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Lead in the western South China Sea: Evidence of atmospheric deposition and upwelling

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RESEARCH LETTER

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Key Points:

- Lead concentration in the western South China Sea has increased 2–3 times since the 1950s
- China contributes around 40%–60% of lead in the western South China Sea estimated by isotope ratios
- Ocean circulation regulates the temporal variability of lead in the western South China Sea

Supporting Information:

- Supporting Information S1

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Lead in the western South China Sea: Evidence of atmospheric deposition and upwelling

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Abstract In recent decades, rapid industrial developments have increased lead (Pb) inputs to the South China Sea. To quantify the increasing variability, we investigated 170 years of skeletal Pb and Pb isotopes from an offshore, central Vietnamese coral. The Pb/Ca in the coral was 10–16 nmol/mol before the mid-1950s and increased to more than 30 nmol/mol by 2000. While the regional phaseout of leaded petrol commenced in 2000, coral Pb/Ca continued increasing until 2004, possibly due to regional upwelling and the transport of previously emitted Pb from tropical Pacific waters. The ²⁰⁶Pb/²⁰⁷Pb ratio in the coral was 1.191–1.195 before mid-1950s, suggesting natural sources. Since then, the ratio decreased, reaching ~1.165 in 2004. Lead isotopes show high linearity between natural and Chinese emitted Pb, with the latter contributing ~40%–60% of the skeletal Pb after 2000.

1. Introduction

Lead (Pb) in the present ocean is dominated by anthropogenic sources [Echegoyen *et al.*, 2014; Flegal, 1986; Patterson and Settle, 1987], and it is primarily derived from leaded petrol, coal, and high-temperature industrial activities. The variability of Pb content and isotopic composition in oceanic location depends on regional historical anthropogenic Pb emissions and atmospheric and oceanic transport [Alleman *et al.*, 1999; Weiss *et al.*, 2003]. As a result the temporal and spatial dependent patterns of Pb in oceans can be used as a tracer demonstrating how metals move through the ocean [e.g., Boyle *et al.*, 2014]. To date, direct seawater Pb measurement remains sparse, and continuous monitoring stations are even rarer. Fortunately, the temporal variation of surface ocean Pb can be inferred from corals, which has been demonstrated in various ocean basins in response to historical Pb emissions, including the North Atlantic Ocean [Kelly *et al.*, 2009; Reuer, 2002], the Indian Ocean [Lee *et al.*, 2014], the Caribbean Sea [Desenfant *et al.*, 2006], the Singapore Straits [Chen *et al.*, 2015], and the western Pacific [Inoue and Tanimizu, 2008; Inoue *et al.*, 2006].

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

To address this issue, we reconstructed a 170 year record of Pb and Pb isotopes in the western SCS from an exposed site to the east of central Vietnam. The Pb/Ca in the coral is compared to historical and recent Pb emissions in the region, and the Pb isotopes in the coral are compared with potential sources such as leaded petrol, Pb ore, and other natural sources.

2. Sampling and Analysis

Hon Tre Island (Figure 1c) lies to the east of central Vietnam in the western SCS and is within the influence of East Asian Monsoon (Figure 1b) [Chang, 2004]. From November to March, northeast winds prevail [Dippner

et al., 2007; Xie et al., 2003], originating in China and northern Vietnam, whereas from June to September, southwest winds prevail originating in Southeast Asian countries and southern Vietnam (Figure 1b). During the Southwest Monsoon, upwelling occurs at $\sim 12^{\circ}\text{N}$ off the central Vietnamese coast [Xie et al., 2003], bringing deeper water [Dippner et al., 2013] with possibly older Pb to the site.

A 2.4 m long core was obtained from a *Porities lutea* coral off the northeastern side of Hon Tre Island on March 2011 at 2.5 m depth ($12^{\circ}12'49.90''\text{N}$, $109^{\circ}18'17.51''\text{E}$). The coral was sampled from the side of the island directly facing open ocean water ($>200\text{ m}$), 12 km from the Nha Trang Bay, and was the furthest point from potential runoff (Cai River [Dung, 2007]). The west side of the Hon Tre Island was developed into a resort [Nguyen et al., 2013], while the northeastern side of the island remains undeveloped. The Sr/Ca on the coral shows excellent agreement with satellite HadISST centered at 12.5°N and 109.5°E [Rayner et al., 2003; Bolton et al., 2014]. The chronology of the coral was determined by counting the annual density bands revealed by X-ray imaging and confirmed by paired seasonal paleoclimate analysis [Bolton et al., 2014]. We subsampled the coral using a diamond-coated saw based on the semiannual banding in the X-radiographs. To ensure sufficient sample size, the $\sim 8\text{ mm}$ thick coral slab is subsampled at a minimum of 10 mm in length by 10 mm in width. Due to varying extension rates, we cut the coral to cover either ~ 12 , 18, or 24 months. The midpoint of each subsample is the reported date. After subsampling, the corals were cleaned using the method laid out in Shen and Boyle [1987], subsequently described by Lee et al. [2014] and Chen et al. [2015]. In brief, coral pieces were crushed into small fragments (2–4 mm for primary and 280–700 μm for final cleaning) and were cleaned extensively using alternating $\text{NaOH-H}_2\text{O}_2$ oxidant, HNO_3 , and hydrazine-based reductant. During the cleaning process, each sample was divided into three subsamples. The cleaned coral fragments were then dissolved in ultrapure HNO_3 for Pb/Ca and Pb isotope analyses. The three subsamples were analyzed separately for Pb/Ca to ensure precision. Trace metal clean laboratory, reagents, and plasticware were used throughout the process to ensure no contamination of Pb induced during sample preparation. Contamination control measures have been taken throughout sample preparation, and Pb concentration and isotope blanks were $\sim 1.5\%$ and $\sim 0.05\%$ of the signals and were corrected in the calculation, respectively.

Lead concentration in the coral was analyzed on a quadrupole inductive coupled plasma–mass spectrometer (Q-ICP-MS; VG Plasma Quad 2+) by isotope dilution. After triplicate Pb/Ca were obtained for each sample, the subsample with the lowest Pb/Ca (least contaminated) is chosen for Pb isotope analysis. The lead isotopes were measured by a multiple-collector ICP-MS (MC-ICP-MS; GV IsoProbe) after purifying the dissolved coral samples using an HCl-HBr anion exchange column. Pb isotope data calibration including mass fractionation by the instrument, isobaric interferences, procedural/instrumental blanks, tailing error, and accuracy adjustment were all performed as described in Reuer et al. [2003] and Boyle et al. [2012]. Pb/Ca values range from ~ 10 to 40 nmol/mol with a standard deviation of triplicate measurements of 1.47 nmol/mol . The precision and accuracy of Pb isotope ratios is monitored by measuring our internal lab standard (BAB3deg, calibrated with National Bureau of Standards 981 Standard Reference Material), which gives a relative standard deviation of $^{206}\text{Pb}/^{207}\text{Pb} = 160\text{ ppm}$ ($n = 42$) and $^{208}\text{Pb}/^{207}\text{Pb} = 163\text{ ppm}$ ($n = 42$).

Estimating the average isotopic composition of Chinese emitted Pb is challenging due to the time evolution of Chinese lead sources [Cheng and Hu, 2010; Flegal et al., 2013]. Estimates of Pb isotopic composition from Chinese emissions were compiled using a weighted average of the Pb isotopes in Chinese petroleum, coal, and lead ores with respect to consumption rates. The emission of automobile exhausts and coal combustion were adopted from Lee et al. [2014], while the emissions from Pb smelting were estimated by the amount of lead produced in 2008 [International Lead and Zinc Study Group, 2014] multiplied by the general government's emission guidelines. The $^{206}\text{Pb}/^{207}\text{Pb}$ in Chinese leaded petrol was ~ 1.134 [Lee et al., 2011] since China used alkyl-lead additives mainly from Australian ores [Cheng and Hu, 2010]. The $^{206}\text{Pb}/^{207}\text{Pb}$ in Chinese coal was adopted as ~ 1.166 , which was an average of values reported by Cheng and Hu [2010] and Díaz-Somoano et al. [2009]. The average isotopic values of Chinese Pb ore were estimated as $^{206}\text{Pb}/^{207}\text{Pb} = 1.151$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.133$, which were calculated as the weighted average with respect to the lead production from Liaoning, Hunan, Guangdong, Guangxi, and Yunnan Provinces ($\sim 85\%$ of the country's total production [Mukai et al., 1993; Sangster et al., 2000; Ministry of Land and Resources of the People's Republic of China and China Mining (eds), The distribution of Chinese major Pb-Zn production bases [in Chinese], Retrieved on December 18, 2014, http://www.chinamining.com.cn/report/default.asp?v_doc_id=1102]). In summary, the weighted average Pb isotope ratios for Chinese emitted lead in 2008 were calculated as $^{206}\text{Pb}/^{207}\text{Pb} = 1.159$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.123$.

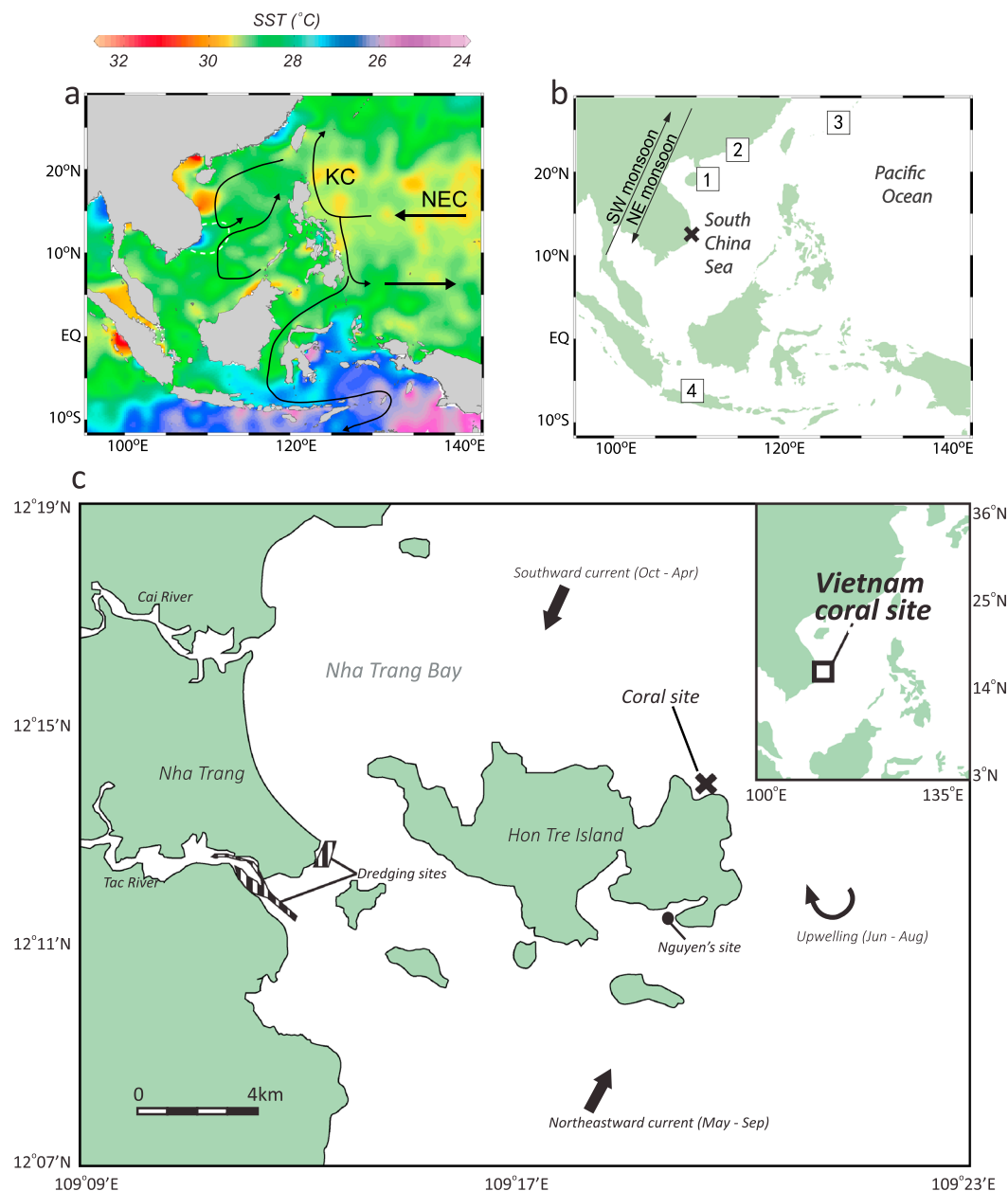


Figure 1. An illustration of our coral site and the atmospheric/oceanographic condition in the surrounding area. (a) Surface current circulation pattern in the South China Sea and adjacent western Pacific with summer sea surface temperature (SST) contour replotted from Bolton *et al.* [2016]. The white dashed line illustrates the area for summer upwelling. The abbreviations are KC = Kuroshio Current and NEC = North Equatorial Current. (b) An illustration of major atmospheric circulation pattern in the region with numbered squares shows the location of other corals published in the literature: 1 = Hainan coral, 2 = Hongkong coral, 3 = Ishigaki coral, and 4 = Jakarta coral [Inoue *et al.*, 2006; Inoue and Tanimizu, 2008]. The Vietnam coral is shown in a black cross. (c) Sampling location of the Vietnam coral (black cross) and its relative location in the South China Sea in the inset map. Major currents of the site are shown in black arrows. The black dot denotes for the location of the coral from a previous study [Nguyen *et al.*, 2013]. Dredging sites on the Tac River are also shown in shaded areas [Nguyen *et al.*, 2013].

3. Temporal Variabilities of Pb/Ca and Pb Isotopes in the Vietnam Coral

Throughout the coral record, the most prominent Pb/Ca feature is a factor of 3 increase over the last 50 years simultaneous to an isotope excursion, indicating anthropogenic Pb input. From the 1840s to mid-1950s, the coral Pb/Ca was low and stable, at 14 ± 2 (1σ) nmol/mol (Figure 2). The Pb/Ca increased abruptly from 14 nmol/mol in 1958 to 22 nmol/mol in 1959 and then plateaued at 20 ± 1.5 (1σ) nmol/mol until the late

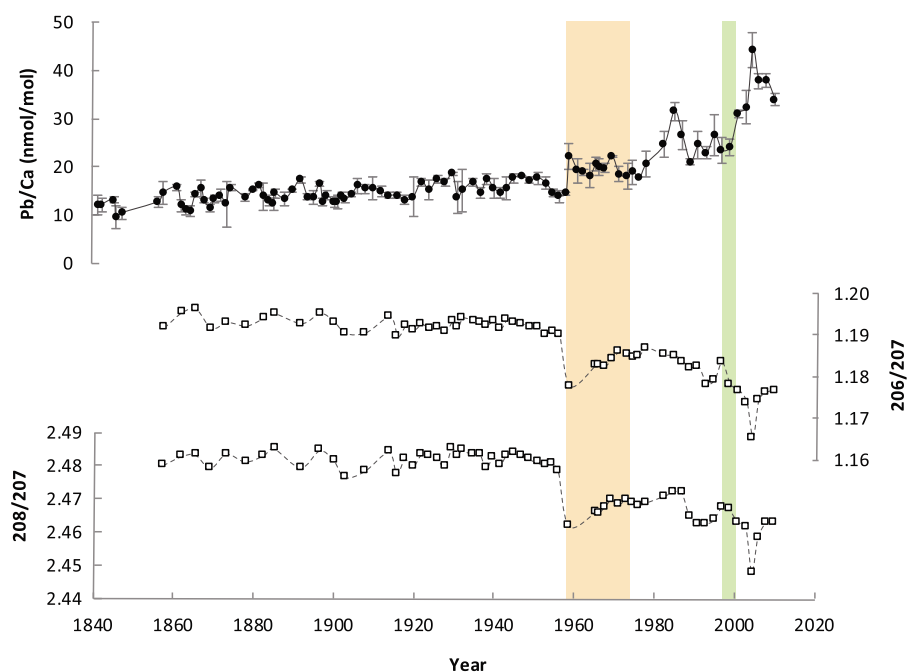


Figure 2. The variations of the Pb/Ca, the $^{206}\text{Pb}/^{207}\text{Pb}$, and the $^{208}\text{Pb}/^{207}\text{Pb}$ in the Vietnam coral. The orange bar marks the timing of the Second Indochina War (1959–1975), and the green bar illustrates the timing of China phasing out of leaded petrol (1997–2000). The error bars in Pb/Ca represent the standard deviation of the triplicates, and the uncertainties in Pb isotopes are within the size of each points.

1970s. After the late 1970s, Pb/Ca increased steadily from 17.6 nmol/mol in 1976 to 24 nmol/mol in 1999 and then increased sharply to 44 nmol/mol in 2004. The annual rate of increase was ~ 0.3 nmol/mol for 1975–1999 and was ~ 4 nmol/mol for 1999–2004. From 2004 to 2010, Pb/Ca in the coral decreased to 34 nmol/mol.

The variations of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are shown together with Pb/Ca (Figure 2). From mid-1910s to mid-1950s, $^{206}\text{Pb}/^{207}\text{Pb}$ was 1.190–1.194 and $^{208}\text{Pb}/^{207}\text{Pb}$ was 2.478–2.486. The $^{206}\text{Pb}/^{207}\text{Pb}$ decreased abruptly to 1.178 at ~ 1958 and then plateaued at 1.185 ± 0.003 (1σ) until the late 1980s. Over the same period, $^{208}\text{Pb}/^{207}\text{Pb}$ decreased to 2.462 and then plateaued at 2.467 ± 0.003 (1σ). The decrease of $^{206}\text{Pb}/^{207}\text{Pb}$ in ~ 1959 coincided with the increase in Pb/Ca in 1959 (Figure 2). From the late 1980s to 2004, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 1.185 to 1.165. The $^{208}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 2.47 to 2.45 in 2004. The sharp decrease in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ coincided with the sharp increase in Pb/Ca from the late 1990s to 2004 (Figure 2). Since 2005, the $^{206}\text{Pb}/^{207}\text{Pb}$ increased again to ~ 1.175 . Throughout the whole record, the Pb/Ca is negatively correlated with $^{206}\text{Pb}/^{207}\text{Pb}$ in the coral with $R^2 = 0.78$ (see supporting information for scatterplots). The correlation is also observed between Pb/Ca and other isotope ratios.

4. Possible Mechanisms for Lead Delivery to the Western SCS

The variation of Pb/Ca and Pb isotopes in the Vietnam coral implies that anthropogenic Pb has invaded the western SCS. The contamination of Pb in the western SCS is quantifiable beginning in the late 1950s. This is earlier than the “takeoff” of the regional economy and industrial development (since the 1970s in this region [UN Data, 2014]). The elevated Pb/Ca in late 1950s coincides with the Vietnamese war (1955–1975 [Department of Defense (DOD), 1998]). It should be noted that a major change in $^{206}\text{Pb}/^{207}\text{Pb}$ in the coral appeared in ~ 1959 , which likely marked the beginning of Second Indochina War (1959–1975), a military struggle with increasing support from the United States (U.S.) [DOD, 1998]. The Pb imprint of the Second Indochina War was not only observed in the Nha Trang coral but also observed in other corals in the northern part of SCS (coral from Xisha Island [e.g., Song *et al.*, 2014]), suggesting that the 1959 event could potentially be used as a stratigraphic marker regionally. During increased military activity, scraps from leaded paint could have possibly contribute to increased coral Pb [Wang *et al.*, 2011], particularly when a U.S. military base was located ~ 30 km south of Nha Trang [Storey and Thayer, 2001]. During the war, Vietnam consumed more

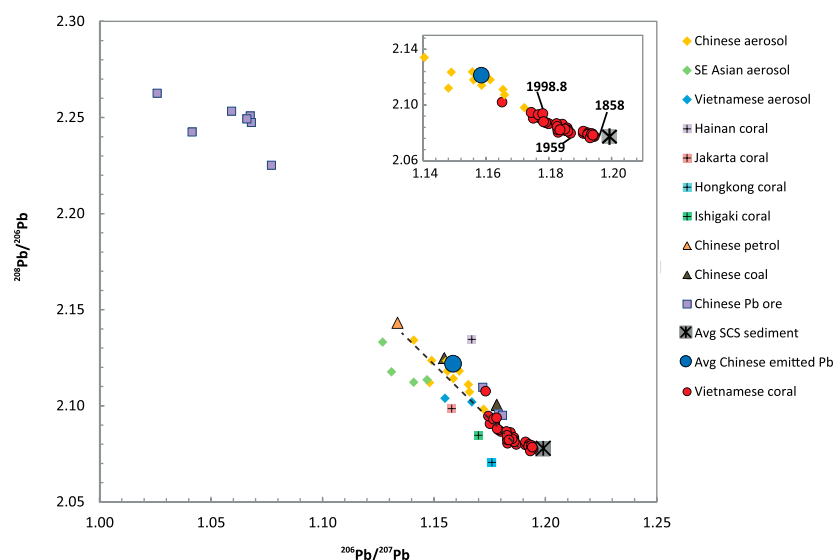


Figure 3. Triple-isotope plot of the Pb in the Vietnamese coral together with potential Pb sources in the South China Sea region. Data include aerosols [Bollhöfer and Rosman, 2000; Cheng *et al.*, 2014; Mukai *et al.*, 1993; Wang *et al.*, 2006], sediments [Zhu *et al.*, 2010], corals (mainly spanning over the 1990s [Inoue and Tanimizu, 2008]), coals [Cheng and Hu, 2010], petroleum [Lee *et al.*, 2011], and Pb ores [Mukai *et al.*, 1993; Sangster *et al.*, 2000]. The two possible end-members are in large symbols with the average Chinese Pb estimated based on emission of 2008 (see text). The dashed line shows the regression using the Pb isotope values in the Vietnam coral after 1959. The R^2 for the regression is 0.83. The inset figure shows a close view of the Pb isotopes in the coral with major end-members. The points representing three key dates are marked out. The three dates in the inset figure mark the timing of beginning of the core (1858), beginning of Second Indochina War (1959), and China phasing out of leaded petrol (1998.8).

leaded petrol than immediately following the war (1976–1979) [Balce, 2000; International Energy Agency, 2014], which may also explain some increased Pb/Ca in the coral in 1955–1975.

Limited changes in Pb isotopes were observed immediately after 1975, indicating that the same type of leaded petrol may have been used during and after the war, as Vietnam imported its leaded petrol from its neighboring countries [ESMAP (Joint UNDP/World Bank Energy Sector Management Assistance Programme), 2002]. Additionally, lead emissions from neighboring countries were 2–10 times higher at this time [Lee *et al.*, 2014]. Combining these effects likely make it difficult to resolve changes in local Pb sources or emissions following the war (Figure 3).

From late 1970s to 2004, the Pb/Ca increased strongly in the coral, implying increased Pb concentrations in surface seawater. A small Pb/Ca peak occurred in the mid-1980s, which coincided with a number of initiatives to decrease Pb content in petrol (see supporting information on countries, years, and detailed initiatives). However, the Pb/Ca peak does not correspond to a significant change to the isotopic composition. The lack of a corresponding change to the Pb isotopes may indicate either that another mechanism is at work or that isotopic exchange with particulate matter may be influencing the isotopic composition [Chen, 2015]. The increase in Pb contamination was most prominent between the late 1990s and mid-2000s, with the highest Pb/Ca value approximately threefold higher than pre-1950 values. These results are in line with the rise of the regional economy since the 1970s [UN Data, 2014]. However, the use of leaded petrol [Lee *et al.*, 2014; Yao *et al.*, 2013] in this region does not seem to correlate with the variation of Pb/Ca. From the estimations from previous studies, peak petroleum Pb emission occurred from 1997 to 2000 in China [Chen *et al.*, 2005; Cheng and Hu, 2010; Lee *et al.*, 2014], 1977 in Thailand [Hirota, 2006], 1980 in Malaysia [Afroz *et al.*, 2003], and 1994 in Vietnam [Balce, 2000]. However, Pb/Ca in the Vietnam coral was still increasing until 2004 (Figure 2), several years later than any of the peak petroleum Pb emissions. China used 10–20 times more leaded petrol than Vietnam, Thailand, or Malaysia [Lee *et al.*, 2014]; therefore, the primary source of the lead in Vietnam coral is likely China. Of note, the Vietnamese lead emissions were <5% of Chinese lead and <30% of Thai lead [Lee *et al.*, 2014]. Therefore, Vietnamese emissions could have been overwhelmed by neighboring countries. Vietnam's efforts in reducing lead emissions in the early 1990s were not clearly shown in the Nha Trang coral,

which also supports Vietnam being a minor Pb source. Therefore, China is considered to be the primary Pb source. The peak coral Pb/Ca was 4–7 years later than the phaseout of leaded petrol in China. The residence time of Pb in oligotrophic surface waters is ~2 years [Bacon *et al.*, 1976; Nozaki *et al.*, 1976] and is estimated to be ~1.8 years in the SCS (data from 18°N, 116°E [Wei *et al.*, 2011]). Therefore, even if the ~2 year residence time for Pb is considered, the Pb/Ca peak still lags the peak lead emission for 2–5 years. Additionally, no significant correlation was observed between Pb/Ca in the Vietnam coral and petroleum lead emission from China, Thailand, Malaysia, or Vietnam, implying that the usage of leaded petrol alone does not fully explain the variation of Pb/Ca in the Vietnam coral.

There are several other possible sources of Pb to the surface ocean at this site including (1) coal combustion, (2) runoff from urban and industrial processes, or (3) advective transport of anthropogenic Pb from other regions that will modify the temporal variability of Pb in the western SCS region. Industrial processes like coal combustion and metal smelting could also contribute Pb to the Vietnam coral. As noted from atmospheric monitoring, the concentration of Pb in Chinese aerosols remained relatively high after phasing out of leaded petrol [Chen *et al.*, 2005; Wang *et al.*, 2006]. An atmospheric monitoring study in Hanoi also concluded that coal combustion could be a major Pb source besides leaded petrol [Gatari *et al.*, 2005]. Lead emissions related to coal combustion or metal smelting (or both) from these countries have been estimated in various studies [e.g., Cheng *et al.*, 2014; Lee *et al.*, 2014; Li *et al.*, 2012; Niisoe *et al.*, 2010; Yao *et al.*, 2013]. The estimated Pb emissions differ greatly (e.g., from ~9000 t/yr to 56,500 t/yr in 2008) because of the choices of emission factor (the amount of Pb emitted per standard amount of coal or ore used) in different studies. It was difficult to evaluate which emission factor is more appropriate because of the significant improvements on emission controls over the last decade [Cheng *et al.*, 2014]. As a result, it is difficult to compare skeletal Pb/Ca and atmospheric emissions quantitatively. But qualitatively speaking, all estimates show an increasing trend since 2000, which is contrary to the decrease in Pb/Ca since 2004. Industrial Pb sources could have some influence on Pb in the Asian region in general but do not appear to be the major source for the Pb leading to the Pb/Ca peak in 2004.

In coastal environments, runoff from urban and industrial catchments could potentially contribute Pb to corals [Chen *et al.*, 2015]. Fluvial Pb inputs do not seem to be significant at our site as both the Tac and Cai Rivers are small and the coastal current directs the river water to the south of Hon Tre Island during its monsoon rains [Ilyash and Matorin, 2007], away from our sampling site. Besides fluvial Pb inputs, the major construction projects carried out in the nearest city, Nha Trang, have been assessed, including the construction of Nha Trang port, several resorts, and dredging of the Tac River (Figure 1c) [Nguyen *et al.*, 2013]. In assessing the influence of the local construction activity on the lead in the coral, the Pb/Ca variability in this study is compared with the bulk lead variability reconstructed using a coral taken to the south of Hon Tre Island facing the Tac River [Nguyen *et al.*, 2013]. As described from Nguyen *et al.*'s [2013] study, the impacts from the major local constructions were not significant until 2006–2008, when the Tac River was extensively dredged, despite scattered construction projects from 2003 [Nguyen *et al.*, 2013]. In Nguyen's study, the coral was sampled from a reef facing the river discharge (Figure 1c) and likely reflects the impacts from local construction. Comparing the two studies, the lead concentration in Nguyen *et al.*'s study started to increase in 2006–2008, while the Pb/Ca in this study between 2006 and 2008 was firmly decreasing, indicating that the impacts from local construction were not observed in our coral. Combining the knowledge on the impacts from local construction and the oceanographic setting around both sites (see section 2 and Figure 1), we conclude that local developments should not have significantly influenced the Pb/Ca in our coral.

Advective transport of Pb is likely modulating the surface ocean Pb at this site. Ocean circulation has been shown to advect Pb [e.g., Alleman *et al.*, 1999; Boyle *et al.*, 1986]. At our coral site, a strong southwestward current prevails from October to April and a northeastward current prevails from May to September [Mitsuguchi *et al.*, 2008; Nguyen *et al.*, 2013]. During midsummer (June to August), the prevailing winds, the topography, and ocean dynamics together develop an upwelling zone [Xie *et al.*, 2003] at ~12°N in the SCS encompassing this study site (Figure 1). Previous studies demonstrated that water masses segregated from the atmosphere (i.e., below the thermocline ~150 m) transport anthropogenic Pb signals over decades [Boyle *et al.*, 2014; Bridgestock *et al.*, 2014]. As suggested by field measurements, the upwelled water mass contains high-salinity North Pacific Tropical Water (NPTW) mixed with the SCS Open Sea Water [Dippner and Loick-Wilde, 2011; Dippner *et al.*, 2007]. The NPTW originates near the center of North Pacific subtropical basin [Cannon, 1966] and intrudes into the SCS via North Equatorial Current and then the Kuroshio Current [Qu *et al.*, 2000] below the surface (~100–200 m [Suga *et al.*, 2000]). No direct measurements were made in

the remote tropical Pacific where NPTW was formed; however, Chinese Pb is likely the main contributor to NPTW as it accounts for ~60% of Pb input to the western Pacific since 1990s [Inoue and Tanimizu, 2008] and ~30% of Pb in urban Californian aerosols [Ewing *et al.*, 2010]. In this case, the temporal variation pattern of Pb in NPTW could be similar to the Chinese leaded petrol emissions and similar to surface SCS. While the frequency and strength of the Kuroshio intrusion vary [Centurioni *et al.*, 2004], the transport time of NPTW from Pacific to Vietnam could be a possible explanation for the 4–7 year offset from the main features of leaded petrol emissions, indicating that a substantial volume of NPTW is regularly surfacing off western Vietnam. Since our site receives water both from surface SCS and NPTW, the transport time of NPTW should be at least 2–5 years to account for the 4–7 year lag between the peak Chinese Pb emission and the peak Pb/Ca in the Vietnam coral, as the residence time of Pb in the upper SCS is ~2 years [Wei *et al.*, 2011]. Similar source and delivery time on upwelling have also been found in the bomb radiocarbon record from the same coral, which showed a broader and lower postbomb ^{14}C peak [Bolton *et al.*, 2016]. Further work on corals from nonupwelling regions in the SCS or using other oceanographic tracers can be done to better constrain the intensity of upwelling and the time scale of the advection of NPTW into the SCS.

5. Sources of Pb to the Western SCS Interpreted From Isotope Records

Lead isotopes provide information on the sources of Pb to the region, allowing for further interpretations of the mechanisms proposed previously. Before the mid-1950s, $^{206}\text{Pb}/^{207}\text{Pb}$ in the coral was 1.191–1.195 and $^{208}\text{Pb}/^{206}\text{Pb}$ was 2.078–2.081. The isotope ratios were invariable and agree with averages from SCS Holocene sediments (average $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.196 and $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.079; Figure 3 [Zhu *et al.*, 2002, 2010]). Considering the limited industrial development in the SCS region during that period [Hirschman and Bonaparte, 2012], Pb in the Vietnam coral clearly originates primarily from natural sources.

From the mid-1950s to 2010, $^{206}\text{Pb}/^{207}\text{Pb}$ decreased to <1.170 , suggesting low $^{206}\text{Pb}/^{207}\text{Pb}$ sources to the western SCS. The $^{206}\text{Pb}/^{207}\text{Pb}$ was negatively correlated with Pb/Ca in the coral, with low $^{206}\text{Pb}/^{207}\text{Pb}$ consistently associated with high Pb/Ca, supporting an anthropogenic Pb source into the region with low $^{206}\text{Pb}/^{207}\text{Pb}$. Lead isotope ratios in the Vietnam coral show high linearity in a triple-isotope plot (Figure 3), which suggests that Pb in the Vietnam coral results from a mixture between the natural Pb with high $^{206}\text{Pb}/^{207}\text{Pb}$ (low $^{208}\text{Pb}/^{206}\text{Pb}$) and an anthropogenic Pb with a low $^{206}\text{Pb}/^{207}\text{Pb}$ (high $^{208}\text{Pb}/^{206}\text{Pb}$). Since 2000, the Pb isotopes in the coral were $^{206}\text{Pb}/^{207}\text{Pb} = 1.174 \pm 0.004$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.095 \pm 0.003$, close to the isotopic composition in both Chinese aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges 1.141–1.177 and $^{208}\text{Pb}/^{206}\text{Pb}$ ranges 2.094–2.134) and Vietnamese aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges 1.155–1.167 and $^{208}\text{Pb}/^{206}\text{Pb}$ ranges 2.101–2.103; Figure 3 [Bollhöfer and Rosman, 2001; Bollhöfer and Rosman, 2000; Chen *et al.*, 2005; Wang *et al.*, 2006]). The similar isotope ratios of Chinese and Vietnamese aerosols make it difficult to evaluate the individual contributions (Figure 3). While we must consider Vietnamese lead emissions as an aerosol source to seawater in Nha Trang, Chinese emissions are likely the dominant signal as Chinese leaded petrol emissions were ~20 times higher than Vietnam and directly upwind from Nha Trang.

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

Little was known about the isotopic composition in NPTW as no direct Pb isotope measurements have been made in the remote Pacific. However, the seawater measurements from recent GEOTRACES cruises on the North Pacific [Zurbrick, 2014] and the western Philippine Sea [Ho, 2016] show a prominent peak in Pb concentration at ~200 m, particularly at the sites where NPTW penetrates [Suga *et al.*, 2000]. The corresponding isotope ratios were $^{206}\text{Pb}/^{207}\text{Pb} < 1.160$ and $^{208}\text{Pb}/^{206}\text{Pb} > 2.110$, implying significant Chinese Pb contribution (average Chinese Pb has $^{206}\text{Pb}/^{207}\text{Pb} = 1.159$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.123$). Inferring from these studies on the neighboring basins, the Pb isotopes in the Vietnam coral would be close to a mixture of natural Pb and Chinese Pb even though we see a delayed time stamp caused by upwelling.

A linear fit between the average emitted Pb and natural Pb in the SCS passes within error of the values obtained from the Vietnam coral (Figure 3), supporting the previous argument that Chinese Pb is the major source of anthropogenic Pb in the region. Using the Chinese emitted Pb ($^{206}\text{Pb}/^{207}\text{Pb}=1.159$ and $^{208}\text{Pb}/^{206}\text{Pb}=2.123$, based on 2008) and natural SCS ($^{206}\text{Pb}/^{207}\text{Pb}=1.193$ and $^{208}\text{Pb}/^{206}\text{Pb}=2.079$) as the two end-members, the weightage calculation shows that Pb into the Vietnamese coral after 2000 ($^{206}\text{Pb}/^{207}\text{Pb}=1.176$ and $^{208}\text{Pb}/^{206}\text{Pb}=2.095$) contains around 40%–60% of Chinese emitted Pb.

6. Conclusion

The temporal variabilities of Pb and Pb isotopes in the western SCS over the last 170 years were inferred from a coral east of Nha Trang Bay, central Vietnam. From the 1840s to mid-1950s, the Pb/Ca in the coral was 10–16 nmol/mol and the $^{206}\text{Pb}/^{207}\text{Pb}$ was ~ 1.195 , inferring natural Pb sources. Since the late 1950s, Pb/Ca started increasing and reaching 44 nmol/mol in 2004. Correspondingly, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from ~ 1.195 to 1.165, suggesting the invasion of anthropogenic Pb sources. The variation in Pb in the coral involved several periods, including natural variations, the Vietnamese war, increasing development and usage of leaded petrol, and then the phasing out of leaded petrol. The decrease in Pb/Ca was 4–7 years later than peak emissions of Pb in this region, possibly due to the upwelling of the Pacific tropical waters in the western SCS. The delayed Pb peak in the coral also implies that the transport time of NPTW into Vietnamese upwelling region is at least 2–5 years. The Pb isotopes in the Vietnam coral showed high linearity on the triple-isotope plot, suggesting that Pb in the coral was a mix between natural Pb and Chinese emitted Pb. The average Chinese Pb contributes to 40–60% of the Pb in the coral in 2000s. This is the first study addressing the century-scale variation of Pb in the South China Sea using both the Pb/Ca and Pb isotopes.

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