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

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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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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

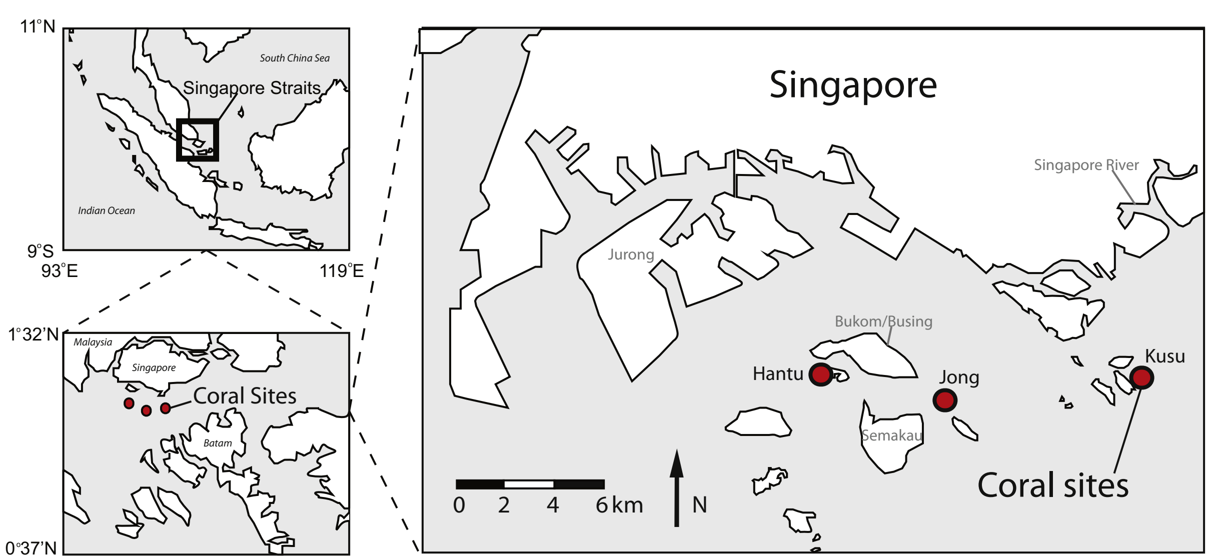

Fig. 1. Map of the study site. On the top left corner is a map of Singapore Straits and its relative location in Southeast Asia; on the bottom left corner is a zoomed map of Singapore Straits with respect to the countries and regions in its vicinity, the adjacent countries and ocean basins are denoted. 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).