Transport of Heavy Metals between Soil and Rice in the Jiulong River River Basin

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Abstract Diet is one of the main pathways for heavy metals to enter the human body, so studying the content of heavy metals in agricultural products and evaluating them is of great significance. When farmland soil is contaminated with heavy metals, the heavy metals accumulated in the soil will be absorbed by the roots of rice plants growing on it, and will migrate and transform between different tissues and organs of rice plants. There is a significant correlation between heavy metal pollution in soil and the content of heavy metals in rice. The migration and enrichment of heavy metals in the agricultural soil rice system is a complex process that is influenced by many factors, such as the physical and chemical properties of the soil, the content and occurrence forms of heavy metals in the soil, and the physiological characteristics of rice plants. In actual field environments, these influencing factors have significant spatial differences and are relatively complex. Therefore, it is necessary to conduct practical analysis of the various influencing factors in actual field environments. Based on actual data analysis, studying the heavy metal content in rice and the characteristics of heavy metal accumulation and migration in rice plants is of great significance for improving the food safety of rice.

Key words Enrichment and migration characteristics; Soil Rice System; Heavy metals

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The heavy metals in the agricultural soil rice system pose a serious threat to the safe production of rice worldwide[1]. Heavy metal pollution is currently one of the focuses of environmental research, and due to the toxicity, persistence, and bioaccumulation of heavy metal elements, it has attracted widespread attention worldwide[2–3]. The discharge of waste from industrial activities, the discharge of wastewater from mining activities, the extensive use of fertilizers in agricultural activities, and the discharge of domestic wastewater from residents have caused soil pollution in agriculture[4]. The heavy metal elements released by human activities such as industry and agriculture ultimately accumulate in the soil and remain for a long time[5–6]. The global cultivation of rice covers an area of approximately 160 million hectares, and rice is the staple food for more than half of the world's population[7]. Approximately 92% of rice is produced in Asia[8]. Heavy metal pollution in paddy soil systems and its continuous accumulation in different parts of rice plants (roots, stems, leaves, grains, *etc.*) have been found in different rice growing countries[9]. Therefore, it is of great significance to systematically study the distribution of heavy metal content in paddy soil and its migration and transformation in the agricultural soil rice system[10].

Materials and Methods

Sample collection and preprocessing

To study the characteristics, source analysis, and health risk assessment of heavy metal pollution in the farmland soil rice system in the Jiulong River Basin, samples of farmland soil and rice plants were collected during the rice ripening period in the summer of 2017 in the Jiulong River Basin. The specific distribution of sampling points is shown in Fig. 1. Among them, there were 71 samples of arable soil layer, 45 samples of rice plants, and 6 samples of soil profile.

Rice plant samples: Rice plant samples were collected simultaneously at soil sampling points, and 10 mature rice plants were collected around the sampling points as mixed samples. The rice plant samples were brought back to the laboratory and rinse with ultrapure water. Each rice plant sample was divided into roots, stems, leaves, rice husks, and brown rice samples, which were packed in bags. Each sample of rice plants was dried with a constant temperature dryer to a constant weight, and then crushed with a grinder.

Experimental methods

Total heavy metal extraction in soil: The content of 19 heavy metals (Be, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Mo, Cd, Ba, Pb, Th, U) in the soil was digested with mixed acid. Approximately, 0.2 g of soil sample was accurately weighed into a PTFE digestion tube. Next, 10 ml of mixed acid solution (made in a ratio of hydrofluoric acid : hydrochloric acid : nitric acid = 1 : 1 : 3) was added to the sample, which was then covered with a lid, and pre-digested at 110 – 120 ℃ for 2 – 3 h. After cooling, 1 ml of hydrochloric acid, 3 ml of nitric acid and 2 ml of perchloric acid were added, and the sample was covered with the lid to continue digestion at around 150 ℃ for 2 – 3 h. Next, the sample tube was opened, and the acid was evaporated to near dryness under a condition of 150 – 175 ℃. If there is black substance during the acid driving process, 2 ml of aqua regia will be added in batches until the solution has no precipitation and is a

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homogeneous orange yellow gel with no fluidity. Subsequently, 1 ml of nitric acid and 1 ml of pure water were added while hot for dissolution at 120 ℃ for 1 h in a closed state. After removal of the lid and cooling, the solution was filtered with a 0.45 μm filter membrane to obtain a filtrate, which was diluted to 50 ml with 2% nitric acid.

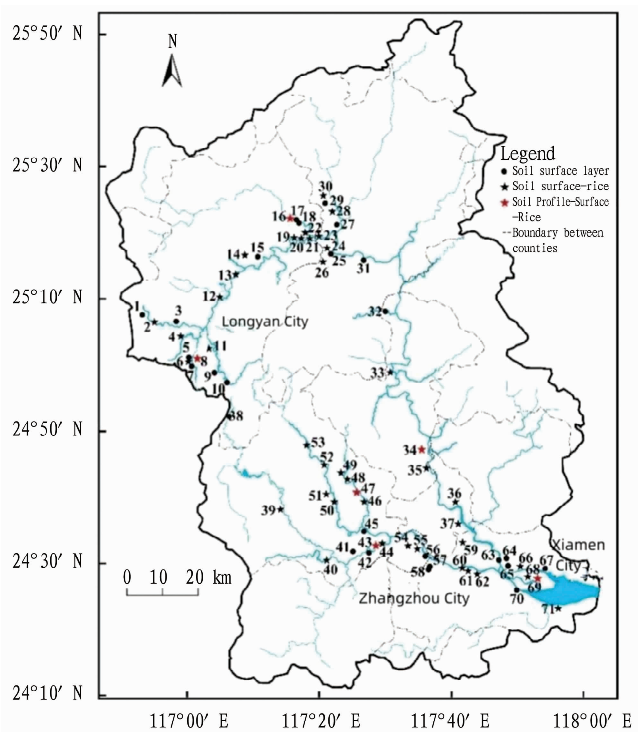

Fig. 1 Sampling locations of agricultural soils and rice from Jiulong River Basin

The mercury content in soil was dissolved in aqua regia water bath. About 0.2 g of soil sample was accurately weighed into a digestion tube, which was then added with 10 ml of freshly prepared aqua regia (hydrochloric acid : nitric acid = 3 : 1), and shaken to mix well. After standing overnight, the test tube was heated in a boiling water bath for 2 h. The digestion solution was filtered with a 0.45 μm filter membrane to obtain a filtrate, which was diluted to 50 ml with 2% nitric acid.

Total extraction of heavy metals in plants: The heavy metal content in rice plant samples was digested using a pressure digestion tank. According to the pre experiment, a certain amount of rice plant samples was accurately weighed into a digestion tank, which was then added with 10 ml of nitric acid and 0.5 ml of perchloric acid accurately to soak the sample overnight in a ventilated kitchen. Next, the digestion tank was covered with an inner cover, and after the stainless steel jacket was tightened, the digestion tank was heated in a constant temperature drying oven with a temperature of 160 ℃ and a duration of 5 h. After digestion, the digestion tank was cooled naturally in the constant temperature drying oven. After cooling to room temperature, the digestion tank was opened, and the inner tank was removed. And the digestion tank was soaked in a water bath for 5 min to remove the brown gas. The digestion solution was filtered with a 0.45 μm filter membrane to obtain a filtrate, which was diluted to 50 ml with 2% nitric acid.

Quality control

This study adopted four methods for quality control. Specifically, (1) standard curve: The correlation coefficient of the standard curve should was required to reach 0.999 or above. (2) Internal standard: During the measurement process, with 80% – 120% as the control line, when the internal standard response value during sample measurement is between 80% – 120% of the internal standard response value (*i.e.* internal standard recovery rate) during standard curve measurement, and it is considered that the instrument performance is relatively stable, and the measured data is valid after calibration with internal standard. When the internal standard recovery rate exceeds this range, it indicates that the instrument has drifted or interfered, and the cause needs to be identified and reanalyzed. (3) Blank experiment: Each batch of samples is processed synchronously with the entire reagent blank to reduce error interference; (4) Parallel samples: The precision of the sample analysis process adopted parallel double samples, that is, 10% of the samples were selected for parallel double sample determination in each batch of sample analysis.

Results and Discussion

Correlation analysis of physical and chemical properties

Pearson correlation analysis was conducted on the physicochemical properties of farmland soil in the Jiulong River Basin, including pH, total organic carbon, cation exchange capacity, calcium carbonate content, and electrical conductivity. The results are shown in Fig. 2. According to the correlation analysis results, the soil pH value was significantly correlated with cation exchange capacity, calcium carbonate content, and electrical conductivity at the $P < 0.01$ level. TOC was significantly correlated with calcium carbonate and cation exchange capacity at the $P < 0.01$ level. There was a significant pairwise correlation ($P < 0.01$) between the content of calcium carbonate, cation exchange capacity, and conductivity.

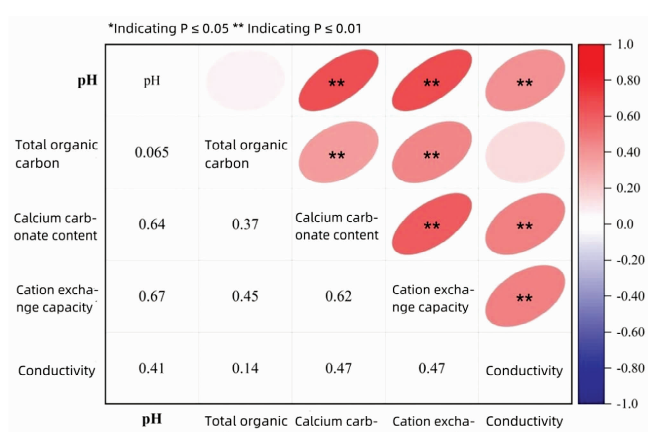

Fig. 2 Pearson's correlation coefficient of soil physical and chemical properties

Heavy metal content in soil

The subject of this study was farmland soil, and the heavy metal content in it should comply with the "Soil Environmental Quality, Agricultural Land Soil Pollution Risk Control Standards (Trial)" (GB15681-2018). The pH value and heavy metal content of farmland soil in the Jiulong River Basin were compared with the standard in this study. The results are shown in Fig. 3. Cd content in farmland soil exceeded the soil pollution risk screening value at 32.4% of sampling points, while Zn, Pb, and Cu content exceeded the soil pollution risk screening value at 15.5%, 14.1%, and 12.7% of sampling points, respectively. This result indicated that there might be pollution risks in some areas of farmland soil in the Jiulong River Basin, and routine monitoring of farmland soil environment and monitoring of pollutants in agricultural products produced in this area should be strengthened.

Characteristics of heavy metal enrichment and migration in rice plants

Bioenrichment factor Bioconcentration factor (BCF), also known as bioconcentration factor, can represent the absorption of heavy metal elements by plants from the soil and their enrichment in the plant's body[11]. The calculation formula is:

$$BCF = C_{plant}/C_{soil} \quad (1)$$

In the formula: BCF is the biological enrichment factor; C_{plant} is the heavy metal content of a certain organ in a plant; C_{soil} is the concentration of heavy metals in the soil.

The bioaccumulation factors of heavy metals in the roots of rice plants in the Jiulong River Basin (BCF roots) and the bioaccumulation factors of heavy metals in rice plants (BCF rice) were calculated separately, as shown in Fig. 4. From the calculation results, it could be seen that there were significant differences in the biological enrichment factors of different heavy metal elements.

For the bioaccumulation factors (BCF roots) of heavy metals in rice roots, they could be roughly divided into two categories based on their numerical values. The first type of BCF roots was generally greater than 1, mainly including Cd and As, which were easily absorbed by rice plant roots from agricultural soil. The average bioaccumulation factors (BCF roots) for Cd and As in the roots of rice plants in the Jiulong River Basin were 4.00 and 3.66, respectively, with the highest values reaching 10.91 and 12.76, respectively. It could be seen that Cd and As in farmland soil are easily absorbed by the roots of rice plants. Studies have also shown that rice plants have a strong ability to absorb Cd in agricultural soil. Even in the middle and later stages of rice plant growth, the absorption of other heavy metals by rice plants weakens, but the absorption of Cd remains strong[3, 12]. The second type of BCF roots were generally between 0.1 and 1, mainly including Cr, Ni, Cu, Zn, and Pb. The ability of rice plant roots to absorb these elements from farmland soil was average. However, it was also found that the bioaccumulation factor (BCF root) of these elements at individual sampling points was greater than 1, indicating that under the influence of other factors such as soil physicochemical properties and agricultural activities, the enrichment ability of rice plant roots to heavy metals may change[13]. The third type of BCF root was basically less than 0.1, mainly composed of Hg, which was difficult for rice plant roots to absorb from farmland soil. Studies have shown that plant roots can chelate with heavy metals through root exudates to prevent heavy metals from being absorbed by the roots in the soil, thereby controlling the migration of heavy metals to plants[14].

For the bioaccumulation factors (BCF rice) of heavy metals in rice plants, they could be roughly divided into two categories based on their numerical values. The first type of BCF rice was generally greater than 0.1, mainly including Cu, Zn, and Cd, which were relatively easy to accumulate from agricultural soil in rice. The second type of BCF rice was generally less than 0.1, mainly including Cr, Ni, As, Pb, and Hg. Rice was relatively less likely to accumulate these elements from farmland soil. Comparing BCF roots and BCF meters, it could be found that BCF roots were much larger than BCF meters. This indicates that after the roots of rice plants absorb heavy metals from farmland soil, a small amount of heavy metals will eventually accumulate in the rice through the migration of roots and stems. Research has shown that rice plants have a tolerance mechanism for heavy metals. In order to avoid the toxic effects of heavy metals, rice plants will produce a series of physiological effects to prevent the migration of heavy metals to the grain part[15].

Migration factor The transfer coefficient (TF) is the ability of heavy metals to transfer from plant roots to stems, leaves, grains, and other locations, and can reflect the situation of heavy metals transferring from plant roots to other aboveground organs of the plant[16]. The calculation formula is:

$$TF = C_s/C_r \quad (2)$$

In the formula: TF is the migration coefficient; C_s represents the heavy metal content in different tissues of rice plants (stems, leaves, rice husks, and brown rice); C_r represents the heavy metal content in the roots of rice plants.

The migration factors (TF) of heavy metals in the aboveground tissues of rice plants in the Jiulong River Basin were calculated separately, as shown in Fig. 5. From the calculation results, it could be seen that there were significant differences in the migration factors of different heavy metal elements in the same tissue, and there were also significant differences in the migration factors of the same heavy metal in different tissues. Overall, the heavy metal migration factors in the stems and leaves of rice plants were significantly higher than those in rice husks and brown rice.

The difference in migration ability of heavy metal elements between different tissues of rice plants may be related to the properties of heavy metals themselves and the physiological mechanisms of rice plants. Cu and Zn are essential elements for plants, and their migration ability is strong in rice plants. From the comparison of migration factors in different parts of rice plants, it could be seen that the differences in migration factors of Cu and Zn in each part were relatively small, and Cd and Hg also had similar characteristics. Rice mainly absorbs Cd from the soil through root cells and transfers it to other parts, ultimately accumulating in the rice. During the absorption process of Cd, the xylem plays an important role in transportation, and Cd is more likely to migrate from the roots to the aboveground parts in rice plants[17]. Studies have shown that rice has a strong ability to accumulate Hg, meaning that the Hg absorbed by rice plants is more easily transferred to the rice[18]. At the same time, it could be seen that there were significant differences in the migration factors of Cr, Ni, and Pb in various parts, especially in the comparison between the roots and rice. This result indicated that after absorbing Cr, Ni, and Pb from farmland soil, the roots of rice plants migrated less to the aboveground parts. This result is consistent with existing research[19-20]. The migration ability of rice plants to As is also very small. Studies have shown that the absorption of As by plants mainly depends on the type of arsenate, which is often blocked outside the root cells, with little absorption. The absorbed As is mainly concentrated in the roots and xylem, and rarely migrates to the grain[21].

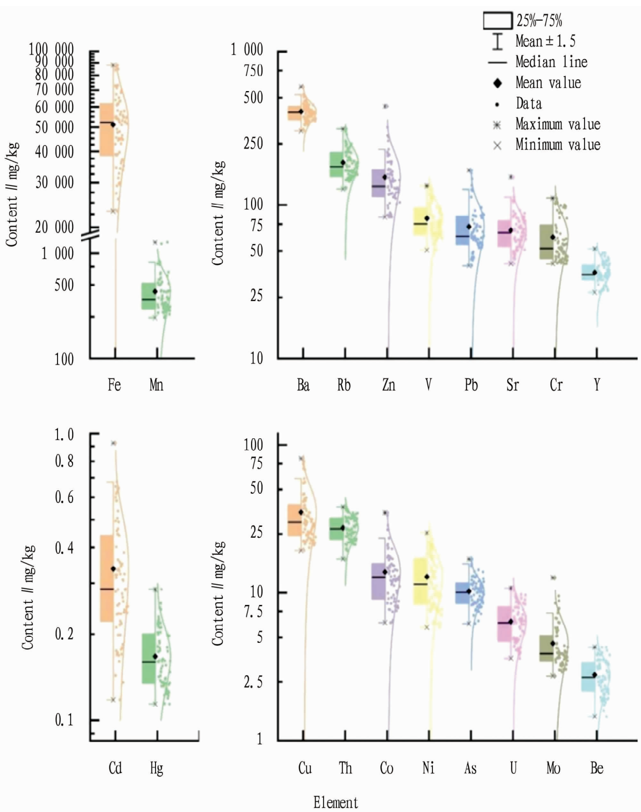

Fig. 3 Concentrations of heavy metals in agricultural soils of Jiulong River Basin

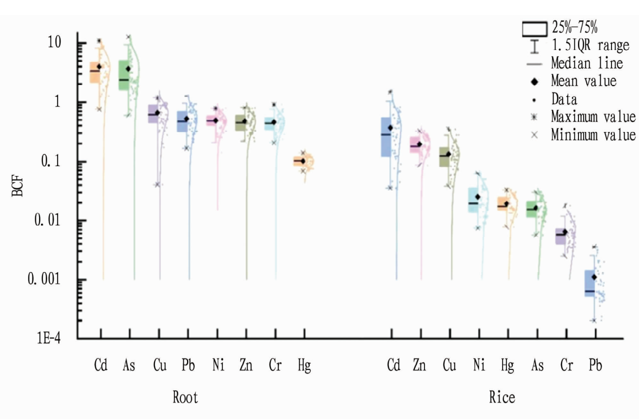

Fig. 4 Heavy metals bioconcentration factors in rice roots in the studied area

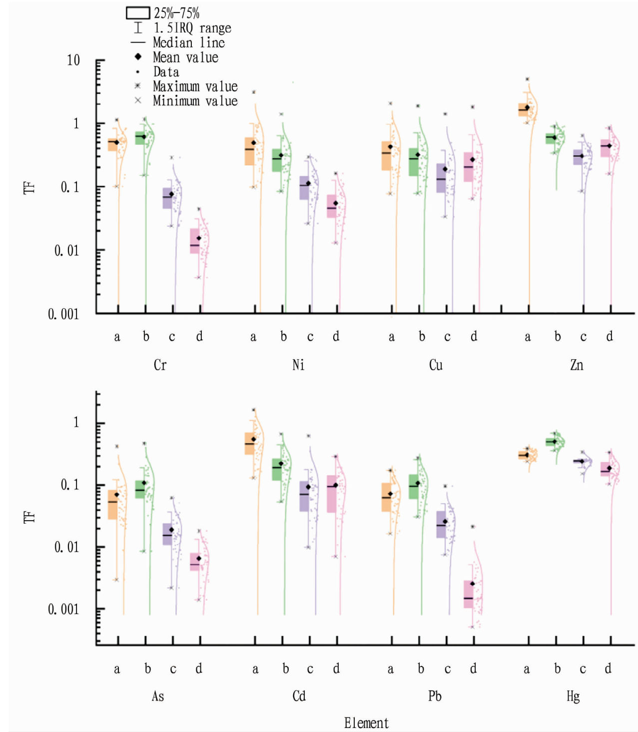

Fig. 5 Heavy metal transport factors of rice plants in the study area

Conclusions

(1) The pH value of farmland soil in the Jiulong River Basin was 4.92–7.94 (average 5.95), mainly slightly acidic. The soil organic matter content ranged from 11.26 to 58.67 g/kg (the average value was 26.94 g/kg), which was at the third level of fertility. The cation exchange capacity was 1.47–16.75 cmol (+)/kg (average 7.33 cmol (+)/kg), and the overall fertility was at a moderate level. The conductivity was 20.45–422.9 μS/cm (average value of 95.95) μS/cm, generally no salt damage occurs (*i.e.* the phenomenon of excessive soil salinity).

(2) Most heavy metals in the soil of the Jiulong River Basin were enriched relative to the soil environmental background values, with significant enrichment of Cd, Pb, Hg, and Sr. The content of Cd, Zn, Pb, and Cu in farmland soil exceeded the soil pollution risk screening value in 32.4%, 15.5%, 14.1%, and 12.7% of the areas, respectively. Therefore, it is necessary to strengthen the detailed investigation of soil heavy metal pollution. The spatial distribution of various heavy metals in farmland soils in the Jiulong River Basin showed significant spatial differences, with some heavy metals exhibiting significant spatial variability and possibly being influenced by more human activities.

(3) There were significant differences in the distribution of different heavy metal elements in various tissues of rice plants. Among them, As and Pb mainly accumulated in the roots; Zn mainly migrated to the aboveground part, while Cr, Ni, Cu, Cd, and Hg had similar abilities to accumulate in the roots and migrate to the aboveground part. The results of bioaccumulation factors indicated that Cd and As were more easily absorbed by roots; and it

was difficult for the roots to absorb Hg, while the ability of the roots to absorb other elements was relatively average. The migration factor results indicated that there were significant differences in the migration factors of different heavy metal elements in the same tissue, and there were also significant differences in the migration factors of the same heavy metal in different tissues. Overall, the migration factors of heavy metals in rice plant stems and leaves were significantly higher than those in rice husks and brown rice.

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