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Using stable lead isotopes to trace heavy metal contamination sources in sediments of Xiangjiang and Lishui Rivers in China

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ABSTRACT

Lead isotopes and heavy metal concentrations were measured in two sediment cores sampled in estuaries of Xiangjiang and Lishui Rivers in Hunan province, China. The presence of anthropogenic contribution was observed in both sediments, especially in Xiangjiang sediment. In the Xiangjiang sediment, the lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ ratio, than natural Pb isotope signature (1.198 and 2.075 for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively), indicated a significant input of non-indigenous Pb with low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$. The corresponding concentrations of heavy metals (As, Cd, Zn, Mn and Pb) were much higher than natural values, suggesting the contaminations of heavy metals from extensive ore-mining activities in the region.

1. Introduction

Located in Hunan province of China, Dongting Lake is the largest interior lake of China, and drains into the Yangtze River, the largest river in China. Dongting Lake is fed by four rivers, which are Xiangjinag, Zishui, Yuanjiang and Lishui (Du et al., 2001). These four rivers cover a large area from south to northwest of the Dongting Lake. China has a long history of metal and non-metal mining activities, and the south China region such as Hunan province is rich in mineral resources including non-ferrous metals (Zaw et al., 2007). Many kinds of ores in Hunan province have been exploited, with mine tailing and wastewater produced and dust emitted, which result in the severe pollution in surrounding environment including rivers and lakes. Phosphate fertilizers were generally regarded as a potential source of Cd, As and Hg contamination of farm fields, and applications of manures and pesticides were found to be a significant non-point source of Cd, Cu, Pb, Zn in the soils (Kachenko and Singh, 2006). This has caused the accumulation of heavy metal in edible part of foods and health risk after human digestion (Zhu et al., 2008; Williams et al., 2009; Li et al., 2011). Mining activities, such as the process of mining exploitation and ore concentrating, are believed to be the major source of metals entering into the environment in Dongting Lake (Liu et al., 2005), although other sources such as wastewater treatment plant, an industrial area, or runoff may also increase the inputs of heavy metal to rivers. It is important to understand and identify the sources of heavy metals in rivers derived from natural or anthropogenic activities so as to control the river contamination and design sustainable management strategies.

Knowing the total concentrations of lead (Pb) may provide useful information about the extent of contamination. However, it is not sufficient for a precise evaluation of contamination sources. Stable Pb isotopes provide a powerful tool that can be used to separate anthropogenic Pb from natural Pb derived from mineral weathering. Pb present in the environment has four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb. While ^{204}Pb is non-radiogenic with a constant abundance on earth in time (Komarek et al., 2008), isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic and produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively. Because the isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes associated with smelting, refining and manufacturing (Ettler et al., 2004), each source of Pb can have distinct or sometimes overlapping isotopic ratio ranges from mixing of local/natural Pb with anthropogenic Pb sources. Investigations of Pb isotope compositions have been well-established in geochemistry and are increasingly used in environmental science (Monna et al., 2000; Komarek et al., 2008). The isotopic composition of Pb has been used as an indicator of anthropogenic contribution in many ecosystems, such as sediments, to investigate the impact of recent Pb smelting and/or

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mining activities on the surrounding environment (Renberg et al., 2002; Monna et al., 1999).

It is probable that in Hunan province, the metallurgical activity is the principal source of soil and river pollution due to many ores exploitation. The studies of Pb and other heavy metal concentrations in river sediments contaminated by mining activities represent the first step in evaluating the extent of pollution (Zhang et al., 1989). To date, no Pb isotopic data are available for river sediments of Hunan province. Tracing contamination sources of heavy metal in river sediments by Pb isotope could be useful for designing sound management strategies to minimize contamination. Therefore, the present study aims to determine the Pb isotopic composition, as well as the contents of heavy metals, of river sediment profiles sampled in the Xiangjiang River, the biggest river and one of the main drinking and irrigation water sources in Hunan Province, and Lishui River, which is believed to be the lightest polluted or unpolluted of the four rivers flowing into the Dongting Lake.

2. Methodology

2.1. Sampling of river sediments

Four sediment cores from each river were collected onboard at estuaries of Xiangjiang (28°50′10″N, 112°52′56″E) and Lishui (29°7′31.6″N, 112°12′2″E) Rivers to Dongting Lake (downstream), Hunan province, China (Fig. 1). The cores were taken using a gravity corer consisting of an acrylic pipe with 8-cm inner diameter and 100 cm length, a sediment catcher and a clear vent. With the slow entry of this corer into the sediment, sediment cores with undisturbed sedimentary column were obtained. Immediately after collection, the sediment cores were cut at 1 cm interval and sealed in labeled plastic bags. After every core was taken, the pipe was replaced for collecting a new sample (Lu and Matsumoto, 2005).

2.2. Sample preparation and analysis of heavy metals

The sediments were air-dried to the constant weight, homogenized. The samples were powdered in the agate mortar, passed through 80-mesh sieve, and then digested with concentrated Aristar Ultra nitric acid (VWR International, West Chester, PA, USA) and hydrogen peroxide (30%) (EM Sciences, Gibbstown, NJ, USA) on a hot plate as described (U.S. EPA, 1996. 3050b; Lorentzen and "Skip" Kingston, 1996). For quality controls, two samples of standard reference materials (SRM) NIST 2710 and 2711 (Montana soils), as well as three blanks without solid samples, were prepared at the same time. After digestion, samples were cooled and then diluted to 50 ml with Millipore ultrapure water (Element A10 and Elix 10, Millipore, Billerica, MA, USA). The samples were then analyzed for total heavy metals including As, Cd, Zn, Mn, Pb, Cu, and Cr using an inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer SCIEX model Elan® DRC II, Waltham, MA, USA). Indium (In) isotope In-115 was used as the internal standard.

2.3. Measurement of Pb isotopes by ICP-MS

A quadrupole-based ICP-MS system (PerkinElmer SCIEX model Elan® DRC II) was used for the isotope ratio measurements according to the reported methods (Margui et al., 2006, 2007). Briefly, the solution digested for total heavy metals were diluted to about 20 μg/kg by high-purity 1% HNO_3 according to the total Pb concentration of samples. For quality controls, two blanks, as well as two United States Geological Survey (USGS) reference materials BCR-2 (Basalt, Columbia River) and AGV-2 (Andesite, Guano Valley), were prepared along with the samples. The standard reference material NIST SRM 981, available in the form of wire, was employed to evaluate the mass bias. Thallium (Tl) isotopes (^{203}Tl and ^{205}Tl) were measured as internal standards. Furthermore, the isobaric interference from ^{204}Hg on ^{204}Pb measurements was monitored. The accuracy of the Pb isotope ratio measurements was evaluated by analyzing USGS SRM BCR-2 and AGV-2. Good agreements were obtained between the lead isotope ratios measured and the certified values for BCR-2 (deviations within 0.2–0.5%) and AGV-2 (deviations within 0.2–0.3%).

3. Results and discussion

3.1. Total Pb and heavy metals in sediment cores

The recoveries in SRM 2710 were As 89%, Cd 81%, Zn 77%, Mn 92%, Pb 83%, Cu 91%, Cr 100% and in SRM 2711 were As 91%, Cd 89%, Zn 96%, Mn 94%, Pb 110%, Cu 96%, Cr 106%. Total metal concentrations in sediment cores from estuaries of Xiangjiang River to Dongting Lake were as follows: As 95.7 mg/kg on average (varied from 48.7 to 153 mg/kg); Cd 12.3 mg/kg (6.3–16.8 mg/kg); Zn 270 mg/kg (123–381 mg/kg), Mn 1806 mg/kg (933–3272 mg/kg) and Pb 133 mg/kg (44.6–257 mg/kg). In contrast, those values for Lishui River are only As 10.8 mg/kg (6.6–16.2 mg/kg), Cd 0.5 mg/kg (0.2–0.7 mg/kg), Zn 85.8 mg/kg (58.7–148 mg/kg), Mn 698 mg/kg

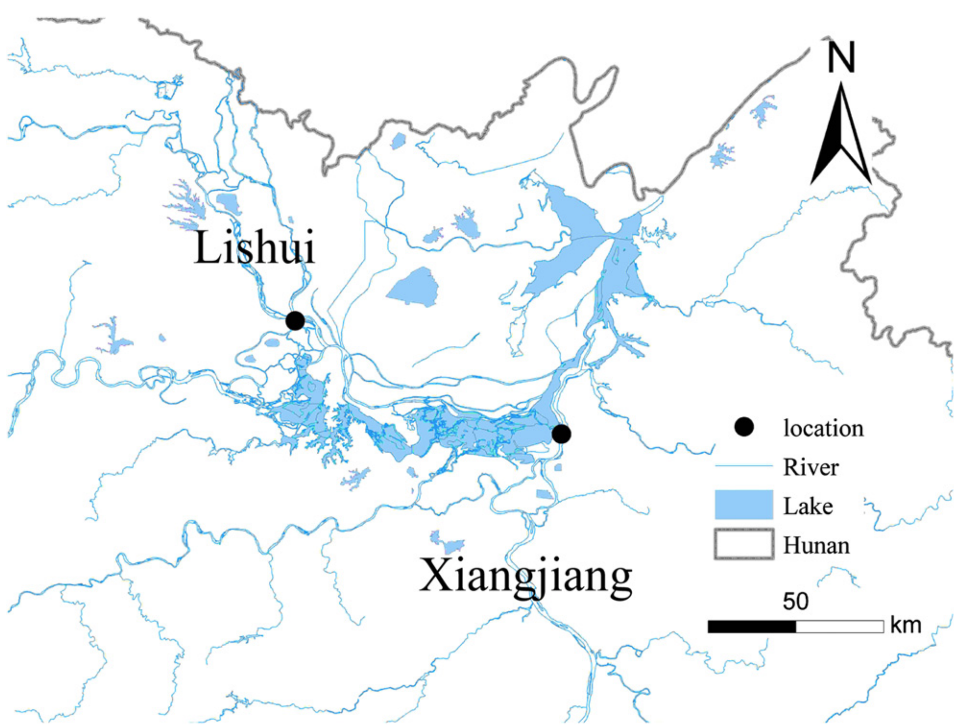

Fig. 1. Location of sampling cores.