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## Baseline

# Source identification of heavy metal contamination using metal association and Pb isotopes in Ulsan Bay sediments, East Sea, Korea



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## ABSTRACT

To determine the characteristics of metal pollution sources in Ulsan Bay, East Sea, 39 surface and nine core sediments were collected within the bay and offshore area, and analyzed for metals and stable lead (Pb) isotopes.

Most surface sediments (>95% from 48 sites) had high copper (Cu), zinc (Zn), cadmium (Cd), and Pb concentrations that were as much as 1.3 times higher than background values. The primary source of metal contamination came from activities related to nonferrous metal refineries near Onsan Harbor, and the next largest source was from shipbuilding companies located at the mouth of the Taehwa River. Three different anthropogenic sources and background sediments could be identified as end-members using Pb isotopes. Isotopic ratios for the anthropogenic Pb revealed that the sources were imported ores from Australia, Peru, and the United States. In addition, Pb isotopes of anthropogenic Pb discharged from Ulsan Bay toward offshore could be determined.

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Heavy metal contamination in the coastal marine environment is a concern for the public and governments because metals may have harmful/toxic effects on humans as well as marine organisms following their bioaccumulation and biomagnification (Förstner and Wittmann, 1981; Kang et al., 1999). Economic development has resulted in industrialization and urbanization in coastal areas, which can result in the discharge of large quantities of metals into the marine environment. To maintain marine ecosystems, management plans considering metal contamination should be established, and they should identify the sources of contamination, transport pathways, and the behavior and fate of metals in the coastal environment. In addition, dispersal patterns including the direction of transport and the extent of dispersal of land-derived contaminants to offshore areas is important to consider in land-ocean interaction studies. Transboundary transport between neighboring nations and coastal environmental protection are also important issues to consider. Chemical tracers and the use of isotopic ratios enable the discrimination of multiple sources of metals, and should be used together with temporal or spatial gradients of metal concentration for the quantitative interpretation of

contaminant dispersal (Bullen and Eisenhauer, 2009; Négrel et al., 2012).

Lead (Pb) isotopes have been used for the discrimination of sources of contamination and to determine the transport pathways of metals in marine materials including seawater, aerosols, organisms, and sediments (Hamilton and Clifton, 1979; Flegal et al., 1987; Hamelin et al., 1990; Labonne et al., 1998; Munksgaard et al., 1998; Hinrichs et al., 2002; Choi et al., 2007a). Pb sources can be differentiated between ore-borne and rock weathered materials. One can also discriminate between different Pb ores because their isotopic ratios vary depending on the age of the ore and the thorium/uranium (Th/U) ratios in parent rocks (Dickin, 1995), and moreover, no fractionation occurs during natural and anthropogenic weathering, and transport in the environment (Hirao et al., 1986).

Widespread metal pollution in seawater, aerosols, organisms, and sediments in Ulsan Bay on the southeastern coast of Korea has been reported, and the source is believed to be nearby industrial plants, including nonferrous metal and oil refineries, shipbuilding facilities, and a large harbor (Lee et al., 1988; Kang and Lee, 1996; Song, 1996; Yang et al., 1996; Kang et al., 1999; Han and Lee, 2000; Moon et al., 2001; Oh et al., 2010). Although air pollution and wastewater control technologies are in place at some facilities, because this area has experienced various levels of industrial activity over the past 40 years, it is likely to be an

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important source of metals to the East Sea through coast–offshore transport and atmospheric pathways (Choi et al., 2006, 2007b).

Although several studies have reported levels of heavy metal contamination and the likely sources in marine materials, no published studies have investigated the sources of metals using Pb isotopes. Choi et al. (2006, 2007b) undertook studies on Pb isotopes in the shelf and slope sediments of Ulleung Basin, which can be used to compare background and anthropogenic Pb isotopes in the sediment.

This study used Pb isotope ratios in Ulsan Bay sediments to identify the sources and transport pathways of metal contamination. In addition, using sediments collected offshore as well as within the bay, this study attempted to identify a signal that would indicate the pattern of coast–offshore transport of Pb-contaminated sediments.

Ulsan Bay is located in the southeastern part of the Korean Peninsula and has a width of 900–2500 m and length of 6.6 km. Its mouth opens directly toward the East Sea. The tidal range of the sea is less than 1 m. The distribution of water temperature and salinity suggests a strong influence of freshwater from the Taehwa River, and the major directions of the tidal currents are southwest and northeast throughout the year (Kwon, 2012). A strong coastal front forms offshore at water depths of 20–80 m in the vicinity of the East Korean Coastal Water current, which is an extension of the South Korean Coastal Water current that moves in a northerly direction, and the East Korean Warm Water current, which is a branch of the Tsushima Warm Current that enters the East Sea through the Korea Strait (Um et al., 2013).

Along the coast of this bay are many industrial sites, including a petrochemical industrial complex, the Ulsan Yongyeon industrial complex, nonferrous industrial complexes, and a shipbuilding company. In the Ulsan and Jangsaengpo harbors, which are located in the northern part of the study area, industries are involved in the welding of steel plates, automobile manufacturing, shipbuilding and painting. A petrochemical complex located in the middle part of the study area contains enterprises involved in machinery and electronic assembly, wheel manufacturing, and shipbuilding. In the southern part of the study area, several nonferrous metal industries, including the Korea Zinc Co., Poongsan Metal Co., and LS Nikko Copper Refinery Co., are located along the coast of Onsan Bay, which also includes Onsan Harbor. These industries use zinc (Zn), copper (Cu), and Pb ores as raw materials, and produce Pb, Zn, cadmium (Cd), and Cu alloys (Song, 1996). Most of the Pb ore consumed in Korea is refined at this location (KIGAM, 2004–2011). Onsan Bay, which is regarded as the center of metal contamination (Kang et al., 1999), almost disappeared due to land reclamation in the past 10 years (Fig. 1; cf. Kang et al., 1999). The transportation of imported ores occurs largely from Onsan Harbor and Ulsan Sin Harbor (Fig. 1).

In 2011, 39 surface sediments and five core sediments (30–70 cm length) were collected at regular distances within Ulsan Bay (Fig. 1) using a Van Veen grab sampler and a gravity corer, respectively. In the same year, four core samples were collected offshore onboard the R/V Tamyang using a box corer (Fig. 1) at a water depth of 30 m and then subsampled using a 50-cm-long acrylic pipe. Two stream sediment samples were collected near the Korea Zinc Co. For the surface sediments, about 2-cm-thick samples were collected using a grab sampler, placed in vinyl zip bags, and preserved in a refrigerator. All the acrylic pipes containing core sediments were tightly capped at the top and bottom, and also preserved in the refrigerator.

The acrylic pipe was cut in a half along its length by hand using an acrylic cutter to prevent the input of any contaminants, and the sediment column was then sliced at 1-cm intervals using a plastic plate. An aliquot of sediment samples, including surface and sliced

core samples, was freeze-dried, powdered with an agate mortar, and stored until analysis.

A method used by Choi et al. (2007a) was adopted for the analysis of iron (Fe), calcium (Ca), cesium (Cs), Cu, Zn, Cd, and Pb concentrations in bulk sediments, and Pb isotopes as well as Cu, Zn, Cd, and Pb concentrations in the 1 N HCl leached fraction. Briefly, 0.2 g of powdered sediments were placed into a 60-mL Teflon digestion vessel (Savillex, Eden Prairie, MN, USA) and then digested overnight with 4 mL of mixed acids ( $\text{HNO}_3:\text{HClO}_4 = 3:1$ ) on a hot plate at 170 °C. After the digested solution was taken to dryness, residual solids were digested with 4 mL of mixed acids ( $\text{HF}:\text{HClO}_4 = 3:1$ ) under the same conditions. The digested solution was taken to dryness, and this step was repeated twice. After evaporation, residual solids were reacted with 1 mL of  $\text{HClO}_4$  and 5 mL of saturated boric acid to remove residual fluorides and then extracted using 20 mL of 1%  $\text{HNO}_3$  solution. For the analysis of leached metals, 0.2 g of powdered samples was placed into 60-mL centrifuge tubes and reacted with 20 mL of 1 M HCl in a horizontal shaker at room temperature for 24 h. After centrifugation, the supernatants were collected and diluted into an appropriate volume.

Metals in both the bulk digested solution and the 1 N HCl leached fraction were quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 4300 DV; Perkin-Elmer Ltd., Waltham, MA, USA) and inductively coupled plasma mass spectrometry (ICP/MS; X-5; ThermoElemental Ltd., Winsford, UK) at the Korea Basic Science Institute (KBSI). The drift and matrix suppression of signals during ICP-MS measurements was corrected using internal standards of  $^{103}\text{Rh}$  and  $^{205}\text{Tl}$  added to the digested solution as much as 10 ng/mL. The external calibration using multi-element standards was adopted to both ICP-AES and ICP-MS measurements. The  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios were measured using multi-collectors inductively coupled plasma mass spectrometry (MC-ICP-MS; Neptune; ThermoFinnigan Ltd., Stoke-On-Trent, UK) at KBSI after spiking with Tl (NIST SRM 997) to correct the instrumental mass bias using a reference  $^{205}\text{Tl}/^{203}\text{Tl}$  value of 2.3871 (Dunstan et al., 1980).

The reproducibility and recovery of metal concentrations were regularly checked using sediment reference material (MESS-3 in National Research Council of Canada) and found to be about 10% and 94–101%, respectively, for all the metals concerned (Table 1). Pb isotope ratios were measured once every five samples in a NIST SRM 981 solution (200 ng/mL Pb). The mean isotope ratios for 120 measurements were deviated by 142 ppm and 346 ppm for  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ , respectively, from Todt et al. (1996) and could be reproduced to within about 0.026% ( $\pm 2$  SD). Pb isotope ratios for MESS-3 were also listed in Table 1 and showed about 0.07% ( $\pm 2$  SD,  $n = 12$ ) reproducibility.

Particulate organic carbon (C) was analyzed using a total organic C analyzer (TOC-V; Shimadzu, Kyoto, Japan) after the removal of inorganic C by reaction with 1 M HCl.

Some parameters related to the geochemical characteristics of sediments such as organic C, Fe, Ca, and Cs, heavy metal concentrations in the bulk and 1 N HCl leached fraction, and Pb isotope ratios in the leached fraction of surface and core sediments are summarized in Supplementary Tables 1 and 2. The spatial distributions of the Fe, organic C, Ca, and Cs concentrations are shown in Supplementary Fig. 1. Because the concentrations of heavy metals vary depending upon the physical and chemical properties of the sediments as well as the existence of contamination sources, it is essential to determine the distribution of physical and geochemical factors in sediments to assess metal contamination (Horowitz, 1991). Generally, heavy metals are more enriched in the finer-grained sediments, and those with a higher content of organic matter, Fe–Mn oxyhydroxides, and clay minerals, but a lower calcium carbonate ( $\text{CaCO}_3$ ) content (Förstner and Wittmann, 1981; Horowitz, 1991; Chester, 2000). The grain size of sediments in

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