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A N I N T E R N A T I O N A L J O U R N A L

Distribution of copper in soil and rice system of Hainan Island, China

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ABSTRACT

This research aimed to discover the distribution and the primary influence factors of Cu in the soil-rice systems of tropical farmland. Soil samples of farmland and rice plant (stalk and polished rice) from the western region of Hainan Island were collected and studied. The results showed that the average Cu content in the topsoil of the study area was 15.75 mg kg^{-1}; the highest Cu content (45.92 mg kg^{-1}) was found in the rice fields of the northern area, where pyroclastic parent material is distributed. Thus, there is a potential for Cu contamination of the rice grown in this region. The average contents of Cu in the rice stalks and polished rice were 16.9 and 5.68 mg kg^{-1}, respectively, indicating that the stalks had a larger capacity for Cu bioaccumulation than the polished rice. The bioaccumulation factor (BAF) of Cu in rice was found to decrease with increased Cu contents in the soil. In regards to the northern farmlands with high Cu contents in the soil derived from pyroclastic deposits, an alkaline fertilizer should be used to prevent the risk of Cu pollution in the polished rice, as soil acidification can promote the uptake and accumulation of Cu to some extent.

Key words: rice; copper; arable land; Hainan

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INTRODUCTION

Heavy metal pollution control is gaining attention, as heavy metal pollution in farmland is becoming an increasingly dire issue (Chen *et al.*, 2011; Xin *et al.*, 2011). In recent years, nearly one fifth of China's farmland has faced heavy metal pollution to some extent, resulting in a drop of more than 10 million tons in the annual food grain output (Zhao, 2004). Copper (Cu) is necessary for the normal growth of plants and animals, but excessive Cu can be harmful (Alloway, 1990; Chen, 1996; Wang *et al.*, 2005). Moderate amounts of Cu in the human body are beneficial and even have anti-cancer properties, but high levels can be harmful (Kabata Pendias and Pendias, 2001; Xia and Lu, 2011).

Because rice is a staple food throughout the world, its Cu content has a significant effect on the Cu intake by human being. Thus, the content distribution of Cu in soil-rice systems is a concern to the academic community (Zhao *et al.*, 2012; Zheng *et al.*, 2005). Rice is a main food crop grown on Hainan Island. In 2011, rice fields made up 74 percent of the island's total food-growing land area (SBHP and SONBSH, 2012), which means the rice's Cu content has a large bearing on the Cu intake of local residents. Previous research projects focused on heavy metal distributions in the soil and ecological risk assessments of some regions of the island (Geng *et al.*, 2012; Tan *et al.*, 2011; Wang *et al.*, 2013), but few studies have investigated the distribution of Cu in the soil-rice systems. Therefore, this research examined the distribution and primary factors influencing Cu in the soil-rice system of the island's western agricultural area. Soil and rice samples collected from this region were studied with spatial analysis techniques. The results of this research can provide a basis for further investigation of the distributions of Cu and other trace elements in soil-rice systems.

MATERIALS AND METHODS

Study area

The study area included four counties in the western region of Hainan: Danzhou, Baisha, Changjiang, and Dongfang, covering approximately 13300 km^2. This area has a tropical monsoon climate with an average annual temperature of 22-26° C and average annual rainfall of 1150-1815 mm. The northwestern study areawas lower in elevation than the southeastern hills and mountainous terrains. In the southeastern part, the primary parent material was residual clastic sediments, covering 12% of the study area. In the western coastal region, the soil was formed from marine sediments, making up 17% of the soil. In the northern region and the central plains area, the soils were derived from pyroclastic deposits (2%) and residual acid igneous rocks (45%), respectively. Fluvial (5%) and acid metamorphic (7%) parent materials were also scattered in study area (Figure 1).

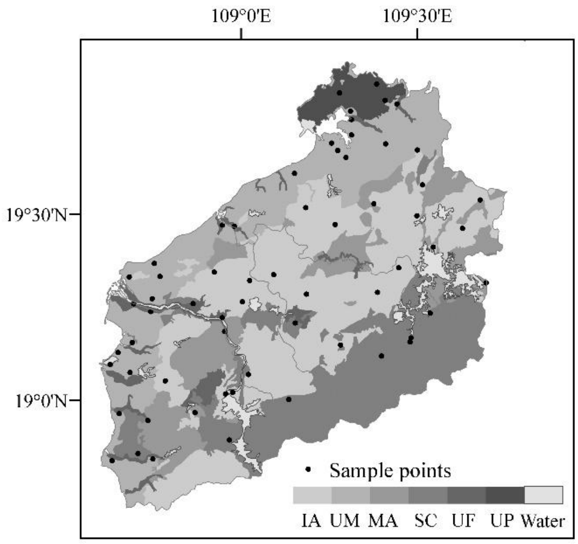

Figure 1 - Distribution of soil parent materials and sample points in the study área.

IA: acid igneous, MA: acid metaprophic, SC: clastic sediments, UF: fluvial, UM: marine, UP: pyroclastic, Water: river and lakes.

Sampling and analyses

A total of 63 top soil samples were collected from upper 20 cm in study area. Each sample weighed 2 kg, and was obtained by quartering a mixture of the soils from 5-10 sampling points. A total of 126 rice samples, including 63 groups of rice stalks and grains, were collected from 10-15 rice plants around the soil sampling points. And the samples were collected at the rice harvest season, since it is the best stage to represent contents distribution of Cu in rice grain and stalk.

After being air-dried at room temperature, the soil samples were crashed and sifted through a nylon sieve (2 mm) for soil pH and cation exchange capacity (CEC) analysis. Then, they were sifted through two additional nylon sieves (0.25 mm and 0.149 mm) to measure the contents of organic matters and total Cu in soil. The rice samples, after being washed with deionized water, were treated for 30 min for deactivation of enzymes at 105° C and then dried at 75° C for one week. The rice grains were threshed by hand and then decorticated and processed by machine to obtain the polished rice. Finally, the stalks and polished rice grains were crushed and sifted through a nylon sieve (0.149 mm) for the measurement of Cu content.

To measure the soil pH using glass electrode, the soil samples were mixed with water at a ratio of 5:1 (w/v). After oxidized by $K_2Cr_2O_7$, the concentration of organic matters in soil was measured by the titration method. The CEC was determined by the Kjeldahl distillation and titration method, after extracted with NH_4OAc. Then, after heating and digesting the soil and rice samples with $HClO_4$ and HNO_3, an analysis of the total Cu amount was conducted using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Lu, 2000).

Statistical analyses

All statistical analyses were performed using SAS 9.0. Analysis of variance was used to assess significant differences between different parameters, the confidence interval for the Student t-test was calculated at α=0.05. The distribution of sampling points and soil Cu content were plotted using the spatial analysis function of ArcGIS 10.0, and the scatter plots were presented with Excel 2007.

The bioaccumulation factor (BAF) of trace elements in plants, the ratio of trace elements contents in plants to soil, can indicate the accumulation ability of trace element of plants. In this study, the BAF of Cu in rice plant was calculated by equation 1:

$$BAF_{\text{Cu in rice}} = C_{\text{rice}} / C_{\text{soil}} \quad (1)$$

Where, C_{rice} and C_{soil} were Cu concentration in rice plant and soil, respectively.

RESULTS AND DISCUSSION

Soil properties and Content of Cu in soil

The soils had weak acidic conditions in study area (Table 1), with soil pH ranging from 4.79 to 8.34, and the average soil pH 6.06. The content of organic matters in soil of research area was 30.62 g kg^{-1}. The CEC was 15.2 $cmol_c$ kg^{-1} and varied from 5.3 to 30.0 $cmol_c$ kg^{-1}(Wang et al., 2014).

Table 1 - Statistical summary of soil properties

	Min	Max	Median	AM±ASD [†]	Geometric mean
pH	4.79	8.34	5.81	6.06±0.87	6.01
Organic matters (g kg^{-1})	13.27	60.51	30.17	30.62±8.51	29.58
CEC ($cmol_c$ kg^{-1})	5.3	30.0	15.2	15.2±5.5	14.2

[†] AM±ASD: Arithmetic mean ±arithmetic standard deviation

The content of Cu in the topsoil of the study area ranged from 2.82 to 49.73 mg kg^{-1} with an average of 15.75 mg kg^{-1} (Table 2). The relatively low content of Cu in the soil suggested a small ecological risk. The content of Cu in the topsoil varied depending on the type of parent material, and its spatial distribution was determined by the distribution of parent materials. In the study area, the soil derived from pyroclastic sediments had the highest content of Cu at 45.92 mg kg^{-1}, compared to 13.24 and 11.29 mg kg^{-1} in the soils derived from clastic sediments and fluvial deposits, respectively. The Cu contents were all lower than 10 mg kg^{-1} in the soils derived from residual acid igneous, metamorphic rocks and marine sediments. In terms of spatial distribution, the soils with high Cu contents were mainly distributed in the northern area of Danzhou and the southern region of Baisha (Figure 2). The distribution of Cu content in the topsoil showed a similarity to the distribution of parent materials, demonstrating that the former was closely associated with the latter. Alloway (1990), Lu *et al.* (2012) and Wang *et al.* (2013) also concluded that the parent material was one of main factors influencing heavy metal concentrations in soil.

Table 2 - Concentrations distribution of Cu in soil of study area

Parent materials	N	Range	Median	AM±ASD†	CV‡
		mg kg-1			%
Acid igneous	20	2.82-18.23	5.13	6.18±4.23 bc	68.4
Acid metaprophic	5	4.15-12.50	7.44	7.88±3.73 bc	47.3
Clastic sediments	8	6.41-19.65	12.92	13.24±4.88 b	36.9
Fluvial	7	7.62-17.21	11.39	11.29±3.50 b	31.0
Marine	20	1.94-14.88	7.00	7.87±4.11 bc	52.2
Pyroclastic	3	35.56-49.73	42.11	45.92±5.39 a	11.7
Total	63	2.82-49.73	7.31	15.75±9.10	57.8

†AM±ASD: Arithmetic mean ± arithmetic standard deviation, values with different superscripts in a column differ significantly (P<0.05). ‡CV: Coefficient of variation.

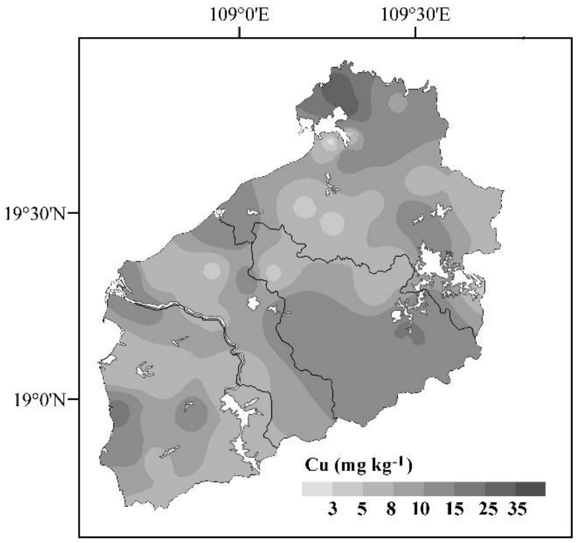

Figure 2 - Spatial distribution of Cu in soil of study area

Content of Cu in the rice

The content of Cu in the rice stalks ranged from 10.79 to 23.65 mg kg^{-1}, with an average of 16.85 mg kg^{-1}; and the Cu content in the polished rice was in the range of 3.65 to 8.43 mg kg^{-1}, with an average of 5.68 mg kg^{-1}, which was much lower than that in the rice stalks (Table 3). This difference demonstrated that the element Cu was more likely to accumulate in rice stalks, consistent with previous research findings (Kang and Xie, 2006). In order to maintain the Cu homeostasis in young leaves, the transport of Cu via xylem to mature leaves was be inhabit while the transport via phloem to young leaves was promoted (Ando *et al.*, 2013; Zheng *et al.*, 2012). Zheng *et al.* (2012) also indicated that Cu was more tend to be accumulated in flag leaf and husk than rice grain in the reproductive stage of rice plant.

The content and distribution of Cu in the rice was not only influenced by the self-regulatory mechanism of the plant, but also by the concentration of Cu in the soil. The results revealed that the Cu content was more in the rice stalks and grains with increased Cu content in the soil. However, the BAF of Cu in rice plant, the ratio of Cu concentration in rice plant to soil, was found to gradually decrease with an increasing Cu concentration in soil (Figure 3), indicating that an increase in the Cu content in the soil reduced the plant's capacity for Cu bioaccumulation. This may be attributed to the Cu saturation in the rice and the down regulation of the plant (Zhao *et al.*, 2003). Thounaojam *et al.* (2012) indicated that doxidative stress of rice plants were induced as Cu concentration in soil elevated, while the stimulated anti-oxidative system of rice, which generate antioxidant enzymes, can set off against Cu induced oxidative stress and inhabit the accumulation of Cu in rice stalks and grains. Therefore, it follows that high Cu contents in soils derived from pyroclastic parent material do not pose a risk of Cu contamination in polished rice due to the rice's self-regulatory mechanism.

Table 3 - Contents distribution of Cu in rice plants

	Range	Median	AM±ASD†	CV‡
	mg kg-1			%
Polished rice	3.65-8.43	5.39	5.68±1.28 b	22.5
Stalk	10.79-23.65	16.80	16.85±2.88 a	17.1

†AM±ASD: Arithmetic mean ± arithmetic standard deviation, values with different superscripts in a column differ significantly (P<0.05). ‡CV: Coefficient of variation.

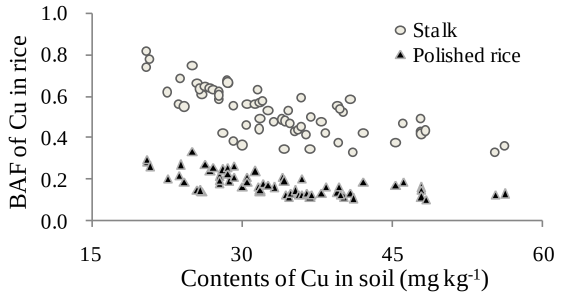

Figure 3 - Relationship between the BAF of Cu in rice and Cu content in soil

The gradual pH decrease in China's farmland soil in recent years demonstrates severe soil acidification (Guo *et al.*, 2010), which greatly impacts the biological availability of certain trace elements in the soil. Since the second national soil survey was conducted in the 1980s, Hainan's farmland has faced serious soil acidification (Wei *et al.*, 2013). Due to the Cu absorbing capability of soil minerals from soil solution was determined by the surface charge carried by adsorbents, and the surface charge was mainly controlled by soil pH, the soil acidification level was one of the most important influence factors to availability of Cu in soil (Kabata Pendias and Pendias, 2001). Studenikina (1999) also indicated that the binding of Cu by soil was highly dependent on soil pH. Therefore, it was necessary to analyze the influence of the soil pH on the bioaccumulation of Cu in polished rice. The results showed that the decrease in soil pH promoted the bioaccumulation of Cu in the polished rice, indicating that soil acidification enhanced the Cu bioaccumulation capacity of the polished rice to some degree (Figure 4). For this reason, farmland with high Cu contents in soil formed from pyroclastic deposits should be properly treated with alkaline fertilizer to avoid excessive Cu bioaccumulation in polished rice due to soil acidification.

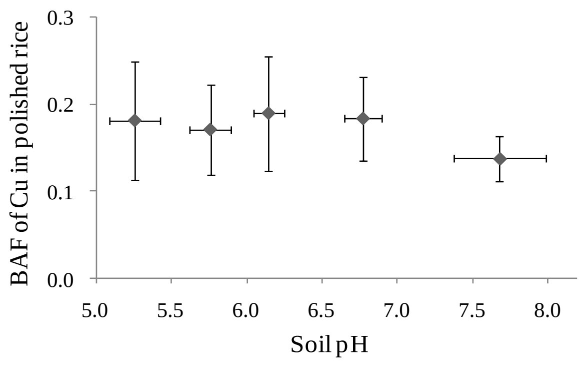

Figure 4 -Relationship between the BAF of Cu in polished rice and soil pH

CONCLUSION

In the western region of Hainan Island, the overall Cu content in the farmland topsoil was generally low although unevenlydistributed. The highest Cu content, found in the northern area where the topsoil was derived from pyroclastic parent material, was measured at 42.47 mg kg^{-1}. The results of the study revealed that the use of chemical fertilizers and pesticides, together with a high multiple cropping index, increased the Cu bioaccumulation in the rice, posing a potential risk of Cu contamination. The rice stalks showed a greater capacity for Cu bioaccumulation than the polished rice. It was also discovered that the Cu bioaccumulation factor of the rice (including stalks and grains) decreased with higher levels of Cu in the soil. In addition, soil acidification was found to promote the Cu bioaccumulation in the polished rice to some degree. Therefore, farmland soil derived from pyroclastic deposits with high Cu contents should be properly treated with alkaline fertilizer to avoid the potential risk of Cu contamination in polished rice that is posed by soil acidification.

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