Baseline

Tracing the recently increasing anthropogenic Pb inputs into the East China Sea shelf sediments using Pb isotopic analysis

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ABSTRACT

This study examined the Pb content and Pb isotopic composition in a sediment core taken from the East China Sea (ECS) shelf, and it was observed that since 2003 the increasing anthropogenic Pb inputs have impacted as far as the ECS shelf sediments. The ECS shelf sediments were generally characterized with low bulk Pb contents (12.5–15.0 µg/g) and relatively lithogenic Pb isotopic signatures (both HCl-leached and residual fractions). However, elevated Pb records along with lighter Pb isotopic signals have occurred in the post-2003 sediments, as a result of a small but increasing anthropogenic Pb contribution from the heavily human perturbed coastal sediments due to the sharply increasing coal consumption in mainland China since 2003.

Leaded gasoline has been phased out around the world between the 1970s and 2000 including in Japan (Mukai et al., 1993), the United States (Shirahata et al., 1980; Nriagu, 1990), Europe (Dörr et al., 1989; Bollhöfer and Rosman, 2001; Renberg et al., 2002) and China (Duzgoren-Aydin, 2007; Wang et al., 2006; Lee et al., 2007). Lead emission was thus reduced, leading to decreased Pb records in the sediments since 2000. Since then, alternative Pb inputs have gradually dominated in the atmosphere, soils, and sediments including those from the combustion of unleaded gasoline and coal, the emission of lead ores, cement, and painting (e.g., Zhu et al., 2010; Widory et al., 2010). A few researchers have used Pb isotopic signatures to reflect the shift in the origin of Pb in aerosols, seawater, and sediments (e.g., Wu et al., 2010; Gallon et al., 2011).

China has been the largest coal producer and consumer in the world for many years. In particular, a sharp increase of coal consumption has occurred since 2003. Indeed, a large quantity of coal has been imported mainly from Southeast Asia starting in 2003, with a sharp increase from ~300 kt/yr in earlier years to 2600 kt in 2003. The coal consumption was relatively low from 1998 to 2002, as indicated by the ~0.66 billion tons of standard coal equivalent (BTCE) per year, but it experienced a sharp increase starting in 2003: it was raised to as much as 0.84 BTCE in 2003, this doubled to 1.98 in 2008, and then to 2.49 in 2012. Indeed, coal consumption presently accounts for ~70% of the total energy consumption (the sum of coal, crude oil, gas and electric power) in mainland China (data from the National Bureau of Statistics of China, http://www.stats.gov.cn/), and ~50% of the total world coal consumption in 2011 (British Petroleum, 2012).

These recently increasing anthropogenic activities potentially impacted coastal sediments, marginal seas and even remote oceans. Previous reports identify increased anthropogenic Pb signals in the nearby coastal sediments of the Yangtze River (YR) (e.g., Zheng et al., 2004; Chen et al., 2005; Zhang et al., 2008; Hao et al., 2008). Some researchers relate the Pb contamination in remote areas to atmospheric deposition from the heavily polluted areas of China (e.g., Gallon et al., 2011; Ewing et al., 2010). Huh et al. (1999) observe relatively lower Pb contamination in the East China Sea (ECS) shelf in the 1990s. However, there is still little information available regarding the impacts of the recently increasing anthropogenic activities in these marginal seas including the ECS.

The ECS is bounded by mainland China on the west, and connects with the North Pacific via Kyushu Island and the Ryukyu Islands. The ECS including the Yellow Sea is one of the largest marginal seas in the world (0.9×10^{12} m^2 in area, 3% of the world's shelf) (e.g., Chen, 1996). Over the past 60 years, the ECS has received freshwater discharges of approximately 900 km^3/y and a sediment load of approximately 390 Mt/y from the YR (historic data from the Ministry of Water Resources of the People's Republic of China, http://www.mwr.gov.cn/zwzc/hygb/zghlnsgb/). The YR, the fourth longest in the world (6300 km), has recently experienced a reduction in both its freshwater and sediment discharges into the sea. The freshwater discharge decreased from a peak of 1220 km^3/y in 1998 to 688.4 km^3/y in 2006, and as low as 667.2 km^3/y in 2011, and the sediment discharges decreased from a peak of 400 Mt/y in 1998 to 84.8 Mt/y in 2006, and as low as 71.8 Mt/y in 2011. Consequently, an increased proportion of sediments have been eroded from the YR lower reaches over the past decade. On the other hand, the YR Delta, including the

Table 1
Pb and Al contents in the bulk sediments, and Pb isotopic ratios (^{208}Pb$/^{207}$Pb, ^{206}Pb$/^{207}$Pb) in the leachates and residuals of the East China Sea shelf sediments. Note: The ages are estimated based on an average sedimentation rate, with an error of 0.5 year.

Depth (cm)	Age (year)	Pb (µg/g)	Al (mg/g)	Leachates		Residuals	
				^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb
1	2008	13.3	0.342	2.4794	1.1847	2.4908	1.1955
3	2007	14.4	0.358	2.4799	1.1851	2.4898	1.1918
5	2006	14.0	0.355	2.4800	1.1851	2.4854	1.1880
7	2006	13.5	0.329	2.4805	1.1855	2.4910	1.1920
9	2005	13.4	0.319	2.4810	1.1853	2.4855	1.1901
11	2004	13.7	0.340	2.4817	1.1862	2.4918	1.1928
13	2003	14.0	0.361	2.4816	1.1862	2.4979	1.1979
15	2003	13.1	0.339	2.4819	1.1866	2.4903	1.1913
17	2002	12.7	0.329	2.4819	1.1867	2.4838	1.1851
19	2001	13.1	0.296	2.4819	1.1866	2.4844	1.1844
21	2001	12.1	0.295	2.4825	1.1869	2.4890	1.1917
23	2000	13.0	0.278	2.4825	1.1869	2.4878	1.1885
25	1999	12.5	0.274	2.4825	1.1868	2.4789	1.1803
27	1998	12.9	0.282	2.4828	1.1869	2.4939	1.1916

metropolitan city of Shanghai with a population of ~23.71 million in 2012 (data from the Shanghai Municipal Population and Family Planning Commission, http://www.popinfo.gov.cn/spfpen), has become the largest and most developed economic region in China since 1980 (e.g., Hao et al., 2008). However, the aerosols, soils and even sediments nearby were also heavily influenced by the anthropogenic activities there. Our study, for the first time, carefully examined Pb content and isotopic composition in a sediment core taken from the ECS shelf, and explored the historic trend of anthropogenic Pb signals in the marginal sea. We demonstrated that anthropogenic Pb signals in the ECS shelf sediments originated mostly from the "polluted" YR lower reaches especially after 2003.

Our study site (123.58°E, 29.28°N) in the ECS shelf is approximately 70 m deep and 300 km from the mega-city of Shanghai) (Fig. 1). It is also located near a mud belt, as deposited by fluvial materials along with the riverine outflow (e.g., Qin et al., 1987; Jin, 1992; Liu et al., 2006) (Fig. 1). The sediments here are dominated with silt and partly mud, consistent with that noted in previous studies (e.g., Liu et al., 2006; Liu et al., 2007). The sampling area is mainly influenced by the southward cold and brackish Zhejiang-Fujian Coastal Current, and slightly by the northward Taiwan Warm Current (Beardsley et al., 1985). The sediments near the sampling site were generally well preserved due to the high sedimentation rates and lack of bioturbation.

The sediment core was taken in a rectangular box corer with a plastic cylindrical core (7 cm in diameter) in August 2009 via the R/V Dongfanghong-2. The core was then sliced in the plastic cylinder at 2 cm intervals, and each slice was collected in a small plastic bag, and stored in a freezer (−20 °C). Back in the laboratory, the samples were then dried in an oven at 60 °C, homogenized, and stored for analyzing the metal content and Pb isotopic composition. The sedimentation rate was dated in the Institute of Earth Sciences, Academia Sinica, Taipei, using a combination of ^{210}Pb and ^{137}Cs radioisotopic techniques, and had an estimated constant value of 2.8 ± 0.3 cm/y. Similar sedimentation rates are also reported in nearby sediments, e.g., 2.14 cm/y (30.36°N, 122.90°E, Liu et al, 2006); 3.1 cm/y (31.00°N, 122.75°E, DeMaster et al., 1985).

The homogenized dry samples (~0.05 g) for the analysis of the metals of Pb and Al were first dissolved in 1 N HCl for 24 h, and the HCl leached fractions were then obtained (hereafter referred to as leachates). The residuals were further dried and dissolved in concentrated HCl, HNO₃, and a small amount of HF, then heated in a 500 °C oven for 12 h, and finally dried and redissolved in 0.3 N HNO₃ (here referred to as the residual silicate fraction). Our measurements showed that the residual fractions accounted for
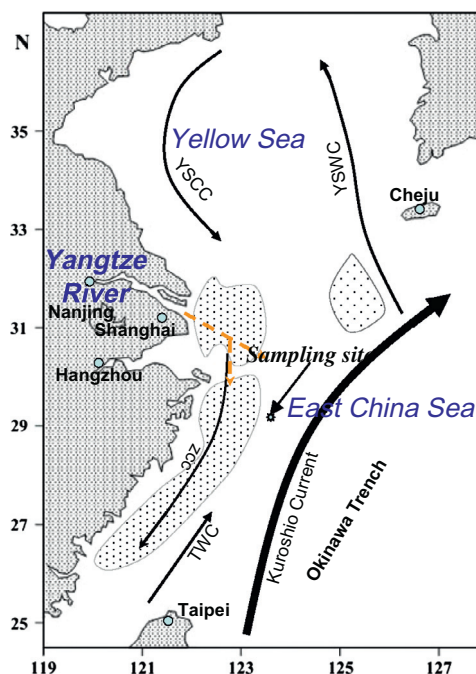

Fig. 1. The sampling site and the general circulation system in the East China Sea and Yellow Sea. Dotted areas represent clay and silt dominated sediments. The large black dot represents the sampling site. ZCC: Zhejiang Coastal Current; TWC: Taiwan Warm Current; YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current; KC: Kuroshio Current.

50 ± 7% of Pb and 95 ± 1% of Al in the bulk sediments. The high Al fractions in the residuals confirmed that the alumino–silicate minerals existed mainly in the residual silicate sediments, consistent with previous reports (e.g., Choi et al., 2007). The leached fraction represents the carbonate and anthropogenic origins (Choi et al., 2007). Here the metal concentrations were measured using ICPMS (Agilent 7500) in Xiamen University via the standard addition method, and the recovery rates of Pb and Al in the NIST reference materials SJ soil were 86% and 92%, respectively. The high-purity acids used in this study were obtained via double distillation (Savillex DST-1000) of ultrapure acids (Merck).

A proportion of solutions (both leachates and residuals) were further processed for Pb isotopic analysis following the method of Reuer et al. (2003). Generally, the samples were dried and

redissolved in 1.1 N HBr. Lead, in $PbBr_4^{2-}$ form, was then separated from the matrixes and purified using Teflon micro-columns loaded with Bio-Rad AG-1X8 (chloride form, 200–400 mesh) anion exchange resin, and finally measured for isotopic composition using multi-collector ICP-MS (high resolution Nu plasma) at Xiamen University and some were also recalibrated at the Institute of Geochemistry, Chinese Academy of Sciences, Guizhou, China. The Pb isotopic measurements were carried out using the Tl doping technique for the mass discrimination correction. All the processes were conducted under a Class-100 hood in a Class-1000 clean room. The measured values for the standard NBS-981 were $^{207}Pb/^{208}Pb = 0.422115 \pm 0.000005$ (2σ, $n = 20$) (certified value = 0.421864) and $^{207}Pb/^{206}Pb = 0.914553 \pm 0.000012$ (2σ, $n = 20$) (certified value = 0.914750). The procedural blank for the bulk samples was less than 5 pg Pb.

All the results are summarized in the Table 1. The sediments in the sampling site were mainly characterized by low bulk Pb and high Al (Pb: 12.5–15.0 µg/g; Pb/Al ratio: 0.27–0.37×10^{-3}, Fig. 2). These Pb records in the ECS shelf sediments were generally lower than those in coastal muddy sediments, e.g., in the YR estuary (31 ± 2 µg/g, Hao et al., 2008), near the YR mouth (40–43 µg/g, Millot et al., 2004), near Shanghai city (35 ± 8.5 µg/g, Choi et al., 2007), in the intertidal zone of the YR estuary (27.3 ± 5.6 µg/g, Zhang et al., 2008; 9–43 µg/g, Bi et al., 2006), and in the coastal muds of the Yellow Sea (40–80 µg/g, Choi et al., 2007).

Our records of Pb concentrations in the sediments also demonstrated two contrasting periods: the pre-2003 period with 12.5–13.7 µg/g of Pb content, and a 0.27–0.30 Pb/Al ratio; and the post-2003 period with 13.8–15.0 µg/g of Pb content, and 0.32–0.36 Pb/Al ratio (Fig. 2). The Pb contents in the deep layers (12.5–13.7 µg/g) were close to those of "pristine" minerals, e.g., the granites near the upper YR (7–12 µg/g, Li et al., 1987), the sediments in the mainstream of the upper YR (Jinshajiang, as low as 5 µg/g Pb, Wu et al., 2008), and the sediments from the upstream of the YR (Tongtianhe, 10.4 µg/g, Wu et al., 2008). On the other hand, slightly elevated Pb contents (13.5–15.0 µg/g) in the post-2003 records reflected the recently increasing anthropogenic Pb impacts, which have resulted from the sharply increasing energy consumption in mainland China since 2003.

The residual fractions in the sediments were characterized with variable Pb isotopic composition ($^{206}Pb/^{207}Pb$: 1.180–1.198; $^{208}Pb/^{207}Pb$: 2.478–2.498, Fig. 4). The large variability in the Pb isotopic signatures in the residuals suggested dynamic lithogenic contributions from the YR upper reaches (Fig. 4). The sediment loads from the YR have decreased by 70% from 400 Mt/y in 1998 to 130 Mt/y in 2008) due to dam and reservoir construction, and particularly the completion of the Three Gorges Dam in 2003 (Yang

et al., 2006). These land use changes in the watershed clearly decrease the lithogenic loads from the upper YR basins, but increase erosion from the YR lower reaches (Dai et al., 2011; Chen et al., 2010) and even the Yellow Sea due to oceanic currents nearby such as the Taiwan Warm Current and the Kuroshio Current. The consistent pattern of residual Pb isotopic signatures with sediment loads from the YR suggested that the Pb isotopic signatures in the residual fractions might serve as a good indicator reflecting the dynamics of sediment discharges from the upper YR reaches.

The Pb isotopic signatures in the leachates demonstrated a stable but slightly decreasing trend of $^{206}Pb/^{207}Pb$ (1.1870–1.1845) and $^{208}Pb/^{207}Pb$ (2.4830–2.4790) with increasing time (Fig. 3). The decreasing pattern of Pb isotopic signatures (increasing radiogenic Pb) with time (Fig. 3) reflected the recently increasing anthropogenic Pb inputs due to the increasing energy consumption. The Pb isotopic signatures in leachates of the pre-2003 deep sediments (15–30 cm) ($^{206}Pb/^{207}Pb$: ~1.187; $^{208}Pb/^{207}Pb$: ~2.482) were similar to those less perturbed sediments or minerals, e.g., the granites in the eastern Cathaysia ($^{206}Pb/^{207}Pb$: 1.183, Zhu et al., 2001), and the Manila Trench sediments and Luzon volcanic Arc ($^{206}Pb/^{207}Pb$: 1.184; $^{208}/^{207}Pb$: 2.480, McDermott et al., 1993). Thus, the pre-2003 deep sediments in the ECS shelf might represent the lithogenic or less anthropogenically perturbed background for Pb.

The leachates of the top sediments (depth 0–15 cm) after 2003 were characterized with increasing anthropogenic Pb signatures ($^{206}Pb/^{207}Pb$: 1.1860–1.1845; $^{208}Pb/^{207}Pb$: 2.482–2.479), which were similar to those in the "polluted" muddy sediments of the YR lower reaches, e.g., the YR estuary ($^{206}Pb/^{207}Pb$: ~1.185, Millot et al., 2004), the YR mouth ($^{206}Pb/^{207}Pb$: 1.185–1.187, $^{208}Pb/^{207}Pb$: 2.480–2.482, Chow et al., 1975), and the YR estuary intertidal zone ($^{206}Pb/^{207}Pb$: 1.186, Zhang et al., 2008). The Pb isotopic signatures in either these leachates of the ECS sediments or the coastal sediments of the YR lower reaches lay between the anthropogenic (coal and unleaded gasoline) and natural lithogenic (e.g., Chinese loess) end members (Fig. 5), suggesting of a mixing of anthropogenic and natural lithogenic origins.

Natural soils in China (e.g., loess) are generally characterized with high Pb isotopic ratios (e.g., bulk $^{206}Pb/^{207}Pb$: 1.211; $^{208}/^{207}Pb$: ~2.501, Jones et al., 2000; Pettke et al., 2000; Godfrey, 2002). Anthropogenic inputs in Asia/China are generally characterized with more radiogenic signals before 2000 as influenced by leaded petroleum (e.g., Bollhöfer and Rossmen, 2001), but less radiogenic signals after 2000 (e.g., Zhu et al., 2010) (Fig. 5), probably due to the fact that Pb sources have shifted from the burning of leaded gasoline to the burning of coal or unleaded gasoline. Using a simple mixing model (e.g., Shirahata et al., 1980), we modeled the
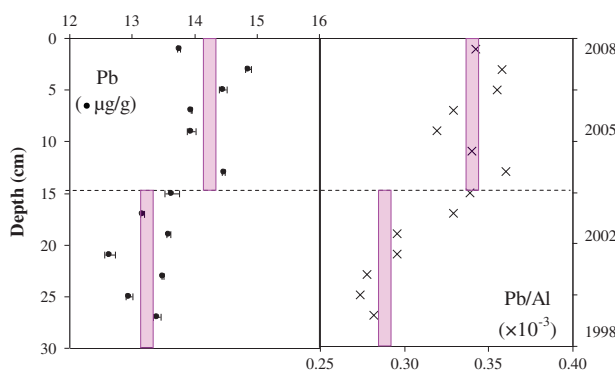

Fig. 2. The downcore profiles of the bulk Pb contents (solid circles, error bars refer to SD, $n = 2$) and the Pb/Al ratios ($\times 10^{-3}$, crosses) in the East China Sea shelf sediments.
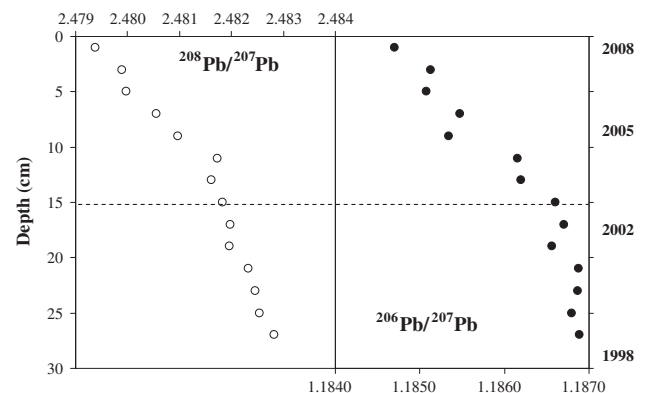

Fig. 3. The downcore profiles of leachate $^{206}Pb/^{207}Pb$ (solid circles) and $^{208}Pb/^{206}Pb$ (open circles) in the East China Sea shelf sediments.

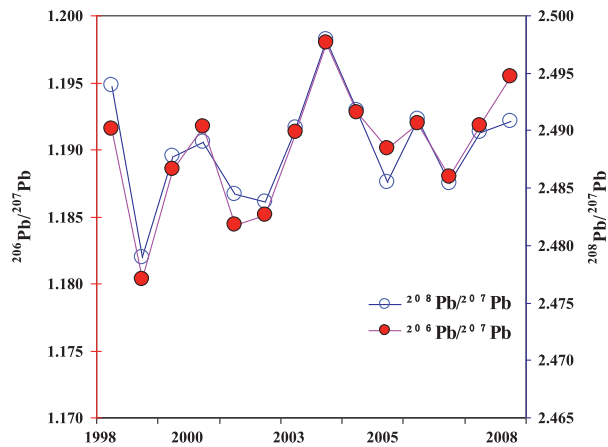**Fig. 4.** Variations of residual $^{206}Pb/^{207}Pb$ (solid circles) and $^{208}Pb/^{206}Pb$ (open circles) with increasing time in the East China Sea shelf sediments.
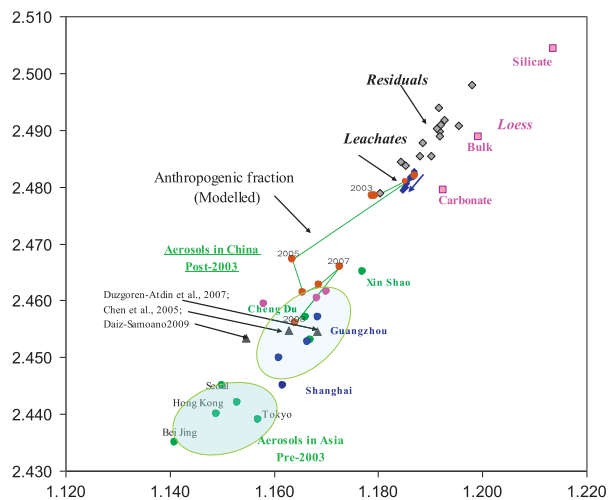

Fig. 5. The plot of $^{208}Pb/^{207}Pb$ vs $^{206}Pb/^{207}Pb$ in the leachates, residuals and modeled anthropogenic fractions in the East China Sea shelf sediments (this study), and in different sources: pre-2003 and post-2003 aerosols, coastal sediments, and coal in China (references therein).

anthropogenic Pb isotopic composition in the top sediments (depth 1–9 cm) based on the leachated Pb, and here the baseline $^{206}Pb/^{207}Pb$ ratio was assumed to have a value of 1.187 in the deep sediments:

$$R_{anthr} = \frac{R_{leachate} - R_{baseline} \times (1-f)}{f}$$

The anthropogenic Pb fraction (f) was estimated using a mixing model as follows:

$$f = (C_{total} - C_{baseline})/C_{total}$$

R denotes the isotopic ratios of Pb in the total leachates, the baseline and current anthropogenic fractions. Thus, the anthropogenic Pb signatures ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) in the top sediments (depth 1–9 cm) could roughly be calculated as 1.164–1.173, and 2.456–2.4673. These Pb signatures were very similar to those aerosols in Asia taken after 2003, e.g., in Guangzhou (1.1684, and 2.4571, Lee et al., 2007), and in Shanghai (1.1617, 2.4450, Chen et al., 2005). Such similarity reflected the fact that the Pb contamination in coastal sediments after 2003, and even marginal seas, originated mainly from the Pb emissions resulting from coal burning in China after 2003.

Some researchers show that Asian aerosols before 2000 (Beijing, Hong Kong, Seoul, and Tokyo, Bollhöfer and Rossmen, 2001) are influenced by leaded gasoline (Fig. 5). China has used alkyl–lead additives supplied by associated Octel (U.K.) in the past (e.g., Cheng and Hu, 2010), and these Pb additives were manufactured from the Pb source ore from Broken Hill, Australia ($^{206}Pb/^{207}Pb$: 1.03–1.10, e.g., Doe, 1970; Cumming and Richards, 1975). By examining Asian aerosols before 2000 (Beijing, Hong Kong, Seoul, and Tokyo, Bollhöfer and Rossmen, 2001), the researchers show similar Pb isotopic signatures in these aerosols to those influenced by leaded gasoline (Fig. 5). Our results demonstrated that the anthropogenic Pb isotopic signatures in the post-2003 records were clearly different from those in either Pb ores or Asian urban aerosols before 2000, e.g., ores in Mexico and Peru ($^{208}/^{207}Pb$: 2.49, Chow et al., 1975), the United States (Mississippi Valley: $^{206}Pb/^{207}Pb$: 1.281–1.396; $^{208}/^{207}Pb$: 2.510–2.612, Doe, 1970), and Australia and Canada ($^{206}Pb/^{207}Pb$: 1.05; $^{208}/^{207}Pb$: 2.33, Doe, 1970; Cumming and Richards, 1975). In addition, these calculated anthropogenic Pb isotopic signatures in the post-2003 records were far away from local Pb sources taken before 2003 in the YR Delta (Fig. 5), e.g., in Shanghai, the coal used ($^{206}Pb/^{207}Pb$: 1.1628; $^{208}Pb/^{207}Pb$: 2.4548, Chen et al., 2005); the coal combustion dust and fly ash produced ($^{206}Pb/^{207}Pb$: 1.1669–1.1655, Chen et al., 2005); the top soils around industrial boilers ($^{206}Pb/^{207}Pb$: 1.170-1.164, Zheng et al., 2004); the metallurgic dust ($^{206}Pb/^{207}Pb$: 1.151–1.180; Chen et al., 2005); and aerosols ($^{206}Pb/^{207}Pb$: 1.1617; $^{208}Pb/^{207}Pb$: 2.4454, Chen et al., 2005). Such differences further emphasized the contribution of leaded petroleum, or those local sources near the mega-city of Shanghai as major Pb contributors to China's coastal sediments or marginal seas.

Summarily, our results clearly demonstrated the shift of anthropogenic Pb from leaded gasoline to coal consumption which occurred around 2003. Along with the complete phasing out of leaded gasoline in Asia in 2000, the anthropogenic Pb sources have shifted to the combustion of coal (and unleaded gasoline) especially after 2003. The recently increasing anthropogenic activities in mainland China after 2003 (mainly as coal consumption) have not only impacted urban aerosols and the coastal sediments in China, but also marginal seas including the ECS.

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