}$ of ~ 1.199 and $^{208}\text{Pb}/^{207}\text{Pb}$ of ~ 2.491 (Zhu et al., 2010). Low anthropogenic enrichment factors were found in these sediment samples, implying little anthropogenic

influence on the sediments, therefore the isotopic composition of Pb in the sediments could reflect natural Pb from the upper crust in this region.

In addition to Pb isotopes in aerosol, seawater, corals and surface sediments, Pb isotopes in coals and Pb ores have been extensively studied and documented. The isotopic composition of Pb from global major coal deposits has been documented by Diaz-Somoano et al. (2009) and the isotopic composition from a number of global major ore deposits has been investigated by Brown in the 1960s (Brown, 1962). A more recent review by Flegal et al. summarized Pb isotopic compositions from major ore deposits across China (Flegal et al., 2013). All of these studies provide an important framework for interpreting our Pb data in Singapore corals.

2. Sampling and methodology

2.1. Site settings

The Singapore Straits is located on the Southwest periphery of the South China Sea and the Northwest side of the Java Sea, and connects to the Eastern Indian Ocean through the Malacca Straits (Fig. 1). The oceanography of the Singapore Straits is dominated by monsoon-driven currents and closely related to the circulation in the above mentioned seas (Pang and Tkalich, 2003). During the northeast monsoon (November to March), the wind in the South China Sea piles water up to the eastern side of the Malay Peninsula and the strong westward

Table 1
General information about the coral cores used in this study.

Site taken ^a	Latitude/longitude ^b	Species	Number of bands ^c	Expected timespan
Kusu	1° 13' 32"N 103° 51' 39"E	<i>Porites lutea</i>	41	1966–2010
Jong	1° 12' 55"N 103° 47' 17"E	<i>Porites lutea</i>	48	1962–2010
Hantu	1° 13' 33"N 103° 44' 45"E	<i>Porites lutea</i>	27	1983–2010

^a The corals were all taken within 5 m depth, with a tidal range of about 2 m.

^b The latitude and longitude show the location of the reefs where our corals were sampled.

^c Annual bands are based on X-ray image and confirmed by fluorescence image.

North Equatorial Countercurrent present near Sumatra and western side of Malay Peninsula (Chen et al., 2005), resulting in a westward current in the Singapore Straits. During the southwest monsoon (April to September), the circulation reverses in South China Sea, Java Sea and northeastern Indian Ocean, resulting an eastward current in the Singapore Straits (Chen et al., 2005). In addition to monsoonal currents, tidal currents reverse these prevalent flows twice a day (Chen et al., 2005; Chia et al., 1988).

Three islands along the east–west transect of the Singapore Straits were chosen for our coral sampling: Kusu to the east, Jong in the middle and Hantu to the west. Kusu is 6.4 km from Singapore's city center and is minimally developed with a one story tortoise sanctuary and a jetty (Sentosa Development Corporation); Jong, ~9 km west from Kusu, remains undeveloped; Hantu is 4.6 km west of Jong and 13.4 km west of Kusu. Even though Hantu itself is minimally developed, it is surrounded by heavily developed islands, including Bokom/Busing (oil refinery), Jurong (industrial), and Semakau (landfill, Fig. 1, Sentosa Development Corporation). Sampling information about the corals used in this study is shown in Table 1, including the location, depth and the species of the corals that were sampled. Seawater samples were also collected at the coral sites to provide a contrast background about the Pb isotope in the environment that corals grew in.

As the Jong coral was the longest record and Jong Island was the only site with no development, the Pb and Pb isotope from the Jong coral should most likely reflect the variability of Pb in the Singapore Straits. The temporal variability of Pb and Pb isotopes in the Jong coral has been discussed elsewhere (in Lee et al., 2014). On top of their discussion, this paper focuses on the spatial variability of Pb and Pb isotopes in the Singapore Straits by comparing the Pb records in three different coral cores.

2.2. Methodology

Both Pb/Ca and the Pb isotopes were analyzed from our coral samples after careful cleaning. Samples went through a series of treatments using trace metal clean reagents in cleaned plasticware. To ensure the precision, all the samples were cleaned and measured for Pb concentrations in triplicate. The cleaning method generally followed the method which has been previously described in Shen and Boyle (1988) with slight modifications due to the improved laboratory techniques. In brief, corals were first crushed into ~700 µm pieces for primary cleaning; and further crushed into 270–700 µm pieces for secondary cleaning. In each cleaning procedure, alternating alkaline-H₂O₂, dilute (0.1 M) HNO₃ and hydrazine-based reductant were applied to selectively dissolve the surface of the coral and to make sure that only the Pb in the carbonate structure remained. The pre-concentration step after the secondary cleaning was skipped as the analysis using quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, VG Plasmaquad 2+) allowed samples to be analyzed at lower concentrations in the presence of a CaCO₃ matrix (10–50 nmol/mol) compared to using graphite furnace atomic absorption (several µmol/mol, Shen and Boyle, 1988). After secondary cleaning, samples were dissolved in trace metal clean HNO₃ for Pb and Ca measurements. From this dissolved solution, Ca was measured by flame atomic

absorption spectroscopy (FAAS) after appropriate dilution, and Pb was measured by Q-ICP-MS with an addition of a known amount of ²⁰⁹Pb enriched spike (Oak Ridge National Laboratory).

For Pb isotope analysis, an Eichrom AG-1X8 (chloride form, 200–400 mesh) ion exchange column was employed to purify Pb from the sample matrix. The column procedure typically recovers 99.98% of the Pb from the sample (Reuer et al., 2003). Although we have no data on Pb isotope fractionation during column separation, given the 99.98% recovery rate of Pb, it should be very small compared to the natural variability of the Pb isotope ratios in the environment.

Pb isotope ratios in these coral separates were measured by multi-collector ICP-MS (MC-ICP-MS, Micromass/GV IsoProbe) with a Daly ion-counting detector measuring ²⁰³Pb. ICPMS mass fractionation was monitored by adding a ²⁰²Tl/²⁰³Tl spike into the post-column sample and corrected using the “beta method”; tailing error was corrected by measuring the monoisotopic element ²⁰⁸Pb at half masses. Tl-acid blanks were measured every 10 samples and interpolated values subtracted from the signal assuming an “on peak zero” condition. To ensure the precision, NBS 981 Standard reference Material was measured at the beginning and at the end of the day to calibrate our isotope ratios with the ratios reported in Baker et al. (2004). Another in-house standard was measured every 5 samples as well as the beginning and the end of the day to constantly monitor the Daly ion counter efficiency. A full description of the mass correction can be found in Reuer et al. (2003) and Boyle et al. (2012).

Pb isotopes in seawater were prepared using the double Mg(OH)₂ precipitation method by adding small amount of vapor distilled ammonia into the sample to enable Mg(OH)₂ precipitation (Reuer et al., 2003). The precipitates were then redissolved using 1.1 M HBr and purified using Eichrom ion exchange column as described above.

Common statistical tools were applied in order to interpret the similarities and differences of the data. The statistical tools involved in this study include: calculating mean and standard deviation, T-test, linear regression, and cross-correlation. Such statistical tools will include legends like: standard deviation (SD), correlation coefficient (*r*), and P-values (*P*).

3. Results

3.1. Pb/Ca variations in Singapore corals

The variations of Pb relative to Ca (Pb/Ca) in the three Singapore corals are shown in Fig. 3. Except for the late 1990s to 2010, spatial variations among the sites were prominent. Kusu had a generally long term decreasing trend (slope = −0.32, *P* = 0.95) while Jong had a rising trend (slope = 0.24, *P* = 0.90). Despite the difference in long term trend, the short term variations in Jong and Kusu appear to be related to each other (*r* = 0.46, after removing the long-term trends).

Hantu had higher Pb/Ca (up to 70 nmol/mol) than Jong or Kusu (Fig. 3), and the temporal variation pattern was less correlated to Jong (*r* = −0.07) or Kusu (*r* = 0.28). Periods of extremely high Pb/Ca in Hantu coral (one standard deviation higher than the mean) coincided with major industrial developments in Singapore (Fig. 3). These

The Pb in coral from multiple islands in the Singapore Strait

Fig. 3. The Pb/Ca in coral from multiple islands in Singapore Strait. The average error of Pb/Ca in Singapore corals is 2.59 nmol/mol, taken from one standard deviation of triplicate sample measurements. The Pb/Ca is arranged geographically with Kusu on the east, Jung in the middle, and Hantu on the west. Gray open arrows indicate a period of Bukom/Busing development (an industrial island 400 m from Hantu, covering the period of 1984–1989, the location of Bukom/Busing is illustrated in Fig. 1) and the black filled arrows indicate the period of Jurong island development (the largest industrial island in Singapore, 5 km from Hantu, 1991–1996, Fig. 1). The small figure on the bottom left corner illustrates the Pb/Ca in corals on the same scale.

developments were in Bukom/Busing Island and Jurong Island. Both islands were on the west side of Singapore Straits, close to Hantu (Fig. 1). To a lesser extent, higher Pb/Ca values during the same period were also observed in other corals.

Temporally, Pb/Ca variability in the Jung and Kusu Singapore corals was positively correlated with the local annual rainfall with a lag time of two years ($r = 0.58$, $P = 0.94$, Fig. 4). The lag may be due to the comparable residence time of Pb in the oligotrophic surface ocean as estimated by ^{210}Pb studies (~ 4 years estimated from ^{210}Pb data in the eastern Indian Ocean, data from Cochran et al., 1983; Ostlund et al.,

1987; ~ 1.8 years estimated from the northeastern part of the South China Sea, data from Wei et al., 2011).

Seasonal variability of Pb/Ca in Singapore corals was investigated using a few samples from the Hantu coral, where the linear extension rate was nearly 2 cm/year. The wet season shows lower Pb/Ca with little variation in isotope ratio (Fig. 5). Such seasonal variation is not seen in the other two corals.

It should also be noted that spatial variation of Pb/Ca from all sites converged (in both magnitude and variation pattern) after the late 1990s (see the small figure on the bottom left corner of Fig. 3). The

Fig. 4. The Pb/Ca from Jung coral (longest record and similar as Kusu, black filled squares) is correlated with local annual rainfall (gray filled squares) with a lag time of 2 years, possibly due to the residence time of Pb in Surface Ocean. Annual precipitation data retrieved from IMDRO Climate data library.

Fig. 5. The variation of Pb/Ca (black diamonds) and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (open squares) in the Hantu coral from 1990 to 1994. Wet seasons (December to March, also called Northeast Monsoon season) are marked in darker color. Such seasonal variation is not clearly seen in other corals.

Pb/Ca in corals all decreased to 20–30 nmol/mol after 2005, a value comparable to 1960s and 1970s.

3.2. Pb isotope variations in Singapore corals

As for Pb/Ca, the temporal Pb isotope variation in Singapore corals also can be categorized into two periods. Before the late 1990s, $^{206}\text{Pb}/^{207}\text{Pb}$ increased from 1.166 to 1.191 and $^{208}\text{Pb}/^{207}\text{Pb}$ increased from 2.442 to 2.484, which generally moved towards higher values. After late 1990s, both temporal and spatial differences between corals were reduced, and coral Pb isotope ratios fluctuated within a narrow range ($^{206}\text{Pb}/^{207}\text{Pb} = 1.185\text{--}1.198$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.464\text{--}2.482$, Fig. 6). The decrease of the long-term trend in these Pb isotope ratios occurs at the same time as the convergence in Pb/Ca.

$^{206}\text{Pb}/^{207}\text{Pb}$ in Kusu and Hantu corals generally agree, while Jong $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were slightly higher than Kusu before late 1990s (average difference = 0.01, SD = 0.005, using 1996 as the point of separation). After the late 1990s, the difference in $^{206}\text{Pb}/^{207}\text{Pb}$ between the 2 sites decreased (average difference = 0.004, SD = 0.004). Similarly, Jong $^{208}\text{Pb}/^{207}\text{Pb}$ was higher than Kusu before the late 1990s (average difference = 0.012, SD = 0.006) but was reduced after the late 1990s (average difference = 0.008, SD = 0.006). No clear difference in $^{208}\text{Pb}/^{207}\text{Pb}$ between the Jong and Kusu corals was noted. As these corals

were processed by the same method in the same laboratory, the differences cannot be caused by the differences in handling or laboratory environment. There was little possibility for contamination, as the Pb/Ca data triplicates were generally within 5% error with no correlation between Pb isotope ratios and Pb/Ca. Furthermore, the isotopic composition in our corals was clearly different from the laboratory environment where they had been processed, which also indicates little contamination. Therefore we attribute the slight difference between Jong and other sites as true variability. Consequently, the results can be summarized as: clear spatial variability in Pb isotopes was observed from the 1960s to the late 1990s, and was diminished after the late 1990s.

4. Discussion

4.1. Pb/Ca variation in Singapore corals

Pb is released from the combustion of leaded gasoline, coal burning, smelting, incineration and high temperature industrial activities in general (Komárek et al., 2008). Also, Pb can be released during the use and disposal of Pb containing materials (such as batteries and lead paint), which can be loosely linked with urbanization. The natural sources of Pb mainly include windblown dusts and volcanogenic particles

Fig. 6. The temporal variation of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Singapore corals. From east to west in the Strait, the sites are Kusu (gray filled circles), Jong (black filled squares), and Hantu (white open diamonds). The average two standard error is 0.0001. Note the Singapore around $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is around 1.147 (measured over a year in 2012), the Southeast Asian around $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is around 1.145, taken between 1994 and 1999 (Bullholzer and Roussin, 2000). The dotted line shows the point of separation between period one and period two. The two periods are differentiated by the magnitude of spatial variability among sites (see text).

Fig. 7. Triple-isotope plot for Pb in Singapore coral and selected sources around the region of study, including various Pb ores (Imre and Taniwata, 2008), aerosols (Bollhöfer and Bourau, 2001; Lee et al., 2014), coals (Diaz-Serrano et al., 2009), and the South China Sea sediments (Zhu et al., 2010). The Kusu water is the seawater sample taken near the coral site in this study. The dashed line highlights the linearity of the Pb isotope ratios in corals.

(Nriagu, 1979). Compared to anthropogenic emissions of Pb, natural sources are much smaller (~4% in global Pb flux, Nriagu, 1989), therefore the long term variation of Pb in Singapore corals is likely a result of the urbanization (including leaded gasoline consumption) and industrialization of Singapore and the neighboring countries. Although there was no universal long term trend observed before the late 1990s, the decrease in Pb/Ca after the late 1990s (particularly after 2005) parallels with the decline in use of leaded gasoline in the Southeast Asian region (see Fig. 2).

The short term variations of Pb/Ca correlated with local annual rainfall (Fig. 4, $r = 0.58$) with a lag time of ~2 years, suggesting that rainfall might be important in regulating the short term variability of Pb/Ca in corals. This observation could be justified as a result of wet deposition which has been identified as one of the major mechanisms for transporting Pb into the ocean (Duce et al., 1991; Flegal, 1986). In addition, rainfall may mobilize non-atmospheric Pb in the soil and transport it into the sea via surface runoff (Joshi and Balasubramanian, 2010).

Lower or even no correlation was found between Pb/Ca in corals and the leaded gasoline from Singapore ($r = 0.43$), Malaysia ($r = 0.03$) and Batam ($r = 0.42$). The low correlation coefficient, together with the deviation of coral Pb isotope from aerosols implies that local leaded gasoline was not the overwhelming source of Pb into Singapore corals.

Although Pb/Ca in three different coral cores did not show a consistent long term trend, the Pb/Ca from the three corals converged beginning in the late 1990s: Pb/Ca in Kusu decreased from ~40 nmol/mol in the late 1970s to ~30 nmol/mol; while Pb/Ca in Jong increased from slightly less than 30 nmol/mol in the 1970s to ~30 nmol/mol.

The long-term variation of Pb/Ca between Kusu and Jong may reflect the spatial variation of the local development. In the 1960s and 1970s, the development in Singapore was largely within the area around the Singapore River and Kallang River (Lay, 2007, Fig. 1). The closer location

of Kusu to the development area may have resulted in higher Pb/Ca in Kusu compared to Jong in the 1960s and 1970s. As the city progressively expanded, corals from both sites should have received a comparable amount of Pb. In this case, it is reasonable to expect the convergence of Pb/Ca between the two sites.

High Pb/Ca ratios in the Hantu coral are likely related to a series of developments on Singapore's major industrial areas (Fig. 3). Both Bukom/Busing and Jurong Islands are close to Hantu and in the shallower region of the Singapore Straits, and the period of development on these two islands (1983–1989 and 1991–1998) coincides with abnormally high Pb/Ca ratios in Hantu coral. It is reasonable to expect that the industrial developments would remobilize some Pb into the water. Moreover, as Hantu is surrounded by other islands (Fig. 1), the relatively stagnant water around Hantu may not have flushed out the Pb from the surrounding industrial islands effectively. Consequently, during these development periods, the Pb/Ca in the Hantu coral was high and the variation pattern deviated from the other two sites.

Seasonal variation of Pb/Ca was investigated in the Hantu coral from 1990–1994. The Hantu coral shows lower Pb/Ca during the wet seasons with little isotope variation. The lower Pb/Ca in wet seasons is consistent with lower turbidity and a lower downward suspended solid flux in the Hantu during wet seasons (Dikoo and van Woelick, 2006); this observation implies that rainfall-induced flushing might be an important factor modulating the Pb/Ca in the Hantu coral. However, the small variance in Pb isotope ratios from dry to wet season indicates that there was little seasonal change in the dominant Pb source.

4.2. Pb isotope variation in Singapore corals and potential Pb sources

Pb isotopes show a high linearity on a triple isotope plot (Fig. 7), suggesting that Pb in Singapore corals might be a result of mixing between

two end members. Therefore a long-term evolution towards higher $^{206}\text{Pb}/^{207}\text{Pb}$ (and $^{208}\text{Pb}/^{207}\text{Pb}$) could be interpreted as an increasing share of the higher $^{206}\text{Pb}/^{207}\text{Pb}$ source in Singapore corals. After the late 1990s, Singapore coral Pb isotopes fluctuated within a relatively narrow range. This observation could be interpreted as a result of a relatively stable supply of the Pb with higher $^{206}\text{Pb}/^{207}\text{Pb}$ to the Singapore Straits. The diminished spatial variability in both Pb isotope and Pb/Ca during this phase supports this interpretation.

In previous decades, there were many sources that potentially contributed to the Pb in Singapore corals. Leaded gasoline was one of the largest sources of Pb and the Pb from vehicle exhausts could enter the surface ocean by atmospheric pathways (Flegal, 1986). Aerosol samples collected in Singapore from June 2011–April 2012, have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.147 ± 0.003 (Lee et al., 2014), significantly different from the isotope ratios in recent corals ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.185–1.198). Although aerosol sampling was performed in 2011/2012, well after the phasing out the leaded gasoline (Singapore in 1997, Malaysia in 1998, Baram in 2003, whole Indonesia in 2006), Pb isotopes in Singapore aerosols were comparable to other Southeast Asian cities between 1994 and 1999 (Kuala Lumpur $^{206}\text{Pb}/^{207}\text{Pb} = 1.141 \pm 0.001$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.410 \pm 0.001$ and Jakarta $^{206}\text{Pb}/^{207}\text{Pb} = 1.131 \pm 0.001$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.395 \pm 0.001$, Bollhöfer and Rosman, 2000). Therefore Pb isotope ratios in the aerosols from this region are consistently too low to dominate the Pb in Singapore corals.

Despite this isotopic difference between corals and aerosols, the coral isotope ratio can still be linked with the aerosols on the lower side of the triple isotope plot (Fig. 7). This implies that atmospheric input was still one of the sources for the Pb in corals, which is normally expected. However, Pb isotope ratios in corals are clearly higher than the ratios in aerosol; this indicates that the atmospheric Pb sources may only account for a small fraction in corals. The higher $^{206}\text{Pb}/^{207}\text{Pb}$ end-member in the triple isotope plot is another unidentified Pb source, and the evolution of Pb isotopes in Singapore corals implies an increasing share of the as yet-unidentified Pb source in Singapore corals, which will be discussed in the following paragraphs.

It would be reasonable to consider that industrial activities and incineration might contribute to the Pb in corals. From the incineration ash samples collected in 2010, the Pb isotope in the fly ash was $^{206}\text{Pb}/^{207}\text{Pb} = 1.148 \pm 0.005$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.424 \pm 0.003$, comparable to the Pb isotope ratios in aerosols. Industrial effluent samples are unavailable as of yet, but previously reported aerosol sampling in Lee et al. (2014) was within 5 km of the largest industrial area in Singapore (Jurong Industrial area), therefore the isotopic departure of aerosol and corals may also imply that neither the aerosol emissions

from industrial activities nor incineration could be a major contributor to the Pb isotope composition of Singapore corals.

Coal burning emits large amounts of Pb to the atmosphere globally; that could also potentially contribute to the Pb in Singapore corals. Indonesia is a large coal consumer, and has also exported more than \$50 billion worth of coal to other countries (COMTRADE, 2012). Since Indonesia is self-sufficient in coal, it is reasonable to expect that Indonesian coal is the main source of coal in Indonesia. Between 2002 and 2012, Malaysia imported more than \$10 billion of coal, mainly from Indonesia (66.9%) and Australia (19.6%) (COMTRADE, 2012). The consumption of coal in Malaysia and Indonesia is nearly 3 orders of magnitude higher than Singapore. Therefore we expect that the major types of the coals used in this region were from Indonesia and/or Australia. Indonesian coals have a $^{206}\text{Pb}/^{207}\text{Pb} = 1.184 \pm 0.004$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.477 \pm 0.006$; while Australian coals have $^{206}\text{Pb}/^{207}\text{Pb} = 1.121 \pm 0.0002$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.487 \pm 0.0001$ (Diaz-Somoano et al., 2009). Both coal sources have an isotopic composition comparable to the Pb in Singapore corals. However, the Pb isotope composition of Singapore corals deviated from that in aerosols, and it is unlikely that Pb from coal enters the ocean (and then corals) without any footprint in aerosols, except possibly from the direct flushing from solid debris released after coal burning. The only coal-based power plant in Singapore was decommissioned in 1962 (Wan and Lau, 2009), and the coal used at that time would likely be Australian coals (for which we can cite no official documentation, and have only heard this by word of mouth). As the $^{206}\text{Pb}/^{207}\text{Pb}$ in Australian coal did not agree with that in corals until the late 1990s, it is unlikely that the Pb from coal was not seen in the corals while the power plant was operating, and has only appeared recently.

Water in the Singapore Straits connects with South China Sea, Java Sea and Northeastern Indian Ocean, and Pb in the Singapore Straits water can be transported from these seas. The seawater sampled in Kusu shows a $^{206}\text{Pb}/^{207}\text{Pb} = 1.199 \pm 0.0003$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.490 \pm 0.0004$, in agreement with the Pb isotopes in corals. In contrast, Pb isotopes in South China Sea water were reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.156 \pm 0.015$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.444 \pm 0.017$ (from the eastern part of the South China Sea, Lee et al., 2014) and in Bay of Bengal water were reported as $^{206}\text{Pb}/^{207}\text{Pb} = 1.149$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.431$ (Lee et al., 2014). Although no seawater Pb isotope data have been reported from the Java Sea, a coral in Jakarta Bay dated between 1998–2001 had $^{206}\text{Pb}/^{207}\text{Pb} = 1.158 \pm 0.007$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.430 \pm 0.010$ (Inoue et al., 2006). Thus Pb isotopes from South China Sea, Bay of Bengal, and Java Sea waters are too low to be a source controlling the Pb isotope composition of Singapore corals.

Fig. 8. The triple-isotope plot of Pb isotopes in corals (filled squares) compared to the most possible end members suggested in this study, including Singapore aerosol (open circle, Lee et al., 2014), South Chinese Pb ore (open triangle, Inoue et al., 2006), natural regional soil (open diamonds, from central catchment reserve of Singapore, unpublished data). The coral data are divided by every 10 years. The dashed line illustrates the linearity of these possible sources to Singapore corals.

Scrapings from boat paints and dockyard activities might also be a source of Pb contributing to corals. A recent study reported that the Pb content in 6 paints from Asia was higher than 5000 mg/kg (Clark et al., 2006). If vessels happen to use these brands of paint, the scrapings from boat paints could contribute Pb into the marine system. Lead paint contamination in corals has also been discussed previously with corals near a dockyard experiencing one standard deviation higher Pb/Ca during the period of dockyard operation (Wang et al., 2011). The Singapore Straits is one of the busiest shipping routes in the world, and all the coral sites are in the vicinity (within ~10 km) of the Port of Singapore. Although it is difficult to characterize the role of ship paint to Pb in Singapore marine waters, until we have evidence to the contrary we have to consider that vessel paint and dockyard operations may potentially contribute Pb in Singapore Straits. We have no information on the Pb isotopic composition of these paints, so we cannot even speculate whether they contribute to the anomalous Pb isotope composition of Singapore marine waters.

Runoff from various small urban and industrial catchments around the Singapore Straits may also discharge a small amount of water (but concentrated in heavy metals) to the Singapore Straits, potentially contributing Pb to Singapore corals. A recent study of Singapore surface runoff has identified that the runoff from industrial catchments contains more than five times more Pb than residential catchments (Joshi and Balasubramanian, 2010). Singapore was one of largest importers of "unwrought Pb" (Harmonized Commodity Description and Coding Systems: HS-96-7801, International Trade Statistics, 2014) from 2000 to 2009 (the 2nd largest trade products containing Pb, comprising 22.8% of total amount of Pb traded in Asia Pacific), and 73% of Singapore's unwrought Pb was from China (UNEP, 2011). The Pb isotope ratios in South Chinese Pb ore were $^{206}\text{Pb}/^{207}\text{Pb} = 1.187 \pm 0.0059$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.475 \pm 0.0038$ (Inoue et al., 2006; Flegal et al., 2013) which are comparable to Singapore coral and seawater. The isotope agreement between the imported Chinese Pb and the Pb in corals implies that Chinese Pb in Singapore may be transported to Singapore waters via rainfall and surface runoff from industrial catchments without any footprint in aerosols.

High $^{206}\text{Pb}/^{207}\text{Pb}$ isotopes in Singapore corals might also be a result of isotope exchange between the Pb in seawater and crustal materials that generally have high isotope ratios. Although little is known whether this process occurs in Pb isotopes, a similar isotope exchange mechanism has been proposed for Sr and Nd isotopes (Oelkers et al., 2011, 2012; Jones et al., 2012). This possible isotope exchange could alter the isotopic ratio of Pb to be more "crustal-like" without requiring an increase in the total Pb concentration. Little is known about the local Singapore crustal material, but the sediment samples in the South China Sea have $^{206}\text{Pb}/^{207}\text{Pb}$ of ~1.199 and $^{208}\text{Pb}/^{207}\text{Pb}$ of ~2.491 (Zhu et al., 2010), in agreement with the Pb isotopes found in Singapore corals and seawater (Fig. 7). Based on salinity measurements, the Singapore Straits is within the influence of Johor River (Soeriatmadja, 1956), the crustal materials from Johor River and other rivers in western Malaysia can then be transported just offshore into the Singapore Straits. Furthermore, deforestation, land reclamation and dredging have also increased the sedimentation to the Straits (Thia-Eng et al., 2000). The re-suspension of bottom sediments due to tidal currents has also been noted (Van Maren and Gerritsen, 2012). All these mechanisms provide an abundant supply of crustal material with which isotope exchange could happen. In this case, despite lower $^{206}\text{Pb}/^{207}\text{Pb}$ in local aerosols and in seawater from adjacent seas, the isotopic composition of Pb in Singapore Straits water may have been modified to higher values as observed in our Singapore corals. The isotope exchange with crustal materials was previously hypothesized in Lee et al. (2014). The isotope exchange hypothesis could explain the high $^{206}\text{Pb}/^{207}\text{Pb}$ observed in corals compared to aerosols, it could also explain the correlation between Pb/Ca and rainfall without an isotope response. In this case, the isotope exchange hypothesis should be considered as a plausible hypothesis which should be tested by studies of the particles from the river mouths near the

Singapore Straits (e.g.: Johor River), indigenous crustal materials, and assess their capability of isotope exchange with seawater.

4.3. Possible attribution of different Pb sources

We suggested that the Pb in the Singapore Straits is the result of mixing of two end-members. Pb carried by aerosols (mainly from leaded gasoline) is considered as one end-member, and the other end-member is either: 1) the Pb from South Chinese Pb ores that was delivered to the Singapore Straits via surface runoff, or 2) the natural crustal Pb that exchanges Pb isotopes with seawater in the Singapore Straits. The attribution of these two possible Pb sources can be estimated by calculating the weightage of isotope ratios from the coral with respect to the end members. As discussed, the possible end member includes either "aerosol + Chinese Pb" or "aerosol + natural Pb". Although the attribution of different atmospheric Pb sources to Singapore corals varies largely by the selection of the possible end members (Fig. 8, the actual data is provided in Supplementary material), they both show an ongoing decreasing contribution of atmospheric related Pb sources.

If the Pb in Singapore corals were from aerosol Pb (average $^{206}\text{Pb}/^{207}\text{Pb} = 1.147$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.424$, Lee et al., 2014) and South Chinese Pb (average $^{206}\text{Pb}/^{207}\text{Pb} = 1.187$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.475$), the calculation shows that the contribution from Chinese Pb to corals was ~72% in 1970s and 1980s; and rose to more than 98% in 2000s. In contrast, aerosol Pb contributed ~28% in 1970s and 1980s, and decreased to less than 2% in 2000s. These calculations agree with the trading statistics as Singapore has imported 1.4×10^{10} kg of Pb-containing products during the 2000–2009 period (UNEP, 2011), 7 orders of magnitude higher than the gasoline emissions (in the order of 10^3 kg, Fig. 2). The amount of imported Pb was so large that even a small fraction of it entering the Singapore Straits could result in huge change in the Pb isotopes in corals.

If the Pb in Singapore corals was from aerosol Pb and natural crustal Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.215$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.506$, unpublished data from ongoing work), the calculation shows that the contribution from natural sources was ~43% in the 1970s and progressively increased to ~60% in 2000s. On the other hand, the aerosol Pb contributed ~57% in the 1970s, and decreased to ~41% in 2000s. The decreasing contribution of atmospheric related Pb is in general agreement with the decrease of leaded gasoline emissions (Fig. 2).

5. Conclusion

Variations of Pb in the Singapore Straits were reconstructed from three corals located on an east–west transect of the straits. The temporal and spatial variations of Pb/Ca have been discussed, and the Pb isotopes in corals were compared with Pb sources in the region. The following points can be concluded:

1. Large spatial variations are observed among corals, yet no clear agreement in the 50-year trend in Pb/Ca is observed. Because the spatial variability of Pb/Ca among sites was associated with only minor variations in Pb isotopes, the spatial variation in Pb/Ca may be a reflection of an uneven distribution of Pb sources between the sites. The spatial variation seems to diminish after the late 1990s.
2. Short term variations of Pb/Ca in corals positively correlate with local annual precipitation after a two-year lag is considered. Seasonal variability of Pb/Ca in Hantu coral has shown a lower Pb/Ca during wet seasons, while only minor changes in Pb isotopes have been observed. These facts suggest that rainfall is an important factor modulating the amount of Pb delivered to the coral sites.
3. From the 1970s to the late 1990s, $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore corals increased from 1.166 to 1.191. $^{208}\text{Pb}/^{207}\text{Pb}$ from 2.442 to 2.484. Since the late 1990s, the long-term trend diminished and $^{206}\text{Pb}/^{207}\text{Pb}$ fluctuated between 1.185–1.198, $^{208}\text{Pb}/^{207}\text{Pb}$ fluctuated between 2.464–

- 2.482. Spatial variations in Pb isotopes were small between sites, especially after the late 1990s.
- Recent $^{206}\text{Pb}/^{207}\text{Pb}$ values in Singapore corals are similar to the isotopic composition of Singapore Straits seawater, but deviate in the positive direction from local aerosols or in seawater from South China Sea, Java Sea or Bay of Bengal. However, Pb isotopes in Singapore corals plot linearly in triple isotopic space, implying a two-source-mixing scenario. The Pb isotope data in Singapore corals in 1960s and 1970s fall on the lower $^{206}\text{Pb}/^{207}\text{Pb}$ side, and can be linked with the Pb isotope in aerosols and incineration ash. Pb isotopes in more recent part of the corals show higher $^{206}\text{Pb}/^{207}\text{Pb}$ and ratios, possibly suggesting a second source of Pb dominating the region. The possible second source is hypothesized as either direct scrap from leaded paint on vessels or dockyard activities or the surface runoff of industrial Pb from various catchments around the Singapore Straits or as a result of isotope exchange of anthropogenic Pb with crustal materials. All of these hypotheses are possible; however the surface runoff and the isotope exchange hypotheses remain the most probable.
 - The contribution of possible Pb sources varies with respect to different choices of end members, while the decreasing contribution of atmospheric related Pb was prominent.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2014.10.007>.

Acknowledgments

The research described in this project was funded in whole by the Singapore National Research Foundation (NRF) through the Singapore-MIT Alliance for Research and Technology (SMART) Center for Environmental Sensing and Modeling (CENSAM). We thank Dr. Jani Tazili who helped with collecting the Singapore coral samples; National Environmental Agency for collecting the incineration ash samples; and Associate Professor Nathalie Goodkin for her constructive criticism. This is EOS contribution number 82.

References

- Afrin, R., Hassan, M.N., Ibrahim, N.A., 2003. Review of air pollution and health impacts in Malaysia. *Environ. Res.* 92 (2), 71–77.
- American Association of Port Authorities, 2006. World port rankings retrieved on July 28, from: www.aapa-ports.org.
- Baker, J., Foster, D., Wright, T., Meyers, C., 2004. Pb isotope analysis of standards and samples using a ^{206}Pb – ^{207}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chem. Geol.* 211 (3–4), 275–303.
- Bohlhöfer, A., Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochim. Cosmochim. Acta* 64 (10), 2251–2262.
- Bohlhöfer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. *Geochim. Cosmochim. Acta* 65 (11), 1727–1740.
- Bohlhöfer, A., Rosman, K.J.R., 2002. The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres. *Geochim. Cosmochim. Acta* 66 (8), 1375–1386.
- Boyle, E.A., John, S., Alouchami, W., Adkins, J.F., Echegyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, R., Gallon, C., Galer, S., Gauth-Ringaki, M., Lacan, F., Radic, A., Rehkemper, M., Rosset, O., Seltzer, V., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. CHOTRACES ICI (IAT5): contamination-free trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr. Methods* 10, 653–662.
- Brown, J.S., 1962. Our leads and isotopes. *Econ. Geol.* 57 (3), 673–720.
- Chen, M., Murali, K., Khoo, B.C., Liu, J., Kumar, K., 2005. Circulation modelling in the Strait of Singapore. *J. Coast. Res.* 21 (5), 960–972.
- Chia, L.S., Khan, H., Chou, L.M., 1988. (Eds.) The Coastal Environmental Profile of Singapore. Manila, ASEAN/US Coastal Resources Management Project; Technical Publication Series No. 3. ICLARM Tech. Rep. 21, p. 92.
- Church, T.M., Verron, A., Patterson, C.C., Settle, D., Erel, Y., Maring, H.R., Flegal, A.R., 1990. Trace elements in the North Atlantic troposphere: shipboard results of precipitation and aerosols. *Glob. Biogeochem. Cycles* 4 (4), 431–443.
- Clark, C.S., Rumpel, K.G., Thappil, V., Chen, C.K., Clark, B., Roda, S., 2006. The lead content of currently available new residential paint in several Asian countries. *Environ. Res.* 102 (1), 9–12.
- Cocharn, J.R., Bacon, M.P., Krishnaswami, S., Turekian, K.K., 1983. ^{210}Pb and ^{210}Po distributions in the central and eastern Indian Ocean. *Earth Planet. Sci. Lett.* 65, 433–452.
- COMTRADE (Commodity Trade Statistics Database), 2012. United Nations Statistics Division retrieved on May 12, 2012 from: <http://comtrade.un.org/data/retrieval.do?commodityresults.aspx?pc=142&cc=2791>.
- Diaz-Somoano, M., Kylander, M.E., López-Arocas, M.A., Suárez-Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Rober, B., Weiss, D.J., 2009. Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing. *Environ. Sci. Technol.* 43 (4), 1078–1085.
- Dikou, A., van Woesik, R., 2006. Survival under chronic stress from sediment lead: spatial patterns of hard coral communities in the southern islands of Singapore. *Mar. Pollut. Bull.* 52 (1), 7–21.
- Douc, R.A., Liu, P.S., Merrill, J.T., Atlas, E.L., Buu-Monard, P., Hicks, R.R., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galway, J.N., Hansen, L., Jekeli, T.D., Knapp, A.H., Reinhardt, K.H., Schneider, B., Seidlitz, A., Tokon, J.J., Tsanogai, S., Wellart, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. *Glob. Biogeochem. Cycles* 5 (3), 203–250.
- Durgam-Hyatt, N.S., Li, X.D., Wong, S.C., 2004. Lead contamination and isotope signatures in the urban environment of Hong Kong. *Environ. Int.* 30 (2), 209–217.
- Ewing, S.A., Christensen, J.N., Berner, S.T., Vancuren, K.A., Cliff, S.S., Depaolo, D.J., 2010. Pb isotopes as an indicator of the Asian contribution to particulate air pollution in urban California. *Environ. Sci. Technol.* 44 (23), 8911–8916.
- Fleegal, A.R., 1986. Lead in tropical marine systems: a review. *Sci. Total Environ.* 58 (1–2), 1–8.
- Fleegal, A.R., Gallon, C., Ganguli, P.M., Christopher, H.C., 2013. All the lead in China. *Crit. Rev. Environ. Sci. Technol.* 43 (17), 1880–1944.
- Hou, Y., Guo, Z., Yang, Z., Fan, D., Fang, M., Li, X., 2008. Tracking historical lead pollution in the coastal area adjacent to the Yangtze River Estuary using lead isotopic compositions. *Environ. Pollut.* 156 (3), 1325–1331.
- Hilton, F.G., 2006. Poverty and pollution abatement: evidence from lead phase-out. *Ecol. Econ.* 56, 125–131.
- Hirata, K., 2006. Review of lead phase out for air quality improvement in the third world cities: lessons from Thailand and Indonesia. *J. Stud. Res. Sci.* 32 (2), 527–541.
- Hsu, S.C., Chen, L.S., Jeng, W.L., Chou, C.C.K., Hsu, B.T., Huang, Y.T., Chen, V.W., 2006. Lead isotope ratios in ambient aerosols from Taipei, Taiwan: identifying long-range transport of airborne Pb from the Yangtze Delta. *Atmos. Environ.* 40 (20), 5393–5404.
- Inoue, M., Tanizawa, M., 2008. Anthropogenic lead inputs to the western Pacific during the 20th century. *Sci. Total Environ.* 406 (1–2), 123–130.
- Inoue, M., Hata, A., Suzuki, A., Nohara, M., Shikazono, N., Yim, W.W., Hamano, W.S., Dengchul, S., Kawahata, H., 2006. Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent sea derived from coral skeletons. *Environ. Pollut.* 144 (3), 1043–1052.
- International Energy Statistics, A total coal consumption by year retrieved on July 1, 2014 from: <http://www.eia.gov/countries/data.cfm>.
- Iq, C.M., Li, X.D., Zhang, G., Wu, D.W.H., Li, Y.S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ. Pollut.* 147 (2), 311–323.
- Jones, M.T., Pearce, C.R., Oelkers, E.H., 2012. An experimental study of the interaction of acidic, marine particulate material and seawater. *Geochim. Cosmochim. Acta* 77, 108–120.
- Joshi, U.M., Hulschrumpfe, R., 2010. Characteristics and environmental mobility of trace elements in urban runoff. *Chemosphere* 80 (3), 310–318.
- Kelly, A.E., Rosen, M.K., Goodkin, N.F., Boyle, E.A., 2009. Lead concentrations and isotopes in corals and water near Bermuda, 1780–2000. *Earth Planet. Sci. Lett.* 283 (1–4), 93–100.
- Kondrak, M., Erlin, V., Chastny, V., Mihajlovic, M., 2008. Lead isotopes in environmental sciences: a review. *Environ. Int.* 34 (4), 562–577.
- Lay, L.T., 2007. Shaping Singapore's cityscape. *Innovation* 7 (2), 32–35.
- Lee, J.M., Boyle, E.A., Huhner, I.S., Pfeiffer, M., Metzman, A.J., Szwargald, B., 2014. Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. *Earth Planet. Sci. Lett.* 298, 37–47.
- Li, Q., Cheng, H., Zhou, T., Lin, C., Guo, S., 2012. The estimated atmospheric lead emissions in China, 1980–2009. *Atmos. Environ.* 60, 1–8.
- Ministry of the Environment Singapore, 1987–2000. Pollution Control Department: Annual Report.
- Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K., Hashimoto, Y., 1993. Characterization of sources of lead in the urban air of Asia using stable lead isotopes. *Environ. Sci. Technol.* 27 (7), 1347–1356.
- Ng, O.-H., Tan, B.C., Oldham, J.P., 2008. Lichens as bioindicators of atmospheric heavy metal pollution in Singapore. *Environ. Monit. Assess.* 122 (1–3), 61–74.
- Nilsson, T., Nakamura, E., Harada, K., Ishikawa, H., Hironaka, T., Watanabe, T., Wang, Z., Kikunori, A., 2010. A global transport model of lead in the atmosphere. *Atmos. Environ.* 44 (14), 1806–1814.
- Nriagu, J.O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279 (5712), 409–411.
- Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338 (6210), 47–49.
- Oelkers, E.H., Gálvez, S.R., Eriksson, E.S., Jones, M., Pearce, C.R., Jeandel, C., 2011. The role of marine particulate material on the global cycles of the elements. *Appl. Geochem.* 26, S365–S369 (Suppl.).
- Oelkers, E.H., Jones, M.T., Pearce, C.R., Jeandel, C., Eriksson, E.S., Gálvez, S.R., 2012. Riverine particulate material dissolution in seawater and its implications for the global cycles of the elements. *Comput. Rendus Geosci.* 344 (11–12), 646–651.
- Ostlund, H.G., Craig, H., Broecker, W.S., Spencer, D., 1987. GOSSECS Atlantic, Pacific and Indian Ocean expeditions. Vol 7 Shorebased Data and Graphic (Washington, D.C.).
- Pang, W.C., Thialth, P., 2003. Modeling tidal and monsoon driven currents in the Singapore Strait. *Singap. Marit. Port J.* 151–162.
- Rosen, M.K., Boyle, E.A., Grant, B.C., 2003. Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS. *Chem. Geol.* 200 (1–2), 137–153.
- Santosa, S.J., Oladun, T., Tanaka, S., 2008. Air pollution and urban air quality management in Indonesia. *Clean: Soil, Air, Water* 36 (5–6), 466–475.