Analysis of Lead Sources in Farmland Soil and Rice Based on Isotope Ratios

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Abstract Microwave digestion-inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze the sources of lead in farmland soil and rice in the Jiulongjiang River Basin. The results suggested that the source of lead in rice was differ from that in soil. There were four main sources of lead in farmland soil: natural source, agricultural source, industrial source and fossil fuel source, among which natural source, agricultural source and industrial source contributed more. There were four main sources of lead in rice: natural, agricultural, industrial and fossil fuel sources, and more importantly, fossil fuel sources. The comparison of lead isotope composition with potential sources($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{208}Pb/^{207}Pb$) can provide a scientific basis for the identification and treatment of heavy metal lead pollution sources in farmland soil and rice in the Jiulong River Basin.

Key words Lead isotopes; Source resolution; Farmland soil; Rice; Fujian Province

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In recent decades, food security has become a high-priority issue[1]. The Jiulong River Basin is an important rice-producing area in China, and the soil is seriously polluted by heavy metals due to factors such as long-term cultivation and the use of chemical fertilizers. When the content of some heavy metals in farmland soil is high, the growth and development of rice will be greatly inhibited and even difficult to survive[2]. Heavy metals in farmland soil may also be absorbed by crops planted on them, and eventually cause excessive heavy metal content in edible parts, which in turn affects human health[3-4]. Therefore, it is urgent to analyze and study the sources of heavy metal pollution.

The sources of heavy metals in soil are complex, which can be divided into natural sources[5] and anthropogenic sources[6-8]. At present, there are many methods for the analysis of the source of heavy metals, including traditional multivariate statistical analysis[9], receptor models developed on the basis of multivariate statistical analysis[10] and stable isotope tracing[11].

Lead isotopes have 4 isotopes in nature: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Its isotopic composition is only related to the Pb isotopic composition characteristics of the source region, with a special "fingerprint" characteristic. It has been used in many fields[12-16], and it can be used to trace the source of contamination.

In this study, microwave digestion-inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze the sources of lead in farmland soil and rice in the Jiulong River Basin, and the lead isotopic composition was compared with the lead isotopic composition of the potential source ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{208}Pb/^{207}Pb$), aiming to provide a certain scientific basis for the identification and treatment of heavy metal lead pollution sources.

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Materials and Methods

Sample collection and pretreatment

In order to study the analysis of the source of lead in farmland soil and rice in the Jiulongjiang River Basin, samples of farmland soil and rice plants were collected in the Jiulongjiang River Basin during the summer maturity of rice in 2017, and the specific sampling points are shown in Fig. 1. In specific, 71 samples of farmland soil tillage, 45 samples of rice plants and 6 samples of soil profile were obtained.

Soil samples of cultivated layer of farmland: According to the distribution of farmland in the Jiulong River Basin, the sampling points were determined. A bamboo shovel was employed to collect 5 soil samples (0 – 20 cm) around the sampling point and mix them into a mixed sample, and then take an appropriate amount (about 1 kg) according to the quarter method. Each sample were put into a clean polyethylene sealed bag, with the information of the sampling point (latitude and longitude, surrounding environment, *etc.*) accurately recorded. After the soil samples were brought back to the laboratory, they were placed on a clean test bench for air drying. Each sample was gently crushed with clean wooden sticks to remove stones and grass roots. Part of the sample was taken by the quarter method, ground with an agate mortar, and then passed through a 0.075 mm nylon sieve. The samples were determined for the isotope ratios.

Soil profile samples: According to the distribution of farmland in the Jiulongjiang River Basin, a total of 6 soil profile samples were collected in the Beixi Basin, Xixi Basin and estuary area, and were named P1-P6. Their corresponding relationships with the surface soil were as follows: P1 (8), P2 (16), P3 (34), P4 (47), P5 (43) and P6 (69). During sampling, soil profile samples were collected at 7 horizons of 0 – 5, 5 – 10, 10 – 20, 20 –

30, 30 – 40, 40 – 50 and 50 – 60 cm with a soil sampler. Each soil sample was mixed thoroughly in a clean, and sealed in a polyethylene bag. The pretreatment for the stratified samples from each profile was the same as that for soil samples of the cultivated layer.

Rice plant samples: Rice plant samples were collected at the soil sample sampling point at the same time, and 10 mature rice plants were collected around the sampling point as a mixed sample. Rice plant samples were brought back to the laboratory and rinsed with ultrapure water.

Rice samples: Each rice plant sample was divided, and the rice sample was kept and packed in bags. The rice samples were dried to a constant weight in a thermostatic desiccator and then crushed in a pulverizer.

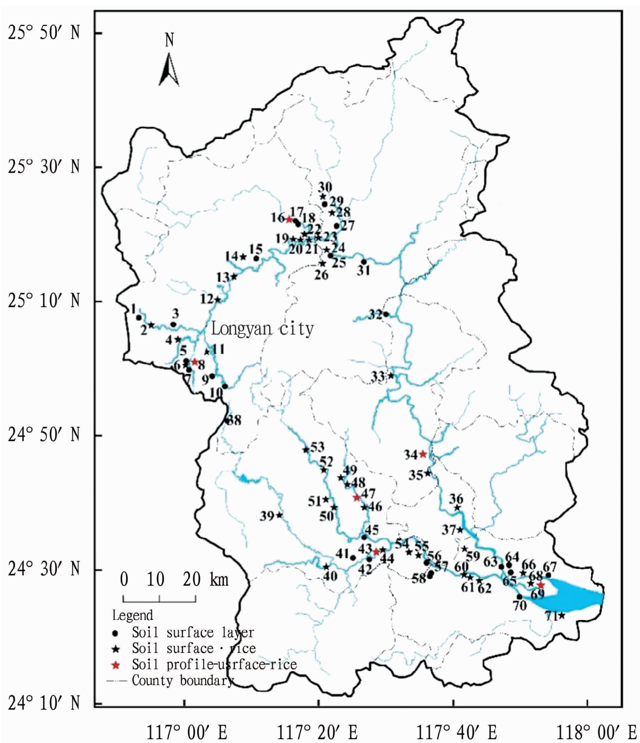


Fig. 1 Sampling locations of agricultural soils and rice from Jiulong River Basin

Experimental methods

Determination of lead isotope ratio: According to the measured Pb content in the extraction solution of each total amount and occurrence form, the volume of the digestion liquid required for the final volume to contain about 20 μg/L of Pb was estimated, and it was placed in an electric hot plate to evaporate to near dryness. Next, 1 ml of HCl was added, and evaporation was continued on a hot plate to near dryness. Subsequently, 1.5 ml of 0.5 mol/L hydrobromic acid solution was added into the digestion tube, which was heated for 1 h, and centrifuged after cooling[17]. The obtained supernatant was centrifuged with Bio-Rad AG1-X1 anion exchange resin (200 mesh). The separated and purified solution was evaporated to near dryness in an electric hot plate, reconstituted with 1 ml of HNO_3, cooled and diluted to 50 ml with pure water. The lead isotope ratio was then determined using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700) in an isotope ratio mode.

Quality control

In this study, quality control was carried out in four ways. (1) Blank experiment: When the samples were analyzed, a laboratory blank was made at the same time. The blank measured value was controlled below the detection limit or 10% of the lowest measured value of the batch sample. (2) For parallel samples: 10% of the samples were selected for parallel double-sample determination during the analysis of each batch of samples, and the relative deviation of the parallel double-sample measurement results was controlled below 10%. (3) Substrate spiking: One sample was selected as the spiked sample in each batch of samples, and the recovery rate was controlled between 90% – 110%. (4) Reference material: When the lead isotope was determined, the American Bureau of Standards Lead Isotope Reference Material NIST SRM 981 was measured simultaneously, and NIST SRM 981 was measured for every 5 samples measured for calibration.

Results and Discussion

Lead isotopic composition of potential sources

According to the investigation of the surrounding environment of the Jiulong River Basin, the potential sources of lead in farmland soil and rice in the Jiulong River Basin may include natural sources, agricultural sources, industrial sources, fossil fuel sources and transportation sources. The isotopic composition of lead from each potential source is shown in Fig. 2.

Among them, the natural source samples were the soil parent layer of the watershed, and the $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ were 1.192 3 – 1.201 2 (average 1.195 6), 2.072 2 – 2.088 8 (average 2.078 7) and 2.479 6 – 2.491 3 (average 2.485 2), respectively. Agricultural source samples were commonly used pesticides and fertilizers in the study area (commonly used fertilizers were compound fertilizers and superphosphate, *etc.*). $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ were 1.181 2 – 1.186 7 (average 1.183 5), 2.049 8 – 2.059 8 (average 2.060 3) and 2.425 7 – 2.446 1 (average 2.438 5), respectively. Lead and zinc, as the main metal elements in rocks, are extremely important industrial raw materials, and most of the lead in industrial emissions comes from lead ore. The industrial samples in this study were mainly Fujian lead-zinc ore samples. $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ were 1.175 2 – 1.183 2 (average 1.179 6), 2.100 3 – 2.106 0 (average 2.102 5) and 2.473 1 – 2.485 5 (average 2.480 0), respectively. The fossil fuel source samples were mainly coal-fired samples, including raw coal, fly ash, furnace bottom slag, *etc.* $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ were 1.143 0 – 1.156 3 (average 1.148 7), 2.119 8 – 2.140 1 (average 2.128 2) and 2.426 9 – 2.463 1 (average 2.444 7), respectively. The traffic source samples were mainly automobile exhaust dust, including gasoline exhaust dust and diesel exhaust dust. $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ were 1.111 1 – 1.148 9 (average 1.130 1), 2.031 0 – 2.125 2 (average 2.069 2) and 2.310 4 – 2.361 3 (average 2.337 9), respectively.

Natural sources exhibited the highest values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$. Fossil fuel sources showed the highest $^{208}Pb/^{206}Pb$ values. The lead isotopic compositions of $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ of end member components such as natural, agricultural, industrial, fossil fuel and transportation sources could be well distinguished. Therefore, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$3D models can be used to analyze the source of lead in farmland soil and rice in the Jiulong River Basin.

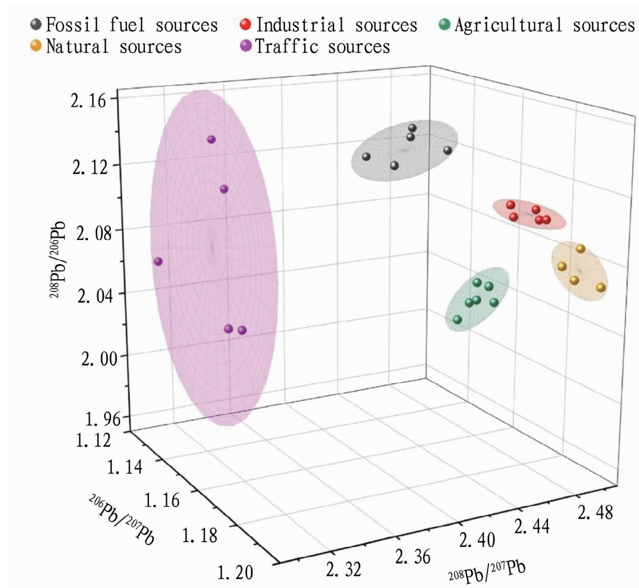
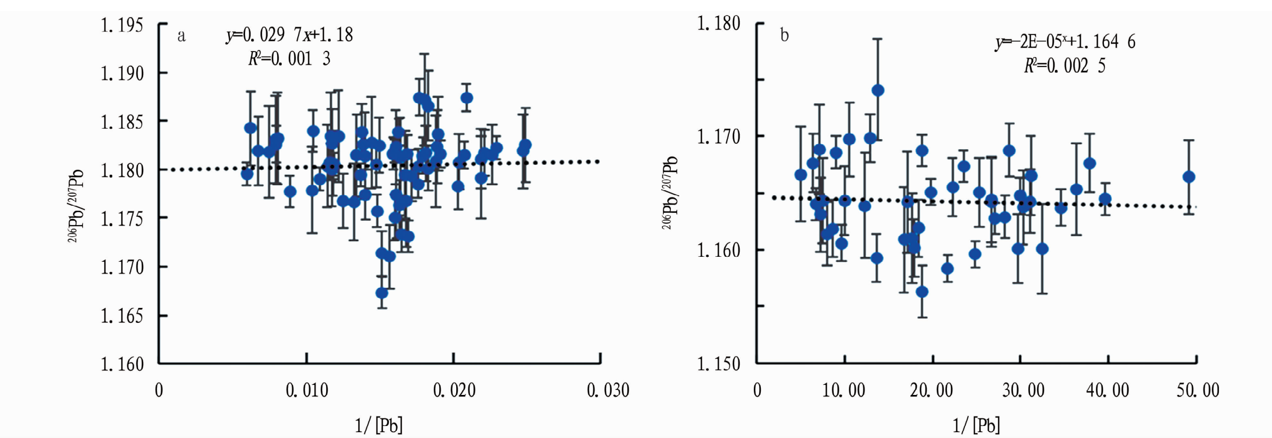


Fig. 2 Pb isotopic composition of potential sources

Analysis of the sources of lead in farmland soil and rice

According to the linear relationship between the lead isotope ratio of $^{206}Pb/^{207}Pb$ and the reciprocal 1/[Pb] of the lead content, it can be used to identify the characteristics of lead pollution sources[18-19]. As can be seen from Fig. 3, the correlation between the ratio of $^{206}Pb/^{207}Pb$ and 1/[Pb] in farmland soil and rice was poor, and the linear fit R^2 was 0.001 3 and 0.002 5, respectively, indicating that there were more than two sources of lead in farmland soil and rice.



a. Farmland soil; b. Rice.

Fig. 3 Linear relationship between $^{206}Pb/^{207}Pb$ and 1/[Pb]

In order to further qualitatively analyze the sources of lead in farmland soil and rice, the lead isotopic composition of farmland soil and rice was compared with the lead isotopic composition of potential sources ($^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$), as shown in Fig. 4. The $^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$ of farmland soil were 1.167 3 – 1.187 4 (average 1.180 4), 2.069 6 – 2.099 0 (average 2.085 3) and 2.447 3 – 2.476 0 (average 2.461 5), respectively, and the $^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$ of rice were 1.156 4 – 1.174 1 (average 1.180 4), 2.087 7 – 2.110 7 (average 2.100 5) and 2.436 0 – 2.454 5 (average 2.445 6), respectively. By comparison, it was found that the lead isotopic composition of farmland soil could be clearly distinguished from that of rice, indicating that the source of lead in rice and soil may be different.

The lead isotopic composition of farmland soils was close to that of natural, industrial and agricultural sources, and might be mainly derived from these three sources. The lead isotope ratio of farmland soil mainly fell in the area composed of natural, agricultural and industrial sources, but some of them exceeded this area, indicating that there may be more than these three sources of lead in farmland soil. When fossil fuel sources were considered, the lead isotope ratios of farmland soils fell within an area composed of natural, agricultural, industrial, and fossil fuel sources. The lead isotope composition of the traffic source was quite different from that of the farmland soil, indicating that the traffic source had no or little contribution to the lead in the farmland soil. Therefore, it could be considered that there were four main sources of lead in farmland soil: natural source, agricultural source, industrial source and fossil fuel source, among which natural source, agricultural source and industrial source contributed more.

The lead isotope ratio of rice also fell largely within the region of natural, agricultural, industrial and fossil fuel sources. However, unlike farmland soils, rice soils had smaller $^{206}Pb/^{207}Pb$ values and larger $208^{Pb}/^{206}Pb$ values, and their lead isotope ratios were closer to fossil fuel sources. Meanwhile, the lead isotope ratio of rice was relatively close to the source of transportation compared with the soil of farmland, and it might also be slightly affected by the source of transportation, but the source of transportation was still not the main source of lead in rice. Therefore, it could be considered that there were four main sources of lead in rice: natural, agricultural, industrial and fossil fuel sources, and more importantly, fossil fuel sources.

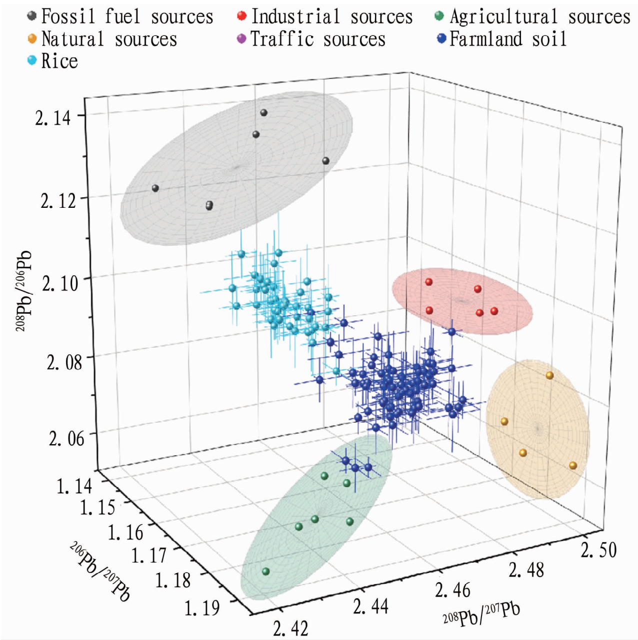


Fig. 4 Isotope compositions in agricultural soils and rice

Studies have shown that the $^{206}Pb/^{207}Pb$ ratio from anthropogenic sources is generally lower than that from natural sources[20-21]. Based on the $^{206}Pb/^{207}Pb$ ratio of the sample, some information about anthropogenic and natural sources could be understood. The spatial interpolation analysis of the $^{206}Pb/^{207}Pb$ ratio of soil and rice in the Jiulong River Basin is shown in Fig. 5. The $^{206}Pb/^{207}Pb$ of farmland soil and rice showed a trend of lower in the lower and estuarine areas and higher in the upstream area, indicating that the lead in farmland soil and rice in the Jiulong River Basin was more affected by anthropogenic sources in the lower reaches and estuarine areas, while more natural sources in the upstream areas.

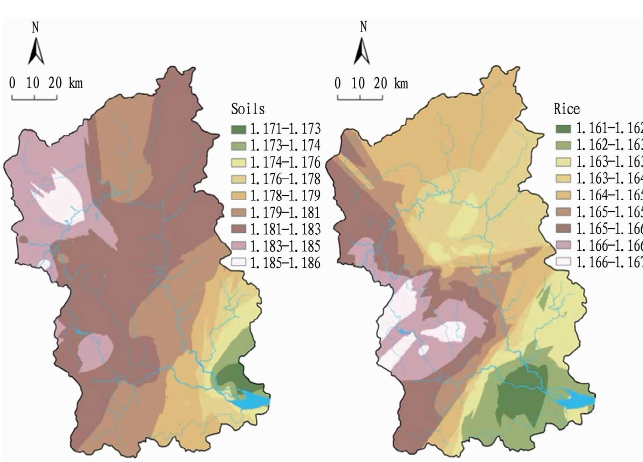


Fig. 5 Spatial distribution of $^{206}Pb/^{207}Pb$ in agricultural soils and rice

Conclusions

(1) The $^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$ values of lead isotope composition of potential sources (end-member components such as natural sources, agricultural sources, industrial sources, fossil fuel sources and transportation sources) in the Jiulongjiang River Basin could be well distinguished, and the 3D models of $^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$ could be used to analyze the sources of lead in farmland soil and rice in the Jiulongjiang River Basin.

(2) According to the comparison of the lead isotopic composition of farmland soil and rice with the lead isotopic composition of potential sources ($^{206}Pb/^{207}Pb$, $208^{Pb}/^{206}Pb$ and $208^{Pb}/^{207}Pb$), it could be seen that the lead isotopic composition of farmland soil could be clearly distinguished from that of rice, indicating that the lead in rice might be different from the source of lead in soil. There were four main sources of lead in farmland soil: natural source, agricultural source, industrial source and fossil fuel source, among which natural source, agricultural source and industrial source contributed more. There were four main sources of lead in rice: natural, agricultural, industrial and fossil fuel sources, and more importantly, fossil fuel sources.

(3) The $^{206}Pb/^{207}Pb$ of farmland soil and rice in the Jiulongjiang River Basin showed a trend of lower in the lower reaches and estuarine areas and higher in the upstream areas, so the lead in the farmland soil and rice in the Jiulongjiang River Basin was more affected by anthropogenic sources in the downstream and estuarine areas, while more natural sources were affected in the upstream areas.

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