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Characteristics of lead geochemistry and the mobility of Pb isotopes in the system of pedogenic rock–pedosphere–irrigated riverwater–cereal–atmosphere from the Yangtze River delta region, China

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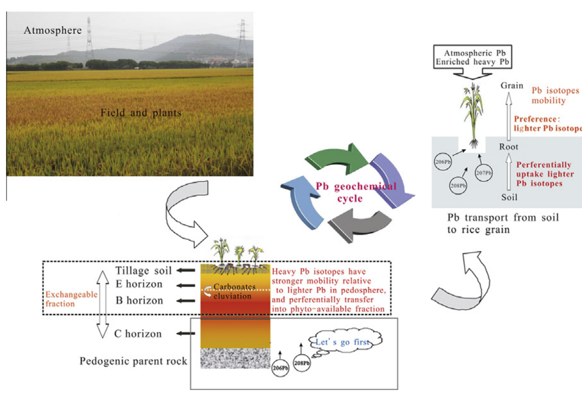
HIGHLIGHTS

- ^{206}Pb is more likely to transport into soil during pedogenic process relative to heavier Pb.
- ^{208}Pb usually shows stronger mobility relative to the lighter Pb in soil.
- Anthropogenic Pb has a significant influence on exist of bio-available Pb in soil.
- Lighter Pb shows stronger transfer ability from soil to cereal relative to heavier Pb.
- Pb isotope estimation shows that 16.7–52.6% of Pb in rice grain is from atmosphere.

GRAPHICAL ABSTRACT



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ABSTRACT

Knowledge of the characteristics of Pb and its isotopic transfer in different compartments is scant, especially for the mobility of Pb isotopes in the geochemical cycle. The present study characterizes differential Pb transport mechanism and the mobility of Pb isotopes in the pedogenic parent rock–pedosphere–irrigated riverwater–cereal–atmosphere system in the Yangtze River delta region, by determining Pb concentration and Pb isotopic ratios of pedogenic parent rocks, fluvial suspended particle matter, tillage soils, soil profiles, irrigated riverwater, fertilizer, Pb ore, cereal roots and grains. The results show that Pb isotopes in the geochemical cycle generally follow the equation of $^{208}Pb/^{206}Pb = -1.157 \times {}^{206}Pb/^{207}Pb + 3.46$ ($r^2 = 0.941$). However, Pb isotopes have different mobility in different environmental matrixes. Whereas in the pedosphere, the heavier Pb (^{208}Pb) usually shows stronger mobility relative to the lighter Pb, and is more likely to transfer into soil exchangeable Pb fraction and carbonates phase. The lighter Pb shows stronger transfer ability from soil to cereal grain via root compared to the heavier Pb. However, the cereal grains have lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ ratios than root and tillage soil, similar to the airborne Pb and anthropogenic Pb, implying that a considerable amount of Pb in cereal grains comes from the atmosphere. The estimate model shows that 16.7–52.6% (average: 33.5%) of Pb in rice grain is the airborne Pb.

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1. Introduction

Lead is a non-essential and toxic element to humans and animals. The geochemical cycle of Pb has been greatly affected by humans. Since the industrial age, Pb pollution has occurred in the soil, atmosphere and agriculture in many regions of the world. The geochemical behavior of Pb and its pollution have been great emphases in the environmental studies (Hao et al., 2008; Dawson et al., 2010; Uzu et al., 2010; Bove et al., 2011).

Lead has four isotopes in nature: ^{208}Pb (52.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{204}Pb (1.4%). Pb isotopes have been used as "fingerprints" for environment pollution (Komárek et al., 2008). Each source of Pb can have its distinct or sometimes overlapping isotope ratio ranges. Pb isotopic studies thus provide a convenient approach for studying and tracing the sources of Pb pollution in different environmental compartments, and this has been the major research direction of Pb isotopes (Bindler et al., 1999; Bollhöfer and Rosman, 2001; Veysseyre et al., 2001; Kaste et al., 2003; Zhang et al., 2007). Besides the application of Pb isotopic radios, the isotope dilution method is also developed for determining Pb geochemical behavior in soil (Gray et al., 2003, 2004). E values and L values analysis shows a good potential for estimating bio-available Pb in soil (Tongtavee et al., 2005). However, the mechanism controlling mobilization and accumulation of Pb in different environmental compartments and the characteristic of Pb isotopes in geochemical cycle are still unclear. Especially, the literature on the characteristic of mobility of Pb isotopes in pedosphere-plants is very limited, and researches on the mechanism of Pb isotopes transfer among the different speciation of Pb in soil are still in blank.

The Yangtze River delta is a well-known river delta with great importance to human civilization. Based on the marine strata (sedimentary rocks) and fluvial alluvial deposits, a series of soils with high maturity had formed on the earth's surface in this area (Soil Survey Office of Jiangsu Province of China, 1995). With the rapid industrial development and enhanced anthropogenic activities, the Yangtze River delta area has transformed from a traditional agricultural area to a typical urban and agricultural agglomeration, and the environment has been contaminated with F, Pb and other heavy metals (Hao et al., 2008; Huang et al., 2009; Wang et al., 2012a,b). Tracing and characterizing the transport mechanism of Pb cycle in pedogenic rock – pedosphere – irrigated riverwater – cereal – atmosphere and the mobility and characteristic of Pb isotopes in the Yangtze River delta area is of great significance to the study of other river deltas.

2. Sampling and experiment

2.1. Study area

The study area is located at between 30°00′N–33°20′N and 119°10′E–121°40′E in East China, covering an area of 109, 650 km^2 with a warm and humid subtropical climate (Fig. 1). The annual mean temperature and rainfall are approximately 15 °C and 1000 mm, respectively. Sedimentary rock (limestone and sandstone) is the predominate rock in the stratum, and is the major pedogenic parent rock. According to the soil classification of the world reference base for soil resources, anthrosol is the major soil order in this area. The rice (*Oryza sativa* L.) and winter wheat (*Triticum aestivum* L.) are two dominant crops grown here.

2.2. Sample collection and preparation

In order to obtain representative and spatially well distributed samples of Pb in the Yangtze River delta region, different kinds of environmental media have been collected. Table 1 lists the samples of the present study, and also some from previous researches for comparison (Mukai et al., 2001; Zheng et al., 2004).

A total of 32 topsoil (tillage soil) and three corresponding wheat (*Triticum aestivum* L.) samples were collected from the study area shortly before wheat harvesting at sites located with the aid of a Global Positioning System in 2009 (Fig. 1). At each site, five topsoil (depth: 0–20 cm) sub-samples were gathered in a 200 m^2 area using a stainless steel trowel, and mixed in a cloth bag.

Soil profiles were taken from six field sites that scattered in the study area shortly before rice harvesting in November 2011. The soil profile sites were chosen based on preliminary geochemical data and assessment of chemical distributions of the topsoil. To characterize the transport of Pb among different environment matrixes, a series of irrigated river water ($n = 5$), fertilizer ($n = 4$), and rice root and grain ($n = 4$) samples were also collected at the corresponding soil profile sites the same time. Samples from soil profiles were collected using a stainless steel soil corer in hand dug soil pits after the sampling face was first scraped clean with a stainless steel trowel. For each profile, four samples were collected from the surface to 1.7 m depth (one topsoil samplein A horizon: 0–20 cm, one sub-tillage soil sample in E horizon: 50–70 cm, and two subsoil samples in B horizon: 100–120 cm and 150–170 cm, respectively). At the soil profile sites P3, P4, P5 and P6, the corresponding rice plant samples (the sampling area is 3 m × 3 m) were collected, then the samples were separated into root and grain samples. The irrigated river water was collected using a 500 mL plastic bottle from the river near to the cropland, four water subsamples were collected during four month (once a month) and mixed into one sample for analysis. The fertilizers were collected from the owner of the corresponding cropland (the surplus fertilizers that after application, 1 kg). Chinese farmer usually use the nitrogenous fertilizer and composited fertilizers that made in the localfactory. As nitrogenous fertilizer generally contains much lower content of Pb than composited fertilizers, we just analyze the latter. The principal ingredient of composited fertilizers is urea, ammonium phosphate and potassium chloride.

The suspended particle matter samples of the lower Yangtze River were collected during the flood (July, 2007) and

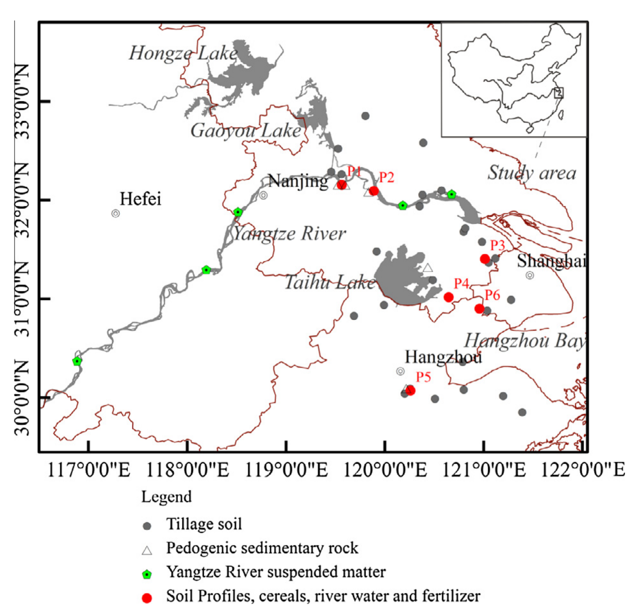

Fig. 1. Study area and sampling locations. At all the soil profile sites except soil profile sites P1 and P2, the corresponding rice, irrigated riverwater and fertilizer samples that applied in the field were collected at the same time.