Marine Chemistry 168 (2015) 49–59

Contents lists available at ScienceDirect

Marine Chemistry

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

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

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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 $^{206}Pb/^{207}Pb$ 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. $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ in triple isotope plots suggests two end-member mixing between the aerosol–Pb as a low $^{206}Pb/^{207}Pb$ end-member and an unidentified source with higher $^{206}Pb/^{207}Pb$. Possible high $^{206}Pb/^{207}Pb$ 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.

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; Duzgoren-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 seawaters (e.g.: Ng et al., 2006); and corals from the western Pacific (e.g.: Inoue 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; 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 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

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http://dx.doi.org/10.1016/j.marchem.2014.10.007
0304-4203/

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 shares 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/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 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/m^3 Pb before 1985; and was reduced to 0.4 kg/m^3 between 1986 and 1989, and to 0.15 kg/m^3 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/m^3 until 1989 (Mukai et al., 1993) and then reduced to 0.3 kg/m^3 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/m^3 (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, ^{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 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

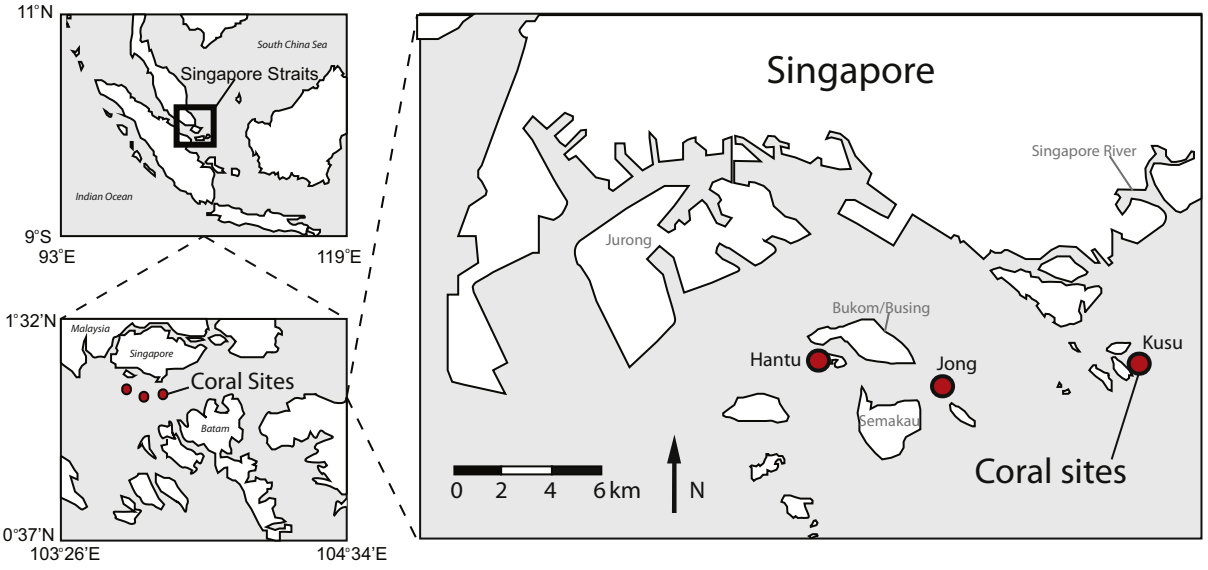

Fig. 1. Map of the study site. On the top left corner is a map of Singapore Straits and its relative location in Southeast Asia; on the bottom left corner is a zoomed map of Singapore Straits with respect to the countries and regions in its vicinity, the adjacent countries and ocean basins are denoted. 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 (Jurong and Bukom/Busing); the landfill (Semakau); and the city center (around Singapore River).

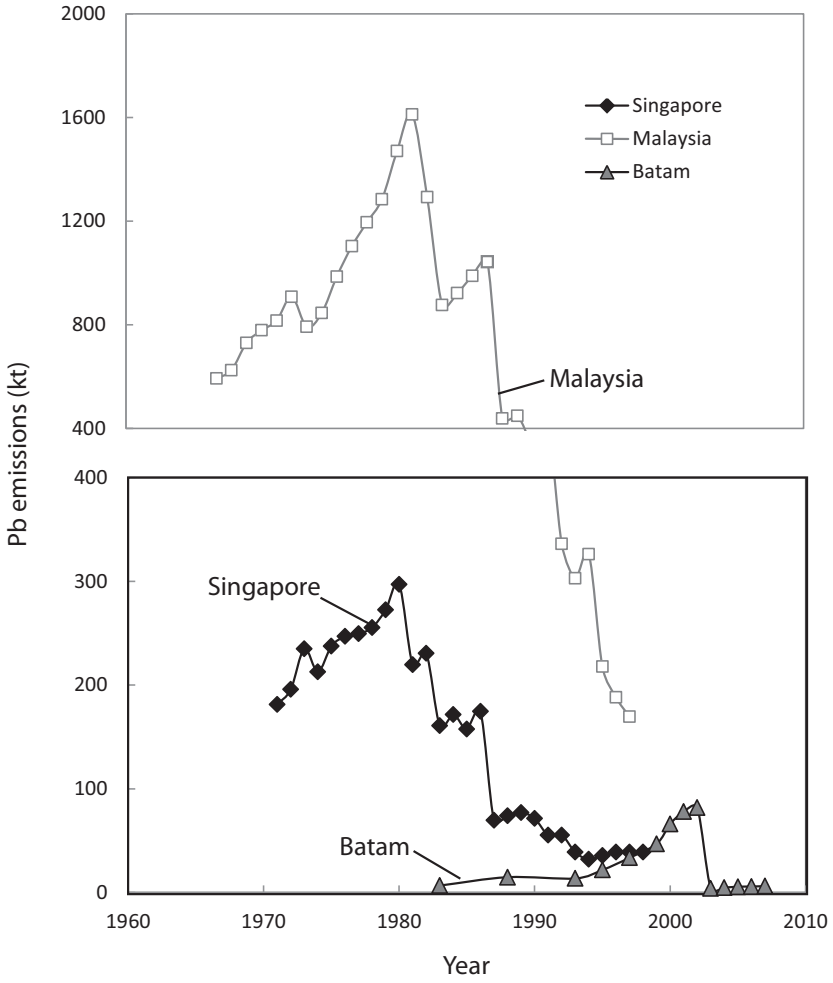

Fig. 2. The estimated Pb emission from gasoline in Malaysia (white open rectangles), Singapore (black filled diamonds) and Batam (gray filled triangles). Data are estimated by the product of: road sector gasoline emissions; the allowable Pb content in the gasoline; the market share of the leaded gasoline; and the tailpipe emission factor. Maximum consumption of leaded 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 $^{206}Pb/^{207}Pb < 1.155$, $^{208}Pb/^{207}Pb < 2.430$. 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 $^{206}Pb/^{207}Pb = 1.147 \pm 0.003$, $^{208}Pb/^{207}Pb = 2.425 \pm 0.003$ (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 $^{206}Pb/^{207}Pb = 1.167 \pm 0.005$, $^{208}Pb/^{207}Pb = 2.491 \pm 0.016$; and a Jakarta coral spanning from 1998–2001 recorded $^{206}Pb/^{207}Pb = 1.158 \pm 0.007$, $^{208}Pb/^{207}Pb = 2.430 \pm 0.010$ (Inoue et al., 2006). Pb isotope ratios in seawater from the central Bay of Bengal were reported as $^{206}Pb/^{207}Pb = 1.149$, $^{208}Pb/^{207}Pb = 2.431$ (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 $^{206}Pb/^{207}Pb$ of ~1.199 and $^{208}Pb/^{207}Pb$ 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 Díaz-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	*Porities lutea*	41	1969–2010
Jong	1° 12′ 55″N 103° 47′ 17″E	*Porities lutea*	48	1962–2010
Hantu	1° 13′ 37″N 103° 44′45″E	*Porities lutea*	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 Bukom/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-H_2O_2, dilute (0.1 M) HNO_3 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 $CaCO_3$ 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 HNO_3 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 ^{204}Pb 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}Tl/^{203}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 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

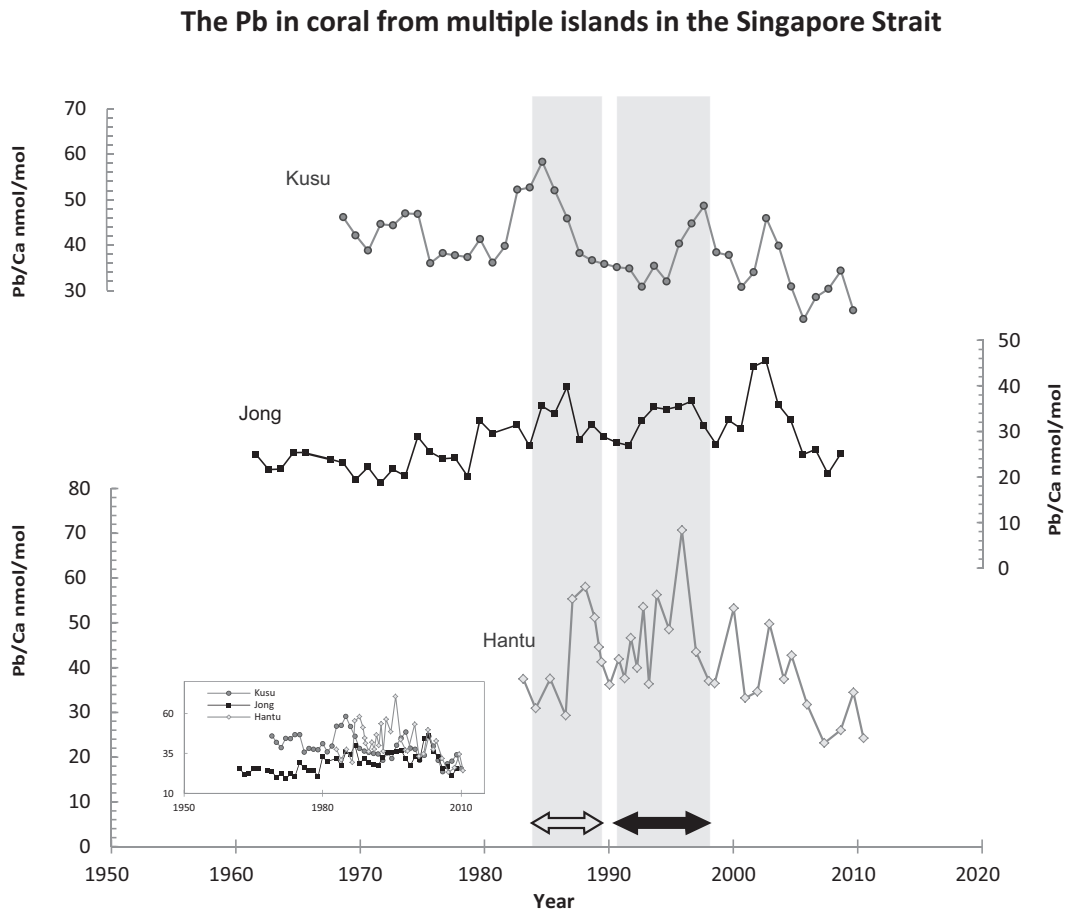

Fig. 3. The Pb/Ca in corals from multiple islands in Singapore Straits. The average error of Pb/Ca in Singapore corals is 2.59 nmol/mol, taken from one standard deviation of triplicate sample measurements. The Pb/Ca is arranged geographically with Kusu on the east, Jong in the middle, and Hantu on the 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, 1991–1998, 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 Jong 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

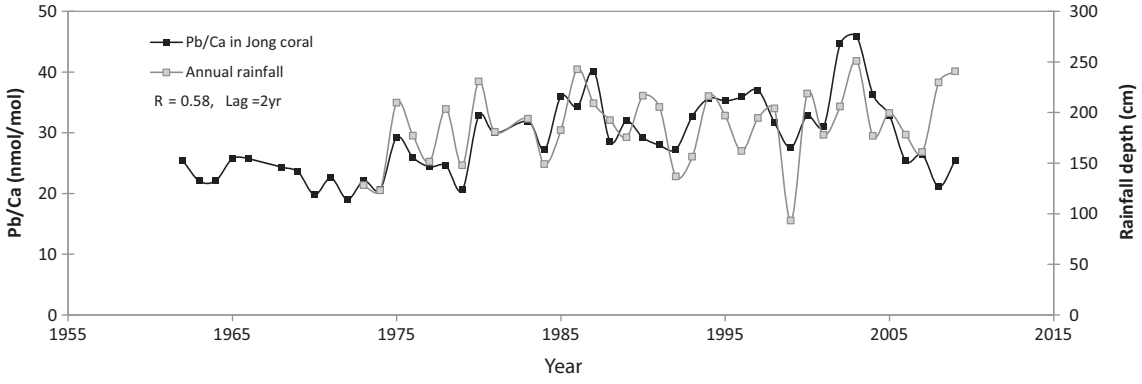

Fig. 4. The Pb/Ca from Jong coral (longest record and similar as Kusu, black filled squares) is correlated with local annual rainfall (gray filled squares) with a lag time of 2 years, possibly due to the residence time of Pb in Surface Ocean. Annual precipitation data retrieved from IRI/LDEO Climate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

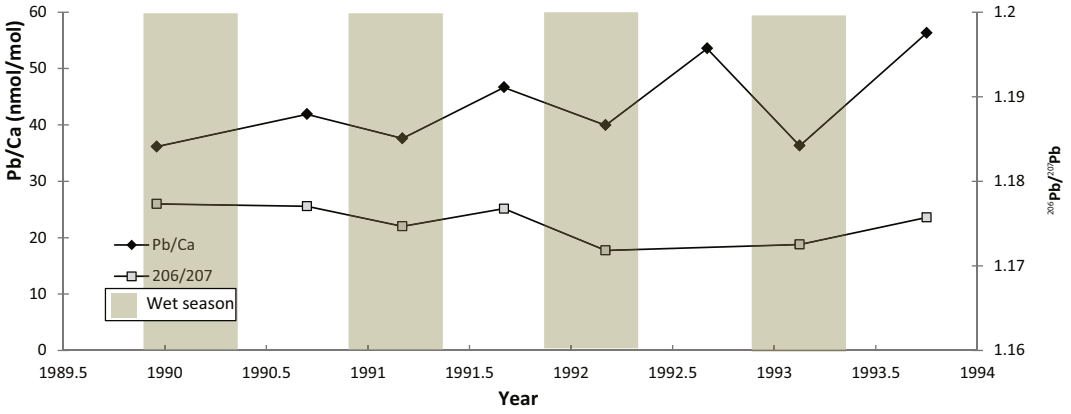

Fig. 5. The variation of Pb/Ca (black diamonds) and $^{206}Pb/^{207}Pb$ ratio (open squares) in the Hantu coral from 1990 to 1994. Wet seasons (December to March, also called Northeast Monsoon season) are marked in darker color. Such seasonal variation is not clearly seen in other corals.

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, $^{206}Pb/^{207}Pb$ increased from 1.166 to 1.191 and $^{208}Pb/^{207}Pb$ 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 ($^{206}Pb/^{207}Pb$ = 1.185–1.198, $^{208}Pb/^{207}Pb$ = 2.464–2.482, 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.

$^{206}Pb/^{207}Pb$ in Kusu and Hantu corals generally agree, while Jong $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ between the 2 sites decreased (average difference = 0.004, SD = 0.004). Similarly, Jong $^{208}Pb/^{207}Pb$ 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 $^{208}Pb/^{206}Pb$ 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

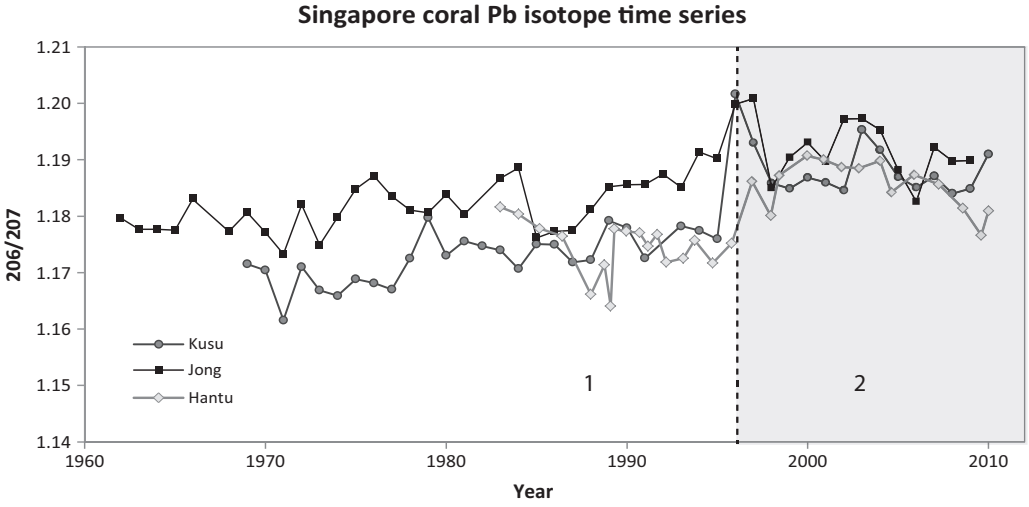

Fig. 6. The temporal variation of 206/207 ratio in Singapore corals. From east to west in the Strait, the sites are Kusu (gray filled circles), Jong (black filled squares), and Hantu (white open diamonds). The average two standard error is 0.0001. Note the Singapore aerosol 206/207 ratio is around 1.147 (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).

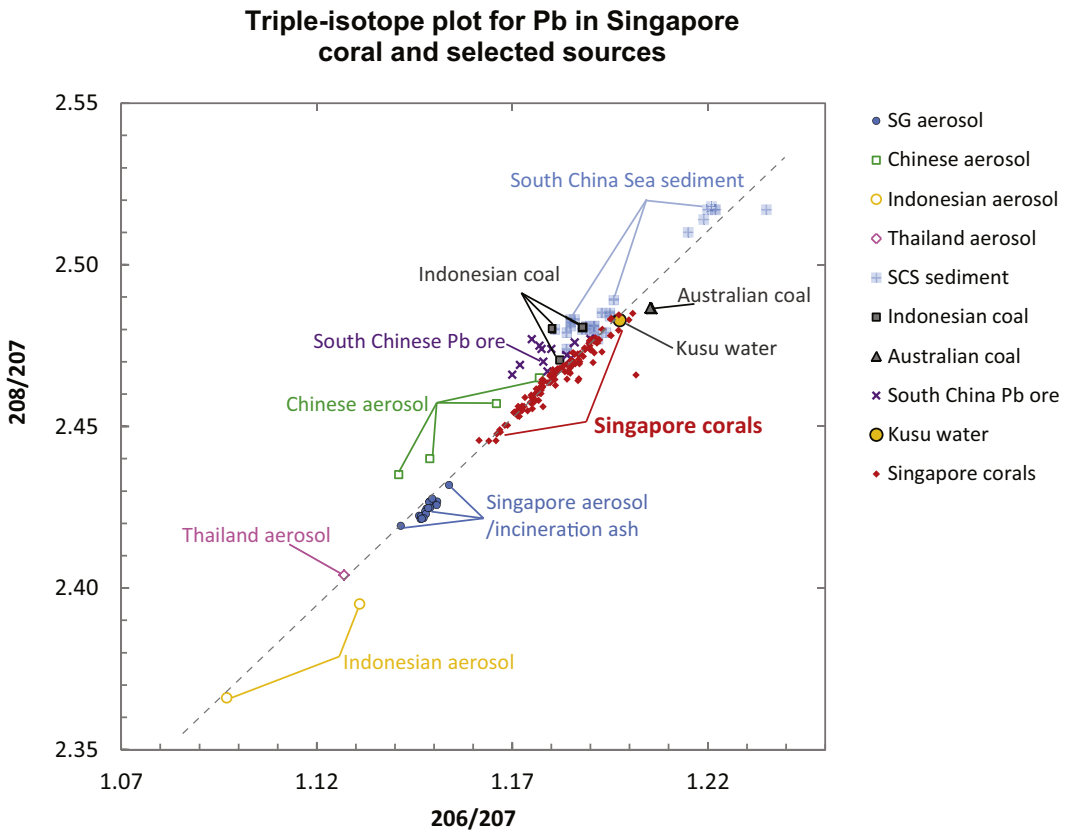

Fig. 7. Triple-isotope plot for Pb in Singapore coral and selected sources around the region of study, including various Pb ores (Inoue and Tanimizu, 2008), aerosols (Bollhöfer and Rosman, 2001; Lee et al., 2014), coals (Díaz-Somoano et al., 2009), and the South China Sea sediments (Zhu et al., 2010). The Kusu water is the seawater sample taken near the coral site in this study. 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 (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. 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 $^{206}Pb/^{207}Pb$ (and $^{208}Pb/^{207}Pb$) could be interpreted as an increasing share of the higher $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ ratio of 1.147 ± 0.003 (Lee et al., 2014), significantly different from the isotope ratios in recent corals ($^{206}Pb/^{207}Pb$ 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, Batam in 2003, whole Indonesia in 2006), Pb isotopes in Singapore aerosols were comparable to other Southeast Asian cities between 1994 and 1999 (Kuala Lumpur $^{206}Pb/^{207}Pb = 1.141 \pm 0.001$, $^{208}Pb/^{207}Pb = 2.410 \pm 0.001$ and Jakarta $^{206}Pb/^{207}Pb = 1.131 \pm 0.001$, $^{208}Pb/^{207}Pb = 2.395 \pm 0.001$, 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 isotopic 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb = 1.148 \pm 0.005$, $^{208}Pb/^{207}Pb = 2.424 \pm 0.003$, 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 $^{206}Pb/^{207}Pb = 1.184 \pm 0.004$, $^{208}Pb/^{207}Pb = 2.477 \pm 0.006$; while Australian coals have $^{206}Pb/^{207}Pb = 1.121 \pm 0.0002$, $^{208}Pb/^{207}Pb = 2.487 \pm 0.0001$ (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 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb = 1.199 \pm 0.0003$, $^{208}Pb/^{207}Pb = 2.490 \pm 0.0004$, in agreement with the Pb isotopes in corals. In contrast, Pb isotopes in South China Sea water were reported as $^{206}Pb/^{207}Pb = 1.156 \pm 0.015$, $^{208}Pb/^{207}Pb = 2.444 \pm 0.017$ (from the eastern part of the South China Sea, Lee et al., 2014) and in Bay of Bengal water were reported as $^{206}Pb/^{207}Pb = 1.149$ and $^{208}Pb/^{207}Pb = 2.431$ (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 $^{206}Pb/^{207}Pb = 1.158 \pm 0.007$, $^{208}Pb/^{207}Pb = 2.430 \pm 0.010$ (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.

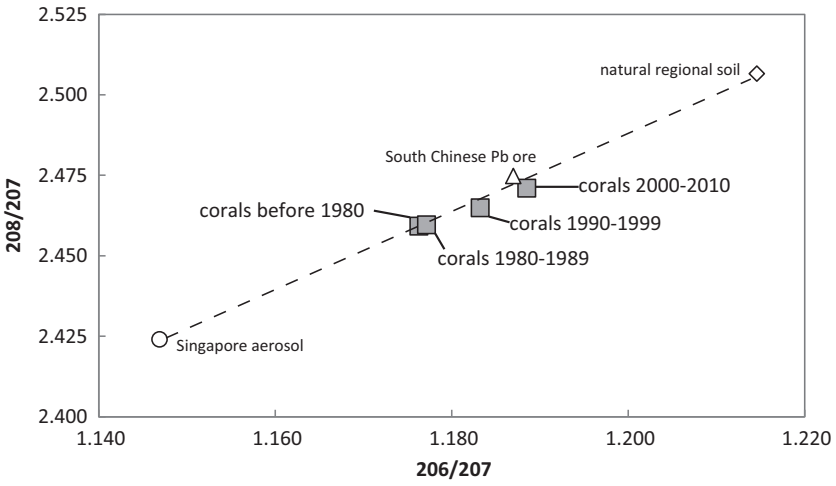

Fig. 8. The triple-isotope plot of Pb isotopes in corals (filled squares) compared to the most possible end members suggested in this study, including Singapore aerosol (open circle, Lee et al., 2014); South Chinese Pb ore (open triangle, Inoue et al., 2006); natural regional soil (open diamonds, from 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 $^{206}Pb/^{207}Pb = 1.187 \pm 0.0059$, $^{208}Pb/^{207}Pb = 2.475 \pm 0.0038$, (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 maybe transported to Singapore waters via rainfall and surface runoff from industrial catchments without any footprint in aerosols.

High $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ of ~1.199 and $^{208}Pb/^{207}Pb$ 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 (Soeriaatmadja, 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb = 1.147$ and $^{208}Pb/^{207}Pb = 2.424$, Lee et al., 2014) and South Chinese Pb (average $^{206}Pb/^{207}Pb = 1.187$ and $^{208}Pb/^{207}Pb = 2.475$), 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^{15} 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 10^8 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 ($^{206}Pb/^{207}Pb = 1.215$ and $^{208}Pb/^{207}Pb = 2.506$, 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, $^{206}Pb/^{207}Pb$ in Singapore corals increased from 1.166 to 1.191, $^{208}Pb/^{207}Pb$ from 2.442 to 2.484. Since the late 1990s, the long-term trend diminished and $^{206}Pb/^{207}Pb$ fluctuated between 1.185–1.198, $^{208}Pb/^{207}Pb$ fluctuated between 2.464–

2.482. Spatial variations in Pb isotopes were small between sites, especially after the late 1990s.

4. Recent $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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 $^{206}Pb/^{207}Pb$ 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.
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.

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 Tanzil 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.

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