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Historical record of heavy metal pollution deduced by lead isotope ratios in core sediments from the Osaka Bay, Japan

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Abstract

Three marine sediment cores from Osaka Bay were analyzed for \textsuperscript{210}Pb geochronology, heavy metal concentrations (Zn, Cu, and Pb) and stable lead isotope ratios (\textsuperscript{206}Pb/\textsuperscript{207}Pb) in order to reconstruct high-resolution heavy metal pollution history from 1900-2006. Anthropogenic metal accumulation in sediments peaked in 1970 in agreement with the high economic growth period in Japan. The comparison of temporal patterns of \textsuperscript{206}Pb/\textsuperscript{207}Pb ratio with other areas of Japan suggested that the heavy metals, imported from several different countries during the periods of economic growth (1955 to 1973), are the main pollution source for the country. For the period 1970-2006, the sediment data reflect the result of stricter environmental regulations applied after the late 1960s. However, heavy metal concentrations in the surface sediments are still elevated to levels several times higher than the levels at the bottoms of the cores. Additionally, the lead isotope ratio does not show significant change after the 1980s. Secondary heavy metal pollution through the mixing of deeper polluted sediment appears to be the likely reason for the deterioration of present time submarine sediment environments. In conclusion, this study has demonstrated that it is difficult to recover over a period of several years the water quality of a bay, once it is heavily polluted.

Keywords: Pollution; Osaka Bay; \textsuperscript{210}Pb dating; Heavy metal; Lead isotope ratio
1. Introduction

Deterioration of the aquatic environment has become a worldwide concern during the last century. Enclosed shallow marine ecosystems in particular have been subjected to significant environmental pollution from increased metropolitan and industrial development. The major sources of pollution include domestic wastewaters, urban runoff, and industrial and agricultural effluents. As a result of these environmental changes, coastal marine environments have deteriorated greatly. To enable better planning of conservation and management of marine environments, the current status and history of pollution needs to be assessed. Once heavy metals are released into shallow marine environments, they are removed from the water column by interacting with suspended particles, and are subsequently deposited as bottom sediments (Callender, 2005). Since heavy metals deposited in sediments are not biodegradable over time, metal profiles of sediment cores, in combination with $^{210}$Pb dating techniques, can be used as records of pollution events (Hung and Hsu, 2004; Lima et al., 2005; Church et al., 2006; Mil-Homens et al., 2006; Cantwell et al., 2007; Ip et al., 2007; Irabien et al., 2008).

Anthropogenic heavy metals could be present in several portions of marine sediments, for example as secondary minerals, or in ion-exchangeable sites of clay and organic fractions. Selective chemical leaching techniques have been used to determine heavy metal partitioning (Callender, 2005). For example, extraction by 0.1 M HCl leaches metals from ion-exchangeable sites on clay, carbonates, and the organic fraction (Kitano et al., 1980). Heavy metals in this fraction are the most readily detachable from the sediments and therefore constitute hazardous wastes that produce an adverse impact on aquatic ecosystems. In addition, 1 M HNO$_3$ + 1.75 M HCl digestion can leach the majority of anthropogenic heavy metals without leaching the metals contained in the original silicates (Graney et al., 1995). This technique has been widely used to reconstruct metal pollution histories (Graney et al., 1995; Lima et al., 2005).

The stable lead isotope ratios (i.e., $^{206}$Pb/$^{207}$Pb) of anthropogenic Pb commonly have different compositions to natural background Pb. This property has recently been used as a powerful tool for judging the presence of anthropogenic Pb in marine sediments (Hung and Hsu, 2004; Ip et al., 2004, 2007; Tang et al., 2008; Komárek et al., 2008). Anthropogenic Pb is commonly sourced from sulphide ore minerals or coals, and is released into the environment as a byproduct of industrial Pb use and through the combustion of fuels and leaded gasoline. Time-dependent changes in lead isotope ratios in sediment profiles sometimes represent transitions in the import sources of ore minerals and coals used for human activities (Hirao et al., 1986; Gallon et al., 2005; Lima et al., 2005). This analysis is also important in assessing if the polluted sediment is able to act as a secondary source of pollution.

In Japan, heavy metal pollution in metropolitan bay areas was targeted in a number of research
projects during the 1970s to 1980s to assess the environmental impact during the period of high economic growth in Japan (1955 to 1973) (Kitano et al., 1980; Hirao et al., 1986; Hoshika et al., 1991; Yasuhara and Yamazaki, 2005). Importantly, these studies have clearly demonstrated that metal pollution in Japanese metropolitan (i.e., Tokyo and Osaka) bays peaked around 1970 and has declined since then. However, there is hardly any data on historical changes in stable lead isotope ratios and metal partitioning characteristics, just few studies at Tokyo Bay, carried out approximately 30 years ago (Kitano et al., 1980; Hirao et al., 1986). The aim of this study was to reconstruct the high-resolution heavy metal (Zn, Cu and Pb) pollution history of Osaka Bay from 1900-2006 on the basis of selective chemical leaching and stable lead isotope techniques. This study also provides important information on the current heavy metal pollution status in Osaka Bay.

2. Study area

Osaka Bay is located on the eastern part of the Seto Inland Sea in central Japan (Fig. 1) with a seawater volume of 41 km³, area of 1,450 km², average depth of 28 m, and maximum depth of 197 m. The bay is semi-enclosed by Awaji Island and is connected to the Pacific Ocean through the Kitan Channel (Fig. 1). The Osaka plain area including Osaka and Kobe Cities is one of the economic and industrial centres of Japan, with a population of around 16 million. The Yodo, Yamato and Muko Rivers are the main inflowing rivers with a total estimated flow of 13.1 km³ yr⁻¹. Of these, the Yodo River is the major source of fresh water into the bay with its estimated flow of 5.14 km³ yr⁻¹, watershed area of 8,240 km², and watershed population of around 11.2 million. A large volume of sewage and industrial wastewater flows into the bay through these rivers.

The depth of the sea water in Osaka Bay increases toward the southwest (Fig. 1). The seawater in the deeper (> 20 m) southwest side of the bay is relatively well mixed due to the strong tidal current through the channels. In contrast, seawater in the shallower (< 20 m) northeast side is rather stagnant. The sea bottom of the inner part of the bay is covered by homogenous fine-grained silt and clay size sediments and contains relatively higher concentrations of organic and inorganic heavy metals than the southwest side of the bay (Sue et al., 1983; Yamada et al., 2006). Accumulation rates of the bottom sediments as determined by ²¹⁰Pb and ¹³⁷Cs chronologies (Matsumoto and Yokota, 1978; Yasuhara and Yamazaki, 2005) displayed wide variation from 0.12 cm yr⁻¹ to 0.61 cm yr⁻¹ all over the bay areas with an average rate of 0.38 cm yr⁻¹ (n = 6). Bulk chemical analysis of some sediment cores has shown that the highest metal concentrations are typically observed in fractions dating from the 1960s-1970s (Hoshika et al., 1991; Yasuhara and Yamazaki, 2005).

3. Methods
3.1. Sediment core sampling

Three sediment cores (OS1, OS2 and OS3) were collected by professional divers from the northeast side of Osaka Bay (Fig. 1) on August 25, 2006. An acrylic core sampler 80 cm in length and 5 cm in diameter was used for the sampling, and about 60 cm sediment profiles were obtained for each site. Each collected core was sectioned at 1 cm intervals. All of the samples were stored in plastic cases, kept on dry ice, and then transported back to the laboratory where they were stored in a freezer room at -30°C. In the laboratory, the frozen sediments were freeze-dried and measured for water contents. Sediment fragments bigger than 1 mm were carefully removed by hand picking. The sizes of the particles in the core samples were analyzed by using a laser diffraction particle analyzer (Beckman Coulter, LS13 320). For heavy metal concentration and isotope analyses, all samples were pulverized in a tungsten carbide vessel using a Herzog HP-MS.

3.2. Sediment dating

The chronology of the sediment cores was determined by the $^{210}\text{Pb}$ method. $^{210}\text{Pb}$ (via $^{210}\text{Po}$) was measured by $\alpha$-spectrometry. $^{209}\text{Po}$ standard obtained from ORNL (Oak Ridge National Laboratory) was added as a yield determinant prior to total digestion of the samples. The $^{209}\text{Po}$ spike was calibrated versus NIST-certified $^{208}\text{Po}$ (SRM-4327). Polonium isotopes were plated onto a silver disc from the sample solution (in 1.5 M HCl, in the presence of ascorbic acid) at 80-90°C for ~1 hour. The counting results were corrected for the decay of $^{210}\text{Po}$ (from the time of plating to counting) and $^{210}\text{Pb}$ (from sample collection to Po plating). The excess $^{210}\text{Pb}$ ($^{210}\text{Pb}_{\text{ex}}$) activity was derived by subtracting the supported $^{210}\text{Pb}$ activity which derived from the near-uniform $^{210}\text{Pb}$ activities at the core bottom. In this study, sedimentation rates were determined by using an advection-diffusion model with the common assumption that fluxes of sediment and the associated $^{210}\text{Pb}$ are reasonably constant on decadal to centennial timescales at a given site (Berger and Heath, 1968; Appleby and Oldfield, 1992; Huh and Su, 1999; Carroll and Lerche, 2003). This method is basically the same as Appleby and Oldfield’s “simple model CF:CS” (Appleby and Oldfield, 1992). Thus, from the trend of the decrease of excess $^{210}\text{Pb}$ with depth in the cores, sedimentation rates can be estimated (Huh and Su, 1999). Since the mixing process was assumed to be negligible, the results of the $^{210}\text{Pb}$-based sedimentation rate should be considered as “apparent” or maximum values.

3.3. Analysis of Zn, Cu, and Pb concentrations

Two kinds of acid solutions were used for heavy metal leaching in the sediments: (1) 0.1 M HCl solution (Kitano et al., 1980) and (2) 1 M HNO$_3$ + 1.75 M HCl solution (Graney et al., 1995). For 0.1 M HCl acid leaching, 0.3 g portions of dried sediment sample were weighed into 5 mL
polypropylene tubes and 3 mL of 0.1 M HCl solution was added. The acid sediment mixtures were homogenized with a vortex mixer for 1 hour, placed in an ultrasonic bath for 30 min, and allowed to react for 12 hours. Subsequently, the leachates were separated by centrifugation. Separated leachates were then moved into Teflon beakers and heated on a hot plate at 100°C until the leachate solutions were completely dry. Finally, dried samples were diluted with 1% high purity nitric acid solution for concentration analysis. This fraction was expected to include heavy metals in the sediment which were leached from ion exchangeable sites of clay minerals, carbonates, small particles of secondary sulphide minerals, and parts of organic compounds (Kitano et al., 1980). The 1 M HNO₃ + 1.75 M HCl acid leaching was performed in the same way as above, and this fraction was expected to include heavy metals from almost all extractable components in the sediments except silicate minerals. This method has been widely used in reconstructing metal pollution histories (Graney et al., 1995; Lima et al., 2005). Heavy metal (Zn, Cu and Pb) concentrations in the solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin-Elmer ELAN 6100DRCII) at the Centre for Advanced Marine Core Research, Kochi University, using indium as an internal standard. Each element was calibrated with mixed standard solutions prepared from commercial 1,000 ppm solutions (CertiPUR®, Merk Tokyo, Japan). Analytical precision for the instrument was better than 2%, and replicate analysis of one of the samples (OS2 depth = 10-11 cm) yield a 5% precision (2σ, n = 22).

3.4. Lead isotope analysis

Stable lead isotope ratios ($^{206}$Pb/$^{207}$Pb) were measured by ICP-MS (Perkin-Elmer ELAN 6100DRCII) using the same solutions used for heavy metal concentration analysis, following the analytical conditions described by Gallon et al. (2005). Briefly, the nebulization rate was set to 1.2 mL min⁻¹ and the signal intensities were measured 400 times over $4 \times 10^{-2}$ s for $^{206}$Pb and $3 \times 10^{-2}$ s for $^{207}$Pb. This procedure was repeated 5 times. An international standard reference material (SRM 981 Common Pb Isotope Standard, National Institute of Standards and Technology) was measured after every three samples for calibration and quality checking. The relative standard deviation (SRD) was better than 0.5% for $^{206}$Pb/$^{207}$Pb ($2\sigma$, n = 30). Mean $^{206}$Pb/$^{207}$Pb values were normalized to certified standard values of $^{206}$Pb/$^{207}$Pb = 1.0933.

4. Results and discussion

4.1. Age dating

The supported $^{210}$Pb activities, the near-uniform $^{210}$Pb activities at the core bottom were 1.32±
0.02 dpm g$^{-1}$ for OS1 and OS2 and 1.12±0.02 dpm g$^{-1}$ for OS3, respectively (Fig. 2). Then the excess $^{210}$Pb ($^{210}$Pb$_{ex}$) activity was derived by subtracting these values from the total $^{210}$Pb as shown in Fig. 2. The $^{210}$Pb$_{ex}$ activity in the upper parts of the sediment column shows a well-mixed layer with constant $^{210}$Pb$_{ex}$ activity in all three cores. The mixing depths in the three cores are 24 cm (OS1), 4 cm (OS2) and 16 cm (OS3), respectively. Below the mixing layer, the profiles of $^{210}$Pb$_{ex}$ show a simple exponential decrease throughout the cores. The cores OS2 and OS3 show reduced $^{210}$Pb$_{ex}$ gradients in the upper sections of the cores. The best estimates of sedimentation rates for these cores are 0.21 cm yr$^{-1}$ (OS1), 1.27 and 0.17 cm yr$^{-1}$ (OS2), and 0.37 and 0.16 cm yr$^{-1}$ (OS3) (Fig. 2). The sedimentation rate based on the lower section of the OS2 profiles is close to the OS1 and OS3 average sedimentation rates, suggesting that the upper part of OS2 may be influenced by the sediment mixing process more intensively than OS1 and OS3. Hence, the sedimentation rates calculated from $^{210}$Pb$_{ex}$ profiles should be conservatively taken as the upper limits. For core OS3, the $^{210}$Pb$_{ex}$ profile shows an abruptly low sedimentation rate at depths of 28-30 cm, which probably implies that an erosion event occurred at the coring site.

The $^{210}$Pb$_{ex}$ inventories were also calculated for the three cores and compared with results from a previous study (Yasuhara and Yamazaki, 2005) in Osaka Bay. The calculated results show that the inventories tend to decrease from the offshore site (OS1; 79.1 dpm cm$^{-2}$) to the coastal site (OS3; 46.78; dpm cm$^{-2}$) (Fig. 2). The $^{210}$Pb$_{ex}$ inventory of OS2 (59.28 dpm cm$^{-2}$) is in agreement with the results obtained by Yasuhara and Yamazaki (2005) at Osaka Bay (56.88 dpm/cm$^2$), and for OS3 the value is just slightly higher than that of the atmospheric input (Osaka: 39.25 dpm cm$^2$; Tokyo: 43.11 dpm cm$^2$; Tsunogai et al., 1985). From a practical point of view, significant deviation in the $^{210}$Pb$_{ex}$ inventory between cores in such a small area should be taken to be the result of sediment redistribution. Thus, the lower inventory of $^{210}$Pb$_{ex}$ at OS3 agrees well with the erosion event conjectured by the $^{210}$Pb$_{ex}$ profile. The estimated sedimentation age was extrapolated in the metal profile for each core (Fig. 3).

4.2. Heavy metal profile for sediment cores

The sediments displayed certain variations in grain size in the overall samples (Fig. 3). In general, the core sediments consisted mainly of silt (69-79%) and clay (14-28%) sized particles and small amounts of sand grains (2-14%). It is sometimes observed that high concentrations of trace metals are associated with smaller particles in sediments (Daskalakis and O’Connor, 1995). However, the sediment cores in the current study do not show any clear vertical changes in grain size (Fig. 3). In Osaka Bay sediments, therefore, there is no clear relationship between the grain size and high concentrations of Zn, Cu and Pb (Fig. 3). Factors other than grain size, i.e., pollution input, are responsible for the increases in heavy metal concentrations in the sediments.
The concentration profiles of Zn, Cu and Pb for the three sediments cores (OS1, OS2 and OS3) (Fig. 3) show significant temporal changes, indicating a changing heavy metal input into Osaka Bay during the last century. These concentration patterns for the three cores are basically the same for all the elements (Zn, Cu and Pb) and for both leaching methods (0.1 M HCl solution and 1 M HNO₃ + 1.75 M HCl solution). The Cu concentration in the OS1 core sample is an exception, it shows a somewhat scattered pattern. Elevated Zn, Cu and Pb concentrations are observed after the 1900s and a significant peak in heavy metal contents is found around 1970 (Fig. 3). For example, Zn, Cu and Pb concentrations in 1 M HNO₃ + 1.75 M HCl leaching solutions from the 1970 portion of the OS2 core (254, 34 and 48 ppm, respectively) are 6.2, 3.1 and 2.3 times greater than those from the portion predating the 1900s. These temporal increases in heavy metal concentrations suggest an increase in pollution input into the bay through industrial emissions and other sources.

A constant decline in the heavy metal contents is observed after 1970 until the present time (Fig. 3). As is well known, Japan faced heavy industrial pollution during the period of high economic growth (1955 to 1973) and pollution became a serious social problem. The observed decline in heavy metal concentrations reflects the results of environmental regulation by the Japanese government enforced after the late 1960s. All of the above features regarding the temporal heavy metal distributions in Osaka Bay correspond well with the previous study carried out in the same coastal area (Yasuhara and Yamazaki, 2005) and also with situations recognized in other areas of the Japanese metropolitan bay (Matsumoto, 1983; Hirao et al., 1986; Hoshika et al., 1991). This clearly indicated that temporal trend of heavy metal accumulation during 20th century is similar over Japanese metropolitan bays and confirmed that our age calculation is satisfactory.

By the year 2006, the Zn, Cu and Pb concentrations, for example, of the 1 M HNO₃ + 1.75 M HCl acid leaching solutions for OS2 core sediments had declined to 189, 30 and 37 ppm, respectively (Fig. 3). These values are clearly lower than the peak values in 1970; however, they are still 4.6, 2.5 and 1.8 times greater than the baseline values. The increases in Zn, Cu and Pb concentrations from 1900-1970 in the core OS2 were calculated to be 3, 0.4 and 0.4 ppm per year. In contrast, the decrease from 1970-2006 was 1.8, 0.2, and 0.3 ppm per year, respectively, for each element. The heavy metal contents at the surface mixing layer are lower than those of the sediments in 2006, but are still significantly higher than those of the baseline values (Fig. 3). Mixing of the deeper polluted sediments (4 to 24 cm depths from the surface) with superficial less-highly polluted sediments can not be neglected as a possible cause of the decline in the rate of attenuation of marine sediment pollution.

4.3. Partitioning of heavy metals in the sediments

A linear relationship was observed between the two different acid leaching solutions for Zn, Cu
and Pb concentrations (Fig. 4). The correlation coefficient was 0.96 for both Zn and Pb. A good correlation was also found for Cu, if a few sample plots which obviously deviated from the major trend were excluded. From the linearity in Fig. 4, the stronger acid solution fraction (1 M HNO₃ + 1.75 M HCl) was calculated to contain 2.1, 3.3 and 2.9 times the heavy metal (Zn, Cu and Pb) concentrations of the weaker acid solution (0.1 M HCl). The bulk analysis of core sediments collected near site OS3 (Fig. 1 for sample location) by Yasuhara and Yamazaki (2005) yielded maximum net increases in heavy metal concentrations from 1904-1962 of 444, 50 and 60 ppm for Zn, Cu and Pb, respectively. Compared with this, the maximum Zn, Cu and Pb concentrations in the stronger and weaker acid solution fractions for core OS3 in 1970 were 413, 51 and 71 ppm and 186, 14 and 23 ppm, respectively. Our results suggest that a large proportion of anthropogenic heavy metals are present in the sediment as exchangeable components other than in silicate minerals. Substantial amounts of heavy metals could also be present in weakly attached forms at the sediment surface, implying a harmful influence to the ecosystem in the marine bottom environment.

4.4. Lead isotope composition of Osaka Bay sediments

The stable lead isotope ratio of ⁰⁶Pb/²⁰⁷Pb for collected core sediments ranges between 1.147 and 1.194. This isotopic variation suggests the contribution of anthropogenic Pb derived from Pb ores which commonly have different lead isotope ratios from those of background geological materials (Ng and Patterson, 1982; Croudace and Cundy, 1995; Farmer et al., 1996; Kober et al., 1999; Eades et al., 2002). The ⁰⁶Pb/²⁰⁷Pb ratio profiles (Fig. 3) display similar configurations between two different acid leaching solutions (0.1 M HCl solution and 1 M HNO₃ + 1.75 M HCl solution). Among the three sediment cores, OS2 shows the most distinct ⁰⁶Pb/²⁰⁷Pb compositional pattern, although the other two cores (OS1 and OS3) follow a similar pattern.

The most notable temporal change in stable lead isotope ratios for the Osaka sediment cores is a drastic decrease in the ⁰⁶Pb/²⁰⁷Pb ratio from 1900-1950 from ca. 1.18 to ca. 1.16, and a subsequent increase in the ratio until the 1980s (Fig. 3). The ⁰⁶Pb/²⁰⁷Pb compositions of sediments before 1900 were rather constant around 1.18. Prior to 1900, the majority of Pb in the sediment must have been transported through erosion of the watershed geology or the use of domestic ore Pb in which the ⁰⁶Pb/²⁰⁷Pb ratios were typically within a range from 1.176 to 1.190 (Mabuchi and Hirao, 1982). Decreased lead isotope ratios after 1900 were confirmed in a sediment core collected at Tokyo Bay (Hirao et al., 1986) (Fig. 5). Hirao et al. (1986) concluded that the steep decline in ⁰⁶Pb/²⁰⁷Pb ratios after 1900 reflected the use of imported Pb ores in addition to domestic Pb ores, i.e. Australian ore deposits, which typically have low ²⁰⁶Pb/²⁰⁷Pb values around 1.05 (Russell and Farquhar, 1960). Monastra et al. (2004) estimated the average decadal isotopic signature of industrial Pb used in Japan during the 20th century, and showed ⁰⁶Pb/²⁰⁷Pb values of industrially used Pb during 1900-1940 to
be around 1.077 to 1.127. It is therefore clear that the decline in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios observed in Osaka sediments during 1900-1950 is attributed to the pollution derived from industrial activities. A similar decline in $^{206}\text{Pb}/^{207}\text{Pb}$ after 1900 was discovered in a coral growth ring collected from the Ogasawara Islands, located about 1,000 km southeast of Japan (Inoue and Tanimizu, 2008) (Fig. 5). This isotope decline after 1900 should be a common feature in and around Japan.

The timing of the end of the decrease and the start of the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that is found in the Osaka sediment cores during 1940-1960 seems a little later than that observed at Tokyo Bay, around 1930 (Fig. 5). There is no clear evidence to explain this gap and further analyses with detailed economic data are needed to solve this problem. However, elevated $^{206}\text{Pb}/^{207}\text{Pb}$ values of industrially used Pb sources during 1940-1970 (av. 1.170; Monastra et al., 2004) showed good agreement with observed $^{206}\text{Pb}/^{207}\text{Pb}$ trend of the core sediments during 1940-1960 (Fig. 5). The high-resolution Osaka data assume that the drastic change in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio around 1940-1960 reflects the fundamental change in the import source of Pb ore after WWII.

The increases in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios during the 1960-1980 suggest a contribution by anthropogenic Pb, which is a mixture of various Pb ores from different countries, imported during the period of high economic growth in Japan (1955 to 1973). Estimated $^{206}\text{Pb}/^{207}\text{Pb}$ values of industrially used Pb sources during 1940-1980 (1.158-1.170; Monastra et al., 2004) correspond well with the observed values in our core sediments (Fig. 5), clearly supporting the above idea. After the 1980s, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the sediments decreased slightly or stayed reasonably constant until the present. The stable lead isotope ratios in the sediments at the surface mixing layer (ca. 1.165) are identical to those of the sediment in 2006. This fact together with low recovery rates of heavy metal pollution suggest the occurrence of mixing of deeper polluted sediments with less polluted surface sediments.

5. Conclusions

The high-resolution analysis of $^{210}\text{Pb}$ chronology, heavy metal concentrations (Zn, Cu and Pb), and stable lead isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) successfully reconstructed the heavy metal pollution history in Osaka Bay. Our results confirmed that the heavy metal pollution peaked in 1970, during the period of high economic growth in Japan. The lead isotope data indicates the changing sources from which ore minerals were imported during 1940-1960. These imported ores were used to support Japanese industrial activities after WWII. A decline in heavy metal pollution was found after the 1970s until 2006, due to environmental regulation enforced by the Japanese government after the late 1960s. However, the heavy metal contents in the sediments have not yet returned to their original levels. The mixing with deeper polluted sediments might cause secondary heavy metal pollution in the surface sediments. Heavy metal pollution of the bottom sediments in Osaka Bay is
still an important subject of concern for environmental preservation and protection.

Acknowledgments

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**Figure Caption**

Fig. 1: Map showing sampling sites of sediments cores and delineation of the Osaka Bay area. The star indicates the sampling site of the sediment core collected by Yasuhara and Yamazaki (2005).

Fig. 2: Profiles of $^{210}$Pb$_{ex}$ activities for cores (a) OS1, (b) OS2 and (c) OS3, including their inventories and sedimentation rates. The sedimentation rates were derived from the linear relationship between depth and $^{210}$Pb$_{ex}$ activities (on a log scale) of the cores.

Fig. 3: Temporal distributions of Zn, Cu and Pb concentrations and $^{206}$Pb/$^{207}$Pb ratios for two different leaching solutions (0.1 M HCl solution and 1 M HNO$_3$ + 1.75 M HCl solution) of the core sediments. Proportions (%) of clay and silt size particles and water content data are also shown.

Fig. 4: Relationship between two different acid leaching solutions for (a) Zn, (b) Cu and (c) Pb concentrations.

Fig. 5: Temporal changes in $^{206}$Pb/$^{207}$Pb ratios for OS2 core sediments. Data for the two different leaching solutions were plotted together. Data from Tokyo Bay core sediments (Hirano et al., 1986) and Ogasawara coral samples (Inoue and Tanimizu, 2008) are shown for comparison.
Fig. 2

(a) OS1

supported $^{210}\text{Pb}$ = 1.32 ± 0.02 dpm g$^{-1}$

mixing layer

0.21 cm yr$^{-1}$

inventory = 79.1 dpm cm$^{-2}$

(b) OS2

supported $^{210}\text{Pb}$ = 1.32 ± 0.02 dpm g$^{-1}$

mixing layer

1.27 cm yr$^{-1}$

0.17 cm yr$^{-1}$

inventory = 59.28 dpm cm$^{-2}$

(c) OS3

supported $^{210}\text{Pb}$ = 1.12 ± 0.02 dpm g$^{-1}$

sedimentation interrupted

0.37 cm yr$^{-1}$

0.16 cm yr$^{-1}$

inventory = 46.87 dpm cm$^{-2}$

mixing layer

total $^{210}\text{Pb}$

excess $^{210}\text{Pb}$
Fig. 4

(a) Zn (ppm)

(b) Cu (ppm)

(c) Pb (ppm)
Fig. 5

- Osaka Bay sediments (OS2; this study)
- Tokyo Bay sediments (Hirano et al., 1986)
- Ogasawara coral (Inoue and Tanimizu, 2008)