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Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century

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Abstract

Anthropogenic lead (Pb) from industrial activities has greatly altered the distribution of Pb in the present-day oceans, but no continuous temporal Pb evolution record is available for the Indian Ocean despite rapidly emerging industries around the region. Here, we present the coral-inferred annual history of Pb concentration and isotope ratios in the surface Indian Ocean since the mid-20th century (1945-2010). We analyzed Pb in corals from the Chagos Archipelago, western Sumatra and Strait of Singapore – which represent the central Indian Ocean via nearshore sites. Overall, coral Pb/Ca increased in the mid-1970s at all the sites. However, coral Pb isotope ratios evolve distinctively at each site, suggesting Pb contamination arises from different sources in each case. The major source of Pb in the Chagos coral appears to be India’s Pb emission from leaded gasoline combustion and coal burning, whereas Pb in western Sumatra seems to be largely affected by Indonesia’s gasoline Pb emission with additional Pb inputs from other sources. Pb in the Strait of Singapore has complex sources and its isotopic composition does not reflect Pb from leaded gasoline combustion. Higher $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios found at this site may reflect the contribution of Pb from coals and ores from southern China, Indonesia, and Australia, and local Pb sources in the Strait of Singapore. It is also possible that the Pb isotope ratios of Singapore seawater were elevated through isotope exchange with natural fluvial particles considering its delta setting.
1. Introduction

Lead (Pb) in our present-day oceans is dominated by Pb produced by human activities, mainly from leaded gasoline combustion and high-temperature industries such as smelting, mining, and coal combustion. Anthropogenic Pb emissions have increased more than an order of magnitude above natural levels during the past century (Nriagu, 1979; Wolff and Peel, 1985; Shotyk et al., 1998), increasing surface ocean Pb concentrations by almost 6-fold in the western North Atlantic (Kelly et al., 2009) and by 3-fold in the western Pacific (Inoue et al., 2006) as a consequence. Previous studies have shown that surface ocean Pb concentrations and isotope ratios have varied in time and space, reflecting the changes in the amount of inputs and sources of anthropogenic Pb (Schaule and Patterson, 1981; 1983; Flegal and Patterson, 1983; Boyle et al., 1986; Helmers et al., 1996; Veron et al., 1998; Wu and Boyle, 1997a; Alleman et al., 1999; Weiss et al., 2003).

Long-term monitoring of surface ocean Pb concentrations and isotope ratios thus enables us to assess the impact of anthropogenic Pb inputs to the ocean and relative importance of various Pb sources, which is informative for marine environmental management. Moreover, by knowing the surface ocean Pb transient, we can interpret the present distribution of Pb in the ocean interior in a historical context, deriving information on the transport and fate of the anthropogenic Pb in the ocean. For example, Pb in the surface North Atlantic Ocean has evolved reflecting historical Pb emissions in North America and western Europe (Schaule and Patterson, 1983; Boyle et al., 1986; Shen and Boyle, 1988a; Veron et al., 1993; 1998; Wu and Boyle, 1997a; Kelly et al., 2009), and this surface Pb transient has been used to trace the transport of North American Pb to the eastern North Atlantic Ocean (Veron et al., 1994; Helmers, 1996; Hamelin et al., 1997), intrusion of anthropogenic Pb to the deep North Atlantic Ocean and its southward
transport (Veron et al., 1998; Alleman et al., 1999; 2001a; 2001b), and to estimate the time scales of those processes (Boyle et al., 1986; Shen and Boyle, 1988a).

However, data on surface ocean Pb is still quite limited, making it difficult to evaluate the impact of anthropogenic Pb inputs in our global oceans. Because of the low concentrations (10^{-10} to 10^{-12} mol kg^{-1}) of Pb in seawater, analysis of Pb requires strict control of Pb contamination during sampling and analysis as well as advanced analytical technique and instruments with low detection limits (e.g., Schaule and Patterson, 1981; Bruland and Coale, 1985; Wu and Boyle, 1997b; Lohan et al., 2005; Sohrin et al., 2008). Because of this challenge, reliable measurement of Pb in seawater became available only after 1976 (Schaule and Patterson, 1981), and even after then, most of seawater Pb data were obtained in the North Atlantic and North Pacific Oceans where Pb pollution was most significant during the 20th century. With the absence of long direct monitoring, the history of the surface ocean Pb longer than a few decades has been reconstructed from annual-banded hermatypic corals, but coral-based Pb records exist only for the western North Atlantic (Shen and Boyle, 1987; Reuer, 2002; Kelly et al., 2009), Caribbean (Dodge and Gilbert, 1984; Desenfant et al., 2006), and western Pacific (Inoue et al., 2006; Inoue and Tanimizu, 2008). Therefore, more direct observations and coral-based reconstructions of surface ocean Pb are necessary to access the evolving global imprint of anthropogenic Pb pollution.

The Indian Ocean is one of the most Pb data-deficient areas in the world ocean. Pb emissions in this region are expected to have increased over the past few decades, however, as a result of the rapid development and urbanization in the countries around the Indian Ocean. Moreover, most countries around the Indian Ocean phased out leaded gasoline in the 2000s (UNEP, 2007), whereas phasing out of leaded gasoline began in the early 1970s and 1980s in most of the developed countries in North America and Europe. There were indications that
increased Pb pollution causes a serious health problem in the countries of this region (e.g., George, 1999; Nriagu et al., 1997), and high Pb concentrations have been found in coastal seawaters off India (Rejomon et al., 2010) as well as the marine aerosols collected over the Indian Ocean (Chester et al., 1991; Witt et al., 2006; Balasubramanian et al., 2013). The first reliable Indian Ocean seawater Pb data were published recently, and the results showed that surface Pb concentrations, particularly in the northern Indian Ocean, are higher than those in the present-day Atlantic or Pacific Oceans, implying large anthropogenic Pb inputs to the Indian Ocean (Vu and Sohrin, 2013; Echegoyen et al., submitted).

The goal of this study is to reconstruct historical changes of Pb concentration and isotope ratios of the surface Indian Ocean in response to the increased anthropogenic Pb emissions in the region. For this purpose, we used annually-banded corals collected from three locations: Chagos Archipelago, western Sumatra, and Strait of Singapore. We analyzed Pb/Ca and Pb isotope ratios from these corals and generated high-resolution 30 to 50 year-long histories of Pb in the surface Indian Ocean since the mid-20th century. We identify potential sources of Pb in the region by comparing our coral Pb/Ca record to historical Pb emissions from the nearby countries, and also by comparing our coral Pb isotope ratios to those of the anthropogenic Pb sources in those countries.

2. Materials and Methods

2.1. Coral collection

The first coral (core GIM; referred to as Chagos coral hereafter) was collected in February 1996 in the lagoon of Peros Banhos Atoll (5°15.8’S, 71°45.3’E), which is the NW-most atoll of the Chagos Archipelago in the central Indian Ocean (Fig. 1). The coral core was retrieved
from a *Porites solida* colony living at a 3-m depth in a channel between Lle Diamant and Grand Ile Mapou, where tidal currents allow good water exchange with the open ocean (Pfeiffer et al., 2009). The coral chronology was assigned based on its annual density bands and the seasonal cycle of the coral Sr/Ca ratios reported in Pfeiffer et al. (2009). The Chagos coral is relatively short (~30 cm) and covers the period of 1973-1996.

The second coral (core LKP-1; referred to as Sumatra coral hereafter) was collected from the northwestern coast of Simeulue Island (2°51.7′N, 95°45.8′E), which is located in the west of Sumatra, Indonesia. The coral core was collected from a *Porites* sp. microatoll, which died in 2004 because of the Sumatra-Andaman earthquake. After cutting the coral into slabs, the chronology was determined by counting annual density bands backwards from 2004 (Meltzner et al., 2010). The coral spans the period of 1945-2004.

The third coral was collected from a *Porites lutea* colony at Jong Island (1°12.9′N, 103°47.2′E) located in the Strait of Singapore in December 2010. The coral has visible brown bands that coincide with high luminescence bands when examined under UV light. Bright luminescence in corals has been linked to the incorporation of terrestrial humic acids into the coral skeleton (Isdale, 1984; Scoffin et al., 1989; Lough, 2011). In the case of the Jong Island coral, its bright luminescent bands correspond to summer when there is higher accumulation of riverine organic materials in the strait. The chronology of the Jong Island coral was determined based on these bands, and the coral spans the period of 1960-2010.

### 2.2. Coral cleaning and analysis

At MIT, coral slabs were physically cleaned with a brush and distilled water, and then approximately 100 mg of samples were cut from each band of the corals using a diamond-coated
cutting wheel and Dremel tool. The most recent layers were not processed due to potential contamination from organic tissues. Surface contaminants and organic materials of the corals were removed using a method modified from the Shen and Boyle (1988b), which includes crushing corals into small fragments (2-4 mm for primary and 280-700 μm for final cleaning), and cleaning the corals with oxidant (alkaline H$_2$O$_2$), reductant (ammonia, hydrazine, and citric acid), and strong acid (HNO$_3$). During the cleaning procedure, crushed coral samples were divided into three subsamples, each with approximately 30 mg of coral.

After cleaning, corals were dissolved in high-purity HNO$_3$. An aliquot of this solution was transferred to another vial and diluted for Pb and Ca analysis, and the rest of the solution was stored for Pb isotope analysis. The Pb concentration was measured by isotope dilution ICP-MS (VG Plasma Quad 2+) after spiking the sample with a $^{204}$Pb enriched spike (Oak Ridge National Laboratory; calibrated with a gravimetric Pb concentration standard). The Ca concentration was measured by flame AAS (Perkin-Elmer 403). Pb and Ca were measured in all three subsamples, and the average standard deviation of the triplicate Pb/Ca measurement was ~0.8 nmol/mol for the samples with Pb/Ca lower than 10 nmol/mol, and ~1.6 nmol/mol for the samples with Pb/Ca higher than 20 nmol/mol.

The remaining aliquot of the dissolved coral solutions were used for Pb isotope analysis. Pb isotope ratios were measured only in one subsample with the lowest Pb/Ca ratios among the three subsamples, because this arguably is likely to be the least contaminated during sample processing. Dissolved coral solutions were evaporated to dryness on a clean hot plate in a recirculating clean air fume hood and re-dissolved in HBr, followed by the purification using HBr-HCl anion exchange chromatography (Kraus and Moore, 1953; Strelow, 1978). Pb stable isotopes ($^{204}$Pb, $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb) were measured in the purified samples by multiple
collector ICP-MS (Micromass/GV IsoProbe). Data processing and corrections were performed as in Boyle et al. (2012), and the details are described in Appendix I. In this manuscript, we will mainly discuss $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, as $^{206}\text{Pb}/^{204}\text{Pb}$ measurement was not as precise as we desire. All the coral data, Pb/Ca and Pb isotope ratios including $^{206}\text{Pb}/^{204}\text{Pb}$, are provided in Supplemental Material I.

2.3. Seawater and aerosol analysis

In order to verify the sources of Pb in corals, Pb concentration and isotope ratios were measured in the seawater samples collected at the Jong Island coral site and in the eastern South China Sea (6 samples from 18-21°N and 116-119°W), and in the aerosol samples collected from the roof of a building in the campus of National University of Singapore in Singapore (see Appendix II for sampling method). Seawater Pb concentrations were measured using single batch nitrilotriacetate (NTA) resin extraction and isotope-dilution ICP-MS (Lee et al., 2011), and Pb isotope ratios were measured by multiple collector ICP-MS after concentrating samples using double Mg(OH)$_2$ precipitation and HBr-HCl anion exchange chromatography (Boyle et al., 2012). Aerosol samples were leached 1N HNO$_3$-1.75N HCl acid mixture (Graney et al., 1995), and Pb isotope ratios were measured in the leachate after HBr-HCl anion exchange column purification.

2.4. Regional settings

All corals used in this study lie in the tropical Indian Ocean, near the equator. The equatorial regime of the Indian Ocean lacks the sustained equatorial easterly winds that are characteristic of the Atlantic and Pacific Oceans (Tomczak and Godfrey, 2003). Instead, winds
and circulation of the tropical Indian Ocean vary seasonally and interannually due to the influence of the regional monsoons and El Niño-Southern Oscillation (ENSO) (Godfrey, 1996; Potemra and Lukas, 1999; Schott et al., 2009). In general, both Chagos Island and the margin sites (Sumatra and Singapore) experience monsoonal winds that blow from the north-northeast during boreal winter monsoon and from the south during the boreal summer monsoon (Schott et al., 2002; 2009; Tomczak and Godfrey, 2003). The air in the southern Indian Ocean is relatively pristine, so most pollutants to the central Indian Ocean (Chagos region) are delivered from South Asia during the winter monsoon, whereas the Sumatra and Singapore sites would have pollutants mostly from Southeast Asia and possibly local sources near the sites.

2.5. Historical Pb emissions from countries around the Indian Ocean

In order to find out how major sources contribute to anthropogenic Pb in the Indian Ocean, we estimated Pb emission histories from the countries around the Indian Ocean. In the North Atlantic Ocean, the dominant source of anthropogenic Pb was found to be automobile exhausts (from the use of leaded gasoline), and Pb/Ca ratios analyzed in Bermuda corals from 1940-2000 closely follow the trend of Pb emissions from leaded gasoline consumption in North America and Europe (Shen and Boyle, 1987; Reuer, 2002; Kelly et al., 2009). On the other hand, coal combustion was suggested as an important source of Pb to the western Pacific (Inoue and Tanimizu, 2008; Gallon et al., 2011), and the same may be true for the Indian Ocean. Therefore, we estimated the amount of Pb emitted from automobile exhausts and coal burning in the countries around the Indian Ocean, particularly those that have high GDP and/or are close to the sample collection area.
Historical Pb emissions from automobile exhausts were estimated using the following formula (Li et al., 2012):

$$E_{\text{gasoline}} = Q_{\text{gasoline}} \times (Pb)_{\text{gasoline}} \times EF$$  \hspace{1cm} (1)

where $E_{\text{gasoline}}$ is the Pb emission from gasoline (t), and $Q_{\text{gasoline}}$ is the road sector gasoline consumption (kilotons of oil). $(Pb)_{\text{gasoline}}$ is the Pb content in gasoline used in corresponding years (g Pb/liter of gasoline), and it changes with time as leaded gasoline is phased out stepwise. EF is the emission factor which is the fraction of the Pb in petrol emitted to the atmosphere, which was assumed to be 76% as in Li et al. (2012). For the unit conversion, 0.74 kg/l was used for the density of gasoline (usually ranging 0.71-0.77 kg/l). $Q_{\text{gasoline}}$ data for the years 1971-2009 were available from World Bank database (http://data.worldbank.org), and $(Pb)_{\text{gasoline}}$ was taken from literature (e.g. Hilton, 2006) or assumed based on the environmental regulations implemented in each country (see Supplemental Material II). If both leaded and unleaded gasoline were in use, the market share of the leaded gasoline was taken into account. If leaded gasoline was phased out on a city-scale, like in India and Indonesia, market share of the leaded gasoline was calculated based on the number of cars (India) or the population (Indonesia) of the cities.

Coal is used in various industries and also domestically for cooking and heating, but most of the coal is used to generate electricity (e.g. Nriagu and Pacyna, 1988). The amount of Pb emitted from coal burning in power plants was estimated based on the following equation (Li et al., 2012):

$$E_{\text{coal}} = P_{\text{coal}} \times C \times (Pb)_{\text{coal}} \times EF$$  \hspace{1cm} (2)

where $E_{\text{coal}}$ is the Pb emission from coal combustion (t), $P_{\text{coal}}$ is the electricity produced from coal sources (kWh, data available from WorldBank database), $C$ is the amount of coals used to...
generate 1kWh electricity (kg), (Pb)\textsubscript{coal} is the Pb content in coals (g Pb/kg coal), and EF is the emission factor. C is assumed to be 0.472 kg per kWh (U.S. Energy Information Administration, www.eia.gov), although it may vary depending on coal Pb content and the efficiency of the power plant. (Pb)\textsubscript{coal} has a large range (3 to over 300 mg/kg) depending on the origin of coals, and 15 mg/kg was used in this study, which is an average Pb content for the coals from Australia, India, Indonesia, and China (Masto et al., 2007; Li et al., 2012; Diaz-Somoano et al., 2009). EF also varies depending on the types of coal-burning stoves used at the power plants, and was assumed to be 80% in this study (Li et al., 2012). Coal combustion devices used for other industrial purposes or domestic use have no lead removal devices (i.e. dust removal and flue gas desulfurization devices), and the emission efficiencies will be higher. Results of the calculations are shown in Fig. 2 and 3, and also provided numerically in Supplement Material II.

3. Results

3.1. Pb/Ca ratios of the corals

Pb/Ca ratios in all corals start to increase in the mid-1970s (Fig. 4-6). Chagos Pb/Ca starts to rise in 1975 (~5 nmol/mol) until it reaches ~11 nmol/mol in 1979. After a slight decrease in 1980-1984, it increases drastically after 1985 with about 3.5-fold increase between 1985 and 1994 (Fig. 4). Unusually high Pb/Ca peaks appear in 1986-1987 and 1989, which are 2.5-fold and 1.6-fold higher than the previous years, respectively. Such rapid changes in the surface ocean Pb concentrations seem unlikely, however, and we have to at least consider the possibility that they might be the result of sample contamination. In the Sumatra coral, Pb/Ca stays relatively constant at 4.3 ± 0.3 (1\sigma) nmol/mol between 1951 and 1977 and starts to increase from 1978 (Fig. 5). Pb/Ca slightly decreases from 6.7 to 5.0 in 1984-1993 and then increases to
~9 nmol/mol in 2004. Pb/Ca of the Jong Island coral is almost constant at 23 ± 2 (1σ) nmol/mol during the period of 1962-1974 (Fig. 6). Despite the large inter-annual variability, Jong Pb/Ca generally increases from 1975 to reach 45 nmol/mol in 2002-2003 and then rapidly drops to 21 nmol/mol in 2008.

These results indicate that Pb contamination of the surface Indian Ocean began to occur at a significant level from the mid-1970s. Among the three studied sites, the contamination effect is most prominent in the Chagos coral given its rapid increases in Pb/Ca ratios (7-fold increase between 1975 and 1994), probably because of the low background of Pb at this remote location. A similar result was found in a preliminary study by Shen and Boyle (1987) for Pb/Ca ratios in a coral from Mauritius. They reported only 6 datapoints spanning from 1968-1978, and saw increased Pb/Ca ratios in samples from 1974 and 1978. However, because of the unusually high Pb/Ca values of these two samples (~3.5 fold higher than the samples from 1968-1972), the authors also cautioned us to be aware of the possible influence of uncleaned refractory phase contaminant Pb that was not removed during cleaning.

The partition coefficient of Pb ($D_p = (\text{Pb/Ca})_{\text{coral}}/(\text{Pb/Ca})_{\text{seawater}}$) for the Jong Island coral was calculated to be 3.8, using the coral Pb/Ca ratio in 2009 (no data from 2010) and the Pb concentration (67.2 pmol kg$^{-1}$) in seawater collected near the coral site in 2010 (this study). Based on this $D_p$, the highest seawater Pb concentration appeared in the Jong Island region in 2002-2003 is estimated to be ~120 pmol kg$^{-1}$. The Pb/Ca ratios of the Chagos and Sumatra corals are lower than the Jong Island coral. However, this does not necessarily indicate lower surface water Pb concentrations in the Chagos and Sumatra region because $D_p$ for these two corals are unknown as no comparable seawater Pb concentration data are available. A range of 2.4-3.7 has been reported for the $D_p$ of Pb for various genus and species of corals (Shen and Boyle, 1987;
Kelly et al., 2009). The corals used in this study are all *Porites* species, but $D_p$ can also vary within one genus (Shen and Boyle, 1987).

3.2. Pb isotope ratios of the corals

Pb isotope ratios found in the Jong Island coral in 2009 (there are no data from 2010) agrees with the Pb isotope ratios of the seawater collected at the coral site in 2010 ($^{206}\text{Pb} / ^{207}\text{Pb} = 1.190$ and $^{208}\text{Pb} / ^{207}\text{Pb} = 2.471$, this study). Thus, the Pb isotope variation in the coral records the changes of the Pb isotope ratio in ambient seawater. No seawater data is available for Chagos and western Sumatra regions for similar assessment. The Pb isotope ratios in three corals appear different from each other, implying that the sampling locations were influenced by different sources of Pb, and the isotope composition of the Pb affecting each region has changed over time.

Pb isotope ratios of the Chagos coral are lower than those in the Sumatra and Jong corals, ranging from 1.138-1.154 for $^{206}\text{Pb} / ^{207}\text{Pb}$ and 2.414-2.429 for $^{208}\text{Pb} / ^{207}\text{Pb}$ (Fig. 4). Both isotope ratios decrease from 1973 to 1985, and increase after 1985 to $\sim 1.153$ for $^{206}\text{Pb} / ^{207}\text{Pb}$ and 2.415 for $^{208}\text{Pb} / ^{207}\text{Pb}$ in 1990 and retain the slightly higher isotope ratios until 1994. This change in the Pb isotope ratios around 1985 coincides with the rapid increase in Pb/Ca of the Chagos coral after 1985. This indicates that the main source of anthropogenic Pb affecting this region changed around 1985, from sources with low isotope ratios to the ones with higher isotope ratios.

In the western Sumatra coral, rather constant isotope ratios are found between 1950 and 1973, $^{206}\text{Pb} / ^{207}\text{Pb}$ around 1.18 and $^{208}\text{Pb} / ^{207}\text{Pb}$ around 2.47 (Fig. 5). After 1973, both isotope ratios generally decrease to 1.147 ($^{206}\text{Pb} / ^{207}\text{Pb}$) and 2.440 ($^{208}\text{Pb} / ^{207}\text{Pb}$) in 2004, indicating that the Pb polluting the Sumatra region had low isotope ratios.
Pb isotope ratios in the Jong Island coral show high variability like its Pb/Ca ratios (Fig. 6). The Pb isotope ratios are relatively low in the 1960s and the early 1970s, with \(^{206}\text{Pb}/^{207}\text{Pb} = 1.179 \pm 0.003\) (1σ) and \(^{208}\text{Pb}/^{207}\text{Pb} = 2.464 \pm 0.003\) (avg. 1962-1974). Then, both isotope ratios generally increase to higher values (\(^{206}\text{Pb}/^{207}\text{Pb} = 1.192 \pm 0.005\) and \(^{208}\text{Pb}/^{207}\text{Pb} = 2.477 \pm 0.005\) in 1995-2009), indicating additional Pb sources with high isotopic ratios. The highest \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{208}\text{Pb}/^{207}\text{Pb}\) ratios appear in 1997, and the second highest ratios appear in 2002-2003, corresponding to the peak in the Jong coral Pb/Ca.

4. Discussion

4.1. Pb in Chagos coral and its potential sources

Chagos coral Pb/Ca ratios increase rapidly from 1985. Given the prevailing wind direction, it is most likely that anthropogenic Pb in this area originated from South Asia. The largest Pb-emitting country in South Asia is India (Fig. 2 and 3), which has the largest population and GDP in South Asia. The number of vehicles in India started to increase from the early 1980s, and Pb emissions from the automobile exhausts also increased rapidly from then (Fig. 2). In addition, India is burning millions of tons of coal annually to supply its abundant power plants and heavy metal industries (Lelieveld et al., 2001; Ramanathan et al., 2001). The coal-based power generation in India has grown much over the past three decades, and Pb emissions from this source are comparable to those from leaded gasoline exhausts in India (Fig. 3).

Chagos coral Pb/Ca ratios are well correlated \((r^2=0.89)\) with the total Pb emissions (sum of vehicle Pb emissions and coal Pb emissions) from India when a 0.5-year lag time is assumed between the Pb emission and the coral Pb/Ca (Fig. 7). Excluding the three datapoints (from 1986, 1987, and 1989) that might possibly represent sample contamination, a higher correlation
(r²=0.93) is achieved between the two data when a 3.5-4 year lag time is assumed. The residence
time of dissolved Pb has been estimated to be a few years in the oligotrophic surface ocean based
on ²¹⁰Pb studies (e.g., ~ 2 years in the Atlantic and Pacific Oceans; Bacon et al., 1976; Nozaki et
al., 1976). Thus, it is reasonable to expect that any changes in the atmospheric Pb flux (e.g.,
changes in India’s Pb emissions) would have observable consequences in the upper ocean (as
observed in the Chagos coral) with a few years of delay, although the residence time of Pb is
unknown for the central Indian Ocean yet. Thus, the increase in the Chagos coral Pb/Ca appears
to be mostly affected by Pb emissions from India’s gasoline and coal combustion. There could be
minor contribution of the Pb from India’s other sources or from other countries, which may
explain the small differences between India’s gasoline and coal Pb emissions and the coral
record, e.g., the abrupt increase in the coral Pb/Ca around 1985 compared to the increase in
India's Pb emissions in 1980-1983.

Pb isotope ratios in the Chagos coral (Fig. 8) are in the same range as the Pb in aerosols
collected from India in 1995 (Bollhöfer and Rosman, 2001), but ²⁰⁶Pb/²⁰⁷Pb is higher (and
²⁰⁸Pb/²⁰⁶Pb is lower) than the urban aerosols from Sri Lanka, Thailand, Indonesia and Australia
in the 1990s (Mukai et al., 1993; Bollhöfer and Rosman, 2000; 2001), supporting the inference
that the Pb emitted from India is the largest contributor to the Pb in Chagos region. The Chagos
coral Pb isotope ratios appear close to the mixing line of Broken Hill (Australia) type Pb ores
and Mississippi Valley (US) type Pb ores (Fig. 8), which are the main Pb ores that were used by
the world’s two largest alkyl-lead suppliers, Associated Octel (Broken Hill type Pb) and Ethyl
Corp. (Mississippi Valley type Pb) (Bollhöfer and Rosman, 2000). This implies that leaded
gasoline combustion is most likely the major source of the Pb in this region. However, the
Chagos coral Pb has slightly higher ²⁰⁶Pb/²⁰⁷Pb (lower ²⁰⁸Pb/²⁰⁶Pb) than this mixing line and Pb
in Indian aerosols, which may reflect the input of coal-derived Pb, because coals generally have high $^{206}\text{Pb}^{207}\text{Pb}$ (low $^{208}\text{Pb}^{206}\text{Pb}$) (Diaz-Somoano et al., 2009). The Pb isotopic signatures of Indian coals are unknown. However, coals imported by India between 1988 and 2000 were mainly from Australia (69%) and Indonesia (10%) (COMTRADE, 2009), and mixing with the Pb from these coals can increase the $^{206}\text{Pb}^{207}\text{Pb}$ and $^{208}\text{Pb}^{207}\text{Pb}$ in the observed direction (Fig. 8).

The drastic change in the Chagos coral Pb isotope ratios around 1985 (Fig. 4) could possibly be caused by increased use of the alkyl-lead supplied by Ethyl Corp. after 1985 compared to those supplied by Associate Octel, but we need further information on the market share of these companies in India during that period to verify this possibility. The increased $^{206}\text{Pb}^{207}\text{Pb}$ and $^{208}\text{Pb}^{207}\text{Pb}$ after 1985 could be also due to the increased coal burning in India (and other countries), as coals have high $^{206}\text{Pb}^{207}\text{Pb}$ and $^{208}\text{Pb}^{207}\text{Pb}$ ratios (Diaz-Somoano et al., 2009), or could be the combined effect of both mechanisms.

Local Pb sources may need to be considered for the Chagos coral record. On the south of the Banhos Atoll (coral site) lies the largest island of the Chagos Archipelago, Diego Garcia. This island contains a large joint UK-US naval support facility with about 1500 military personnel and 2000 civilian contractors, and the activities of this island were suggested to cause high Polychlorinated biphenyls (PCBs) levels in air samples from the Chagos Archipelago (Wurl et al., 2006). The activities on the Diego Garcia may have supplied Pb to the Chagos coral region, but we cannot assess its impact because the amount and the isotope signals of the Pb used on that island are unknown. We suspect this impact would be minimal, though, because the coral Pb record from North Rock Bermuda appear to be unaffected by local sources (Shen and Boyle, 1987; Kelly et al., 2009), although Bermuda was inhabited by more than 60,000 people and housing a US military base until 1995.
4.2. Pb in Western Sumatra coral and its potential sources

Significant Pb contamination started in the western Sumatra region around the mid-1970s given the increasing Pb/Ca ratios and decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios around that time (Fig. 5). Assuming that the “background Pb” of this region is the average of the coral Pb values in 1950-1970, when Pb/Ca and Pb isotope ratios are relatively invariable, we calculated the isotope ratios of the anthropogenic Pb ($R_{\text{Anthro}}$) that contaminated the Sumatra region after the 1970s using a mixing equation (Shirahata et al., 1980):

$$R_{\text{Anthro}} = \frac{(R_{\text{Coral}}x_{\text{Coral}}) - (R_{\text{Background}}x_{\text{Background}})}{C_{\text{Coral}} - C_{\text{Background}}}$$  

(3)

where R and C denote the Pb isotope ratio and Pb/Ca of the coral and the background Pb. The calculated $R_{\text{Anthro}}$ for the years after the 1970 are relatively uniform around $^{206}\text{Pb}/^{207}\text{Pb} = 1.12$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.41$ ($^{208}\text{Pb}/^{206}\text{Pb} = 2.15$). On the triple-isotope plot, these isotope ratios fall onto the range of Indian Pb ores (Sangster et al., 2000) and Pb in aerosols found in Indonesia and Thailand in 1987-89 (Mukai et al., 1993) and 1995-98 (Bollhöfer and Rosman, 2000) (Fig. 8), which were mainly from leaded gasoline combustion. The use of Indian Pb ores was negligible in the countries around the Sumatra region (COMTRADE, 2009). Lead gasoline was phased out in Thailand in the early 1990s (Hirota, 2006), whereas it was widely used until 2006 in Indonesia (Hosono et al., 2011). Thus, the dominant source of Pb affecting the western Sumatra region seems to be the leaded gasoline emissions from Indonesia.

The Sumatra coral Pb/Ca record does not exactly correspond to the vehicle Pb emissions transient from Indonesia, however, because Indonesian Pb emissions decrease in the early 2000s, whereas coral Pb/Ca continues to increase during that period. The decreasing Pb emissions may not have resulted in the decrease in coral Pb/Ca yet because of a lag time between the two
records associated with the residence time of Pb in the water off Sumatra. It is also possible that the decrease of the vehicle Pb emissions was partly compensated by Pb emissions from coal burning and other industrial sources, although we should note that coal Pb emissions from the countries near Sumatra were almost an order of magnitude smaller than vehicle Pb emissions (Fig. 2 and 3). The coral Pb $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb ratios also did not increase to higher values as they would if coal Pb inputs were large. The continual increase of coral Pb/Ca in the 2000s might be also partly ascribed to the upwelling off western Sumatra. Mixing with subsurface water with higher Pb concentrations might have supplied additional Pb to the surface water, although direct Pb inputs from the atmosphere declined.

4.3. Pb in Jong Island coral and its potential sources

Although the data show high variability, Pb/Ca ratios of the Jong Island coral generally increase from the early 1970s to 2002 and decrease after 2003. This overall can be attributable to anthropogenic Pb inputs from the countries surrounding the Strait of Singapore. Pb emissions (gasoline exhausts and coal combustion) from Indonesia, Malaysia, and Singapore were high in the 1980s and early 1990s and decreased in the 2000s after leaded gasoline was phased out in these countries (Afroz et al., 2003; Hilton, 2006; Hosono et al., 2011) (Fig. 2 and 3). However, the detailed pattern of the coral Pb/Ca does not correspond to the Pb transient from a single source. Rather, it seems to be the result of Pb inputs from multiple sources from multiple countries, including industrial sources other than leaded gasoline and coal combustion.

In the triple Pb isotope plot (Fig. 9), Pb in the Jong Island coral falls on a straight line between $^{206}$Pb/$^{207}$Pb = 1.175-1.20 and $^{208}$Pb/$^{206}$Pb = 2.07-2.10, consistent with a hypothesis of two end-member mixing. Pb with low $^{206}$Pb/$^{207}$Pb and high $^{208}$Pb/$^{206}$Pb might be from the
gasoline Pb used in the countries around the Strait of Singapore. Extrapolating the mixing line of the coral Pb overlaps with the Pb in Indonesia, Malaysia, and Thailand aerosols collected in the early 1990s, which were dominated by gasoline Pb (Bollhöfer and Rosman, 2000; Mukai et al., 1997). Relatively low coral $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ in the years prior to 1995 (Fig. 6) might be also attributed to the higher gasoline Pb emissions during that period than the late 1990s and the 2000s (Fig. 2). However, the overall impact of local gasoline Pb to the Singapore regions is probably small, because the $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{206}\text{Pb}$) ratios of the Jong Island coral are all much higher (lower) than the gasoline Pb-containing aerosols (Fig. 9). Pb with high isotope ratios could be from the coals from Indonesia and Australia and the Pb ores from southern China (Fig. 9) that were used in the countries around the Singapore Strait. For example, during 1990-2010, Malaysia imported 67% of its coal from Indonesia and 24% from Australia; Indonesia imported 37% of its coal from Australia and 35% from China (COMTRADE, 2009); and Singapore imported 73% of unwrought Pb from China (UNEP, 2011).

However, a question arises on how this anthropogenic Pb was delivered to the surface water of the Strait of Singapore. It has been known that the Pb in open ocean surface waters is mainly supplied by atmospheric deposition (e.g. Schaule and Patterson, 1981). However, in the Jong Island region, the seawater Pb isotopic signature, which is also recorded in the local coral, does not agree with that of the local aerosol pollutant Pb. As shown previously, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the aerosols collected from Malaysia collected in 1995, Indonesia in 1989 (Mukai et al., 1993) and 1995 (Bollhöfer and Rosman, 2000), and Singapore in 2011-2012 (this study, see Supplemental Material III), are all considerably lower ($^{208}\text{Pb}/^{207}\text{Pb}$ ratios are higher) than the Jong Island coral Pb isotope ratios for the corresponding years (Fig. 9).
There is a possibility that aerosols used in this study were dominated by local sources and do not represent the overall isotope ratios of the Pb emitted from the region. For example, Mukai et al. (1993) show that Pb isotope ratios can vary significantly depending on collection site in some Asian countries. Pb isotope ratios in aerosols collected from a site with heavy traffic (\( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = 1.14 \)) were different from those from a site with low traffic and other industries (\( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = 1.10 \)), although the two sites were only ~10 km apart. It is less likely that the aerosol samples used in this study were all influenced by such localized inputs. However, aerosol sampling covering a wider area, particularly the main industrial areas, is necessary before concluding that aerosols are not the major source of Pb in the Jong Island region.

If not due to local atmospheric deposition, Pb in the Strait of Singapore might have been advectively transported. The Strait of Singapore is a mixture of waters from the South China Sea, Java Sea, and eastern Indian Ocean. Pb isotope ratios of the surface waters in the eastern South China Sea collected in 2000 are \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = 1.156 \pm 0.015, \frac{^{208}\text{Pb}}{^{207}\text{Pb}} = 2.444 \pm 0.017 \) (this study, Supplemental Material III). No seawater data is available for the Java Sea, but a coral sample collected off Jakarta Bay, whose age is from 1998-2001, had Pb isotope ratios of \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = 1.158 \) and \( \frac{^{208}\text{Pb}}{^{207}\text{Pb}} = 2.430 \) (Inoue et al., 2006). Although we don’t have direct information for the eastern Indian Ocean seawater, surface seawater Pb isotope ratios in the open ocean section of the Bay of Bengal (8°31’N, 86°01’E, collected in 2010) were \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = 1.148, \frac{^{208}\text{Pb}}{^{207}\text{Pb}} = 2.431 \) (Lee, 2013). The Pb isotope ratios of these waters are too low to be the source of Pb in the Strait of Singapore.

One possible process of changing the Pb isotope ratios in the waters of the Strait of Singapore is through isotope exchange between seawater and natural fluvial particles. Most of the dissolved \( ^{210}\text{Pb} \) in rivers is scavenged in estuaries (e.g. Turekian, 1977). However, reversible...
exchange equilibrium may occur between the Pb isotopes in riverine particles and seawaters, delivering the riverine Pb isotopic signals to the ocean without increasing seawater Pb concentrations. This process has been suggested to occur for Sr and Nd isotopes (Oelkers et al., 2011; 2012; Jones et al., 2012a; 2012b), and it is also consistent with the similar Pb isotope values found in dissolved and suspended particulate Pb in the water column near Bermuda (Sherrell and Boyle, 1992). Many rivers run into the Malacca Strait and southern South China Sea, or directly into the Strait of Singapore (e.g. the Johor River). Sediment discharges from the rivers in this region are particularly large because of mountainous terrain, erodible strata, and seasonally heavy rainfall (Douglas, 1996; Milliman and Meade, 1983; Milliman et al., 1987). For example, sediment discharge from Sumatra, Java, and Borneo ($2.02 \times 10^9$ t yr$^{-1}$) accounts for 10-12% of the total sediment discharge to the global ocean (Milliman et al., 1999). Little is known about the Pb isotope ratios of the riverine particles of this region, but sediment samples and K-feldspar grains in the rivers of the Indochina Peninsula have been found to have high $^{206}\text{Pb}/^{207}\text{Pb}$ (>1.18) and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (>2.47) (Bodet and Schrärer, 2001; Millot et al., 2004). Thus, if isotopic exchange occurs with these particles, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in the seawater would increase to higher values, as observed in the Jong Island coral. Seawaters and rivers (waters and particles) close to the Strait of Singapore need to be further examined for Pb isotope ratios in order to prove this hypothesis.

There also could be sources of Pb that are directly injected to the Jong Island region. For example, scrapings from boat paints that leach out from transport vessels were suggested as a cause of high Cu and Zn found in the sediments of this region (Goh and Chou, 1997), and they may also release Pb to the seawater. The Strait of Singapore is one of the busiest shipping routes in the world, and Jong Island is in the vicinity (within 5 km) of the Port of Singapore.
5. Conclusions

This study provides the first data on the evolution of Pb concentrations and isotope ratios of the Indian Ocean over the past 30-50 years, where such data has been unavailable in spite of increasing anthropogenic Pb emissions in the region. As expected, unlike the North Atlantic Ocean, where surface Pb concentrations decreased by almost 10 fold after the 1970s (Kelly et al., 2009), Pb levels in the surface Indian Ocean began to increase from the mid-1970s (all sites), continuously until the early 2000s (Sumatra and Singapore sites). Pb in the Chagos coral reflects dominance of India’s industrial (gasoline and coal) Pb in this region. The Sumatra coral record reflects the impact of the gasoline-Pb emissions from Indonesia, with some inputs from unidentified sources. Pb in the Singapore Strait Jong Island coral appears to be affected by Pb emitted from nearby countries, although the major sources could not be identified clearly in this study. In the Jong Island region, Pb could be mainly supplied by advection rather than aerosol deposition, possibly with an increased Pb isotope ratios resulted from the reversible isotope exchange with fluvial particles. Further studies on the Pb in other industrial sources, aerosols, and rivers are required to identify sources and pathways of the Pb in this region.

Among the three corals studied, historical changes in the Pb and Pb isotope ratios of the surface Indian Ocean would probably be best represented by the Chagos coral given its location. The features in the surface Pb transient revealed from the Chagos coral, such as a rapid increase in Pb/Ca and drastic changes in Pb isotope ratios around 1985, provide an important marker for estimating the age of Pb in the Indian Ocean water column. Continuous monitoring of surface seawater and analysis of a coral with a longer time span would provide more information on the
changes of the surface ocean Pb that resulted from the phasing out of leaded gasoline and the
increased use of industrial Pb.

Acknowledgements

We thank Kerry Sieh for arranging for the Sumatra coral collaboration, Jani Tanzil for assistance
in Jong Island coral collection, and Rick Kayser and Jessica Fitzsimmons for ICP-MS
maintenance. The work on the Sumatra coral is Earth Observatory of Singapore contribution 65.
We also thank Steve Galer and two anonymous reviewers for their constructive criticism. This
research was supported by the Singapore National Research Foundation through a grant to
CENSAM/SMART.
References


Appendix I. Pb isotope analysis

Coral, seawater, and aerosol samples that were purified by HCl-HBr anion exchange columns were dried on a hot plate in a recirculating fume hood in a positive-pressure clean lab. On the day of the ICP-MS run, dried samples were re-dissolved in dilute (0.2 M) nitric acid. After spiking the samples with Tl, stable Pb isotopes (204Pb, 206Pb, 207Pb, and 208Pb) in the samples were determined by multiple collector ICP-MS (Micromass/GV IsoProbe). 204Pb was measured with an ion-counting Daly detector with the WARP (Wide Aperture Retarding Potential) filter, with calibration for deadtime (50 ns) and ion-counting efficiency, whereas other masses were measured on Faraday cups. Data processing and corrections were performed as in Boyle et al. (2012), which is the method modified from Reuer et al. (2003). The method includes: (1) elimination of the isobaric interferences of 204Hg, (2) exponential “beta” mass fractionation correction normalized with a 205Tl/203Tl spike, (3) a tailing correction derived from a curve fit to 209Bi at half-mass intervals, and (4) on-peak-zero corrections for instrumental hardware blanks using nitric acid (for Tl isotopes) and Tl-spiked nitric acid (for Hg and Pb isotopes). Within-day Daly counter efficiency variations were monitored by measuring NBS SRM-981 and an independent internal lab standard every 3-5 samples, as well as the beginning and end of each session. The Pb isotope ratios were finally re-normalized to the estimated absolute values reported for NBS SRM-981 (Galer and Abouchami, 1998; Thirlwall, 2000; Baker et al., 2004) to correct for minor differences in Faraday cup efficiencies and isotope fractionation that is not accounted for by Tl correction.

External reproducibility of a Pb standard that has Pb signal intensities comparable to samples was 0.2 permil for 206Pb/207Pb and 0.3 permil for 208Pb/207Pb (1σ, n=51, measured on 4 different days). No replicate measurement was made for the samples, but reproducibility of the
samples should be on the same magnitude as those of the standard, although samples with lower
signal intensities may have higher errors due to the uncertainties in the blank correction. The
$^{206}\text{Pb}/^{204}\text{Pb}$ was not as precise as $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$, e.g., external reproducibility of a
standard measurement was 66 permil for $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (1σ, n=12).

**Appendix II. Seawater and Aerosol sampling**

Seawater samples were collected using a “pole sampler” (sample bottle mounted in clean
plastic holder at the end of a pole) or MITESS “ATE” sampler (Bell et al., 2002). Samples were
filtered through 0.4 µm Nuclepore® filters and acidified with 4x vycor-distilled 6N HCl to pH 2
upon retrieval.

Aerosol samples were collected using a method modified from Bollhöfer et al. (1999).
The aerosols were collected on PTFE filters (37mm 0.45 µm front and 30-60 µm back PTFE
filters, both from Savillex) fitted to the plastic monitors (Millipore Cat. #M000-O37AO) and
suctioned via flexible tubing connected to an electric diaphragm pump. A total of 18 samples
were collected over a period of 10 months, each with 2 days to 4 weeks-long sampling. The
PTFE filters were cleaned by first leaching in ethanol for ~6 h at room temperature to remove
possible organic lead contamination, rinsing with distilled water, and leaching in 1M HCl for
another day at 60°C. After rinsing the filters five times with distilled water, they were left to dry
under a HEPA filtered air stream for one day prior to mounting into the monitors.
Figure captions

Fig. 1. Sampling locations for Chagos, Western Sumatra, and Jong Island corals.

Fig. 2. Historical Pb emissions (t) from vehicle gasoline combustion in the countries around the Indian Ocean. Dotted lines are for the years where data are unavailable.

Fig. 3. Historical Pb emissions (t) from coal burning for electricity production. Singapore, Sri Lanka, and most countries in the Middle East and Africa did not use coal to produce power during the period of 1971-2008. Namibia and Tanzania began coal-based power production in the 1990s, but Pb emitted from them was below 1 tonne. Coal consumed by other industrial facilities and domestic use are not included.

Fig. 4. Time series of Pb/Ca (♦), $^{206}$Pb/$^{207}$Pb (∆), and $^{208}$Pb/$^{207}$Pb (■) ratios in the Chagos coral. Error bars of the Pb/Ca ratios represent the standard deviation of the triplicates. Single measurement was made for Pb isotopes in the sample with the lowest Pb/Ca among the triplicates.

Fig. 5. Time series of Pb/Ca (♦), $^{206}$Pb/$^{207}$Pb (∆), and $^{208}$Pb/$^{207}$Pb (■) ratios in the western Sumatra coral.

Fig. 6. Time series of Pb/Ca (♦), $^{206}$Pb/$^{207}$Pb (∆), and $^{208}$Pb/$^{207}$Pb (■) ratios in the Jong Island coral. Pb isotope ratios of the seawater (∇) collected at the coral growth site are shown together.
Fig. 7. (a) Total Pb emissions (gasoline and coal combustion) from India in comparison with the Chagos coral Pb/Ca ratios, when 0.5 and 4 years of lag-times are assumed between the Pb emission and the coral-Pb calcification. Unusually high coral Pb/Ca in 1986, 1987, and 1988 (open ◊) may be the result of sample contamination. (b) R-squared values from the linear regression between India’s Pb emission and the Chagos coral Pb data when a 0-6 year of lag time is assumed, for all data (□) and for the data excluding the years 1986, 1987, and 1988 (■).

Fig. 8. Triple isotope plot for the Pb in the Chagos and Sumatra corals in comparison with various Pb ores (Sangster et al., 2000; Inoue and Tanimizu, 2008) and coals (Diaz-Somoano, 2009) and the aerosols collected from the countries in South and Southeast Asia (Bollhöfer and Rosman, 2000; 2001; Mukai et al., 1993). Black circles represent typical Australian (Broken Hill) type and US (Mississippi valley) type Pb ores used in alkyl lead (Cooper et al., 1969; Doe, 1970; Cummings and Richards, 1975).

Fig. 9. Triple isotope plot for the Pb in the Jong Island coral in comparison with various Pb ores, coals, and aerosols collected from the countries in Southeast Asia. References are same as Fig. 8, and the Singapore aerosols are from this study.