Distribution of selenium and cadmium in soil-rice system of selenium-rich area in Hainan, China

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Abstract: Rice, which is the staple food in East Asia, is a source of Selenium (Se) and Cadmium (Cd). The distribution of Se and Cd in soil-rice system is significant to human nutrition and public health. This study is to explore the distribution of Se and Cd in arable land soils and their distribution in polished rice and stalks of Se-rich area. A total of 63 soil samples and 126 rice samples (63 groups of rice grains and stalk samples) were collected from West Hainan Island to determine Se and Cd concentrations. The results suggested the concentration of Se in soil was higher than average level in China, and Cd content was lower than the agricultural land-use threshold of China. The distribution of Se and Cd in arable land soil was primarily determined by diagenesis and mineralization. Se and Cd were more inclined to accumulate in stalks than rice grains, and the contents in polished rice were correlated with that in stalk. Acidification of arable land soil will threaten human nutrition and health for the bioaccumulation factor of Se in polished rice decreased significantly with the decrease of soil pH, while that of Cd in polished rice increased significantly. Therefore, application of lime or alkaline fertilizers in arable land soil of Se-rich area can promote the accumulation of Se in polished rice but reduced the intake of Cd in rice crops.

Keywords: Selenium, cadmium, rice, factor analysis, Hainan.

INTRODUCTION

Selenium (Se) is nutritionally essential to physical health. Se deficiency is a cause of Keshan Disease (Beck *et al*., 2003; Gerla *et al*., 2011; Li *et al*., 1982). Rice, as staple food in East Asia, is one of important Se intake sources. Rice contributed over 80 percent of total Se intakes to human body (Tarit *et al*., 2003). The content of Se in human body is largely depended upon rice and finally Se level in soils. Some part of China are Se deficient, and some provinces, have the rice grains Se level are below the critical point standard (Chen *et al*., 2002; Wang and Gao, 2001). It is necessary to identify influencing factors of Se distribution in soil and rice system in order to increase the content of rice grains Se.

Cadmium (Cd) is a common contaminant in arable land soils (Kabata-Pendias and Pendias, 2001; Jia *et al*., 2010). Reportedly, Cd soil contamination and Cd polluted rice were found in several provinces in China (Huang *et al*., 2007; Zhai *et al*., 2008; Zhang *et al*., 2011). As previously stated, rice is staple food in East Asia, thus it is significant to control Cd content in polished rice or arable land soils (Bolan *et al*., 2013; Simmons *et al*., 2005).

Recent survey results indicated that the area of Se-rich soil ($C_{Se} \geq 0.4$ mg kg^{-1}) was 9545 km^2, or 27.5% of total area of Hainan Island (CGS, 2011). The sown area of rice, the most important grain crops in Hainan, was 32.43 km^2, or 72.2% of the total grain crops sown area of Hainan in 2010 (SBHP and SONBSH, 2011). Therefore, it is favorable to develop Se-rich rice in this area. However, soil acidification occurred in Hainan recent years, which was resulted in excessive application of chemical fertilizers (Guo *et al*., 2010; Lesturgez *et al*., 2006). Soil acidification will reduce Se supply ability of soils (Kabata-Pendias and Pendias, 2001; Wang and Gao, 2001) and will also increase Cd availability fraction in soils (de Matos *et al*., 2001; McBride *et al*., 1997; Scheuhammer, 1991). The purpose of this study, taking West Hainan Island as study area, is to explore the distribution of Se and Cd in arable land soils and their distribution in polished rice and stalk, because of importance of distribution of Se and Cd to human nutrition and public health.

MATERIALS AND METHODS

Study area

The study area is located in west Hainan Island, which has four municipal counties, including Danzhou, Changjiang, Baisha and Dongfang (fig. 1). The study area has the typical monsoon tropical climate, with annual mean temperature of 22-26 ºC, and annual average precipitation from 1,000 mm on west to 1,600 mm on east.

Sampling and analytical work

Soil and rice samples were collected in study area in 2012 (fig. 1). Rice plant samples were washed by deionized water and then divided into rice grains and stalks (leaves and stem). Soil samples were also collected from upper 20 cm in each sample site. To avoid local variability, five

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**Corresponding author:* e-mail: dfwang@vip.163.com samples within a 10-meter-diameter sample site were mixed into one sample in the field. A total of 63 soil samples and 126 rice samples (63 groups of rice grain and stalk samples) were obtained.

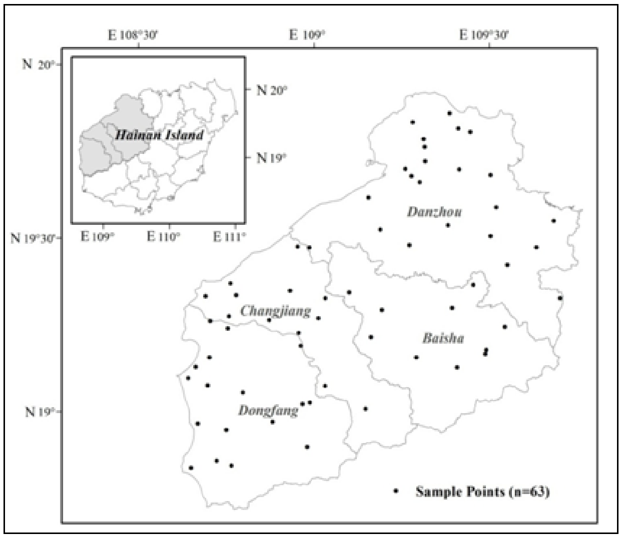

Fig. 1: Study area and sample sites.

The soil samples were air-dried at room temperature, crushed and passed through 2 mm nylon mesh sieve for soil pH and cation exchange capacity (CEC) analysis. Twenty grams of soil sample was ground to pass through 0.25 mm nylon sieve for organic matters (OM) analysis, and 0.149 mm nylon sieve for soil Se, Cd, Pb, Zn, Hg, Si, K, Ca, Mg, Fe and S analysis. The rice plant samples were dried at 75℃ for one week. The stalk and polished rice grain were crushed and passed through 0.149 mm nylon mesh sieve, respectively.

The soil pH was measured using glass electrode, at 1:5 (w/v) ratio of soil: Water (Lu, 2000). After oxidized by $K_2Cr_2O_7$, the concentration of OM in soil was measured by the titration method (Lu, 2000). The CEC was determined by the Kjeldahl distillation and titration method, after extracted with NH_4OAc (Lu, 2000). The concentrations of Se and Hg were determined by Atomic Fluorescence Spectrometry (AFS) and other elements were measured by Inductively Coupled Plasma-Atomic Emission Spectrograph (ICP-AES), after digesting samples (soil and rice) with analytically HNO_3 and $HClO_4$ by electric hot plate (Lu, 2000).

STATISTICAL ANALYSIS

Statistical analysis was performed using the SAS System for Windows 9.00. Analysis of variance was used to assess significant differences between different parameters, the confidence interval for the Student t-test was calculated at α=0.01.The Factor Analysis (FA) allows a considerable reduction in the number of variables and the detection of structure in the relationships of different parameters. FA was applied to reduce the dimensionality of a dataset and to obtain the main influence factors of Se and Cd distribution in soil and rice.

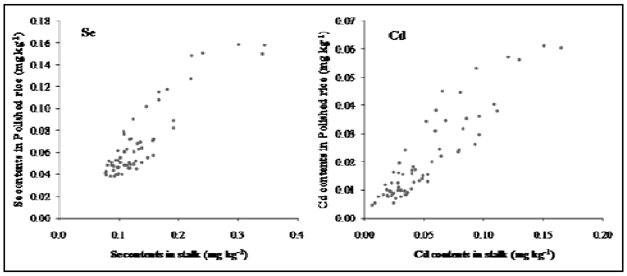

Fig. 2: Relation between the contents of Se, Cd in polished rice and stalk.

RESULTS

Soil properties and contents of Se, Cd in soil

The arable land soils had weak acidic conditions in study area (table 1), with soil pH ranging from 4.79 to 8.34. The organic matters was relative richer in soil, which was 30.62 g kg^{-1}. The CEC was 15.20 $cmol_c$ kg^{-1} and varied from 5.30 to 30.30 $coml_c$ kg^{-1}.

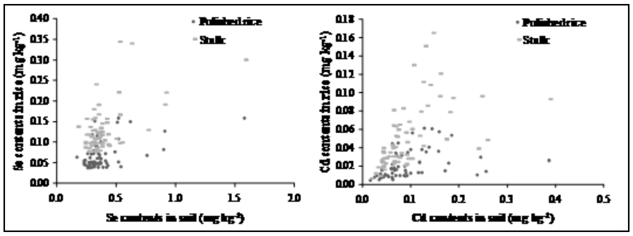

Fig. 3: Relation between the contents of Se, Cd in rice and soil.

Averagely, the content of soil Se of the study area exceeded national averages and Hainan Island means (table 2). However, the concentration of Cd in this study was generally consistent with that of arable land soil of China. According to China's Environmental Quality Standard for Soils, the Cd concentration of all soil samples was lower than 1 mg/kg^{-1}, the agriculture land-use threshold. Soil samples were divided into two groups according to the contents of Se in soil: Se-rich soil ($C_{Se}\geq$ 0.4 mg kg^{-1}) and other soils (C_{Se}<0.4 mg kg^{-1}). The concentrations of Se and Cd significantly differed between Se-rich soil and other soils (table 2).

Contents of Se and Cd in rice

The concentrations of Se and Cd in stalk were significantly higher than polished rice (table 3). The concentration relations of Se and Cd in polished rice and stalk were shown in fig. 2. Both of the concentrations of

Table 1: Statistical summary of soil properties

	Range	Median	AM±ASD [1]	GM±GSD [2]
PH	4.79-8.34	5.81	6.06±0.87	6.01±1.14
Organic matters (g kg^{-1})	13.27-60.51	30.17	30.62±8.51	29.58±1.30
CEC (cmol$_c$ kg^{-1})	5.30-30.00	15.20	15.20±5.48	14.15±1.49

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

[2] GM±GSD: Geometric mean±geometric standard deviation.

Table 2: Statistical summary of Se and Cd concentrations in soil (mg kg^{-1}).

	Se				Cd			
	Range	Median	AM±ASD [3]		Range	Median	AM±ASD	
Se-rich soil [1]	0.41-1.58	0.52	0.62±0.30	A	0.041-0.386	0.158	0.165±0.086	A
Other soil [2]	0.17-0.39	0.31	0.31±0.05	B	0.016-0.144	0.065	0.068±0.030	B
Total	0.17-1.58	0.34	0.39±0.21		0.016-0.386	0.071	0.093±0.065	
Hainan (CGS, 2011)	0.02-4.68	-	0.35±0.30		0.01-3.06	-	0.08±0.09	
China (CNEMC, 1990)	0.006-9.13	0.207	0.290±0.255		0.001-13.4	0.079	0.097±0.079	

Table 3: Distribution of Se and Cd in rice crops (mg kg^{-1}).

		Se				Cd			
		Range	Median	AM±ASD [3]		Range	Median	AM±ASD	
Polished Rice	Se-rich soil [1]	0.04-0.16	0.08	0.09±0.05	A	0.010-0.061	0.028	0.030±0.017	A
	Other soil [2]	0.04-0.15	0.05	0.06±0.02	B	0.004-0.060	0.013	0.018±0.013	B
	Total	0.04-0.16	0.05	0.07±0.03		0.004-0.061	0.015	0.021±0.015	
Stalk	Se-rich soil	0.09-0.34	0.15	0.18±0.09	A	0.028-0.151	0.080	0.078±0.034	A
	Other soil	0.08-0.24	0.11	0.12±0.03	B	0.007-0.165	0.032	0.043±0.031	B
	Total	0.08-0.34	0.12	0.13±0.04		0.007-0.165	0.040	0.052±0.035	

Table 4: Distribution of bioaccumulation factor of Se and Cd in rice plants.

		Se				Cd			
		Range	Median	AM±ASD [3]		Range	Median	AM±ASD	
Polished Rice	Se-rich soil [1]	0.08-0.30	0.13	0.15±0.08	B	0.04-0.73	0.18	0.24±0.19	A
	Other soil [2]	0.10-0.47	0.18	0.20±0.08	A	0.08-0.61	0.23	0.26±0.13	A
	Total	0.08-0.47	0.16	0.19±0.08		0.04-0.73	0.23	0.26±0.15	
Stalk	Se-rich soil	0.17-0.66	0.24	0.30±0.14	B	0.16-1.33	0.48	0.58±0.35	A
	Other soil	0.23-0.82	0.36	0.39±0.13	A	0.25-1.26	0.61	0.62±0.24	A
	Total	0.17-0.82	0.35	0.17±0.82		0.16-1.33	0.60	0.61±0.27	

[1] Se-rich soil: C_{Se}≥0.4 mg kg^{-1} (n=16)

[2] Other soil: C_{Se}<0.4 mg kg^{-1} (n=47)

[3] AM±ASD: Arithmetic mean ±arithmetic standard deviation; Means within a column followed by the different letters were significantly different (Sig.<0.01)

Se and Cd in polished rice were increasing faster when that of stalk increased, as the concentration of Se and Cd were lower in rice stalks. If the concentration of Se was above 0.3 mg kg^{-1}, Cd above 0.1 mg/kg^{-1}, the contents of Se and Cd in polished rice were increasing slowly when that of stalk increased.

The trace elements concentrations in rice stalk and polished rice of Se-rich soil were higher than other soils (table 3). However, no obvious correlation of concentrations of Se and Cd in rice plants was found with soils in this study (fig. 3). There was no direct correlation between the content of Se and Cd in polished rice and stalk with the soil pH, CEC and OM contents in soils.

Bioaccumulation factor of Se and Cd in rice

The bioaccumulation factor (BAF) of trace elements in plants, the ratio of trace elements concentration in plants to soil, can indicate the accumulation ability of trace element of plants. There were differences between the BAF of Se and Cd in different part of rice plant, and the BAF of these two elements in polished rice lower than rice stalk, which was consistent with the contents distribution of Se and Cd in them (table 4). The BAF of

Se in polished rice and rice stalk of Se-rich soil was lower than other soil significantly.

Table 5: Statistical results of factor analysis

		Factor 1	Factor 2	Factor 3	Factor 4
SiO_2		-0.95	0.08	0.12	0.13
K_2O		0.90	-0.04	-0.06	-0.20
CaO		0.83	-0.06	-0.17	-0.02
MgO		0.95	-0.05	-0.08	-0.02
S		-0.27	0.08	0.10	0.86
Fe_2O_3		0.91	-0.04	-0.13	-0.18
Zn		0.22	0.91	0.23	0.10
Pb		-0.31	0.87	0.26	0.08
Hg		-0.08	0.89	0.11	<0.01
Cd		-0.14	0.49	0.45	0.62
Se		-0.10	0.72	0.30	0.55
pH		0.73	0.06	-0.06	0.13
OM		0.03	0.04	0.13	0.94
CEC		0.85	-0.13	-0.02	-0.14
Cd content of polished rice		-0.11	0.04	0.87	0.24
Cd content of stalk		-0.23	0.12	0.77	0.39
Se content of polished rice		-0.02	0.36	0.79	-0.02
Se content of stalk		-0.15	0.35	0.76	<0.01
Initial	Eigen values	7.4	4.2	1.9	1.4
	% of variance	41.0	23.4	10.4	8.0
After Rotation	Eigen values	5.7	3.4	3.1	2.7
	% of variance	31.8	19.1	17.1	14.9

Factor analysis

FA was performed to soil elements concentrations, soil main properties and Se, Cd contents in rice plants by evaluation of principal components and computing the eigenvectors. The first four factors, in which the Eigen values were higher than 1, contribute 82.8% of the total variance in the samples and the high communality estimates suggested that the high portion of variance was explained by the first four factors (table 5).

Table 6: Correlation between Se and Cd contents with other trace elements contents in soil.

	Cd	Pb	Zn	Hg
Se	0.80**	0.77**	0.77**	0.66**
Cd		0.63**	0.59**	0.47**

**Correlation is significant at the 0.01 level (2-tailed); n=63.

Factor 1 explained 31.8% of total variance with a high negative loading from SiO_2, high positive loading from K_2O, CaO, MgO, Fe_2O_3, pH, CEC. Factor 1 may explain the weathering and pedogenesis processes of soil parent materials, due to the loss of SiO_2, and the accumulation of secondary clay minerals in soil. Factor 2, which had the high positive loading on Zn, Hg, Pb, Se, Cd and moderate positive loading on Se concentrations of rice plant (polished rice and stalk), explained the accumulation of trace elements mainly related with diagenesis and mineralization. Factor 3 may explained the accumulation of Se and Cd in rice plants, this factor may also related the distribution of available Se and Cd in soil. Factor 4 displayed the characteristics of soil OM and S contents, and can be considered as the representation of pedogeneis processes. Pedogenesis processes lead to the accumulation of OM and some mineral materials in the soil.

DISCUSSION

The difference of elements contents in Se-rice soil and other soil mainly due to the difference of soil parent materials. The factor analysis results indicated that the contents of Zn, Hg, Pb, Se and Cd in soil were inherited from soil parent materials (table 3), and the concentrations of these trace elements in soil were correlated with each other (table 6). Previous research literature also indicated distributions of soil trace elements were related to the distribution of soil parent materials (Lu *et al*., 2012; Sun *et al*., 2013).

The moderated positive loading from soil Se and Cd contents of factor 4, which reflects the pedogeneis processes, indicated that the accumulation of OM in soil was the other influence factor of Se and Cd contents in soil (table 3). Kabata-Pendias and Pendias (2001) also indicated that the distribution of soil trace elements were related the soil organic matters content.

The Se and Cd were more inclined to accumulate in rice stalk than polished rice. This may be due to the modification mechanism of rice plant, which influences the trace elements distribution in different part of rice plant (He *et al*., 2009), cause the differences of Se and Cd contents in rice stalk and polished rice. As the concentration of Se and Cd was lower than a certain contents in stalk, these two elements in rice plant will easily transfer to seeds. This shows that the rice crops can prevent excessive accumulation of Se and Cd in rice grains. The BAF of Se in rice plant (polished rice and rice stalk) in Se-rich soil was lower than other soil, which also indicated that the rice crop can prevent excessive accumulation of Se when the Se concentration increased in soils. Since the contents of Cd in soil were relatively lower, the Cd BAF of rice plants were not significantly distinct between Se-rich and other soil.

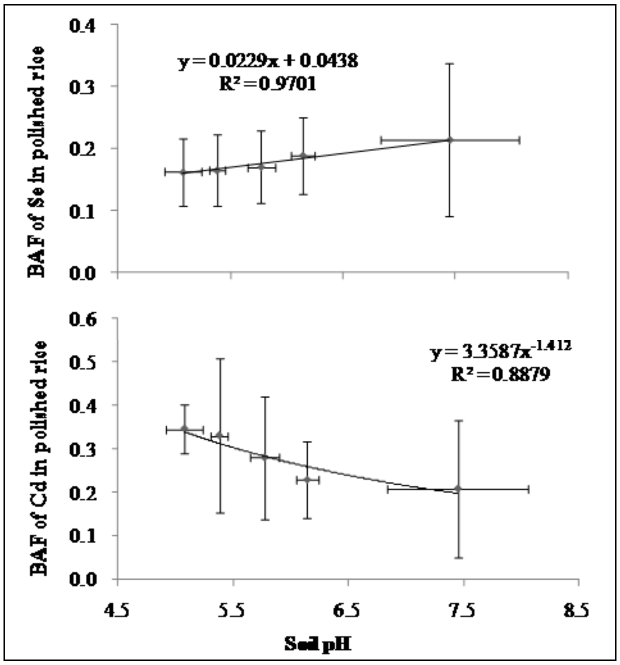

Fig. 4: Relation between the BAF of Se, Cd in polished rice and soil pH.

As previous study, the concentrations of Se and Cd in rice plants increased if their contents in soil increased (Chen *et al*., 2002; Li *et al*., 2005; Yu *et al*., 2006). Although no obvious correlation of concentration of Se and Cd in rice plants was found with soils in this study, factor analysis results indicated that the contents of Se and Cd in rice related the available contents of them in soil (table 3). The contents of Se in rice can be affected by other factors besides the soil Se contents in this study, since the content distribution range of Se in rice plants of Se-rich soil was wider than other soils. Due to the increase of OM contents lead to the organic-bound fraction of Cd accumulation in soil, which was available fraction for plants, the concentration of Cd in rice had positive loading on the factor 4, which reflect the accumulation of soil OM contents.

Although the contents of Se in rice plants (polished rice and stalk) were not closely correlated with the soil pH, due to the bioavailability of Se was sensitive to the change of soil pH (Wang and Gao, 2001), the samples were divided into five groups based on the distribution of soil pH, and the relationship of BAF of Se in polished rice with soil pH was shown in fig. 4. The BAF of Se in polished rice increased when soil pH increased, which reflect there was effects of the change of soils pH on the intake ability of Se in rice plants (Kabata-Pendias and Pendias, 2001).

It is important to increase the content of Se in polished rice, but it shall also be noted that toxicity occurs when polished rice had excessive Cd. It is of necessity to analyze the relation of BAF of Cd with soil pH, since the bioavailability of this contaminant was sensitive to variation of soil pH, too (de Matos *et al*., 2001; McBride *et al*., 1997). In contrary to Se, the BAF of Cd in polished rice increased significantly with the acidification of arable land soil (fig. 4). This attributed that the acidification of soil increased the bioavailability of Cd (Kabata-Pendias and Pendias, 2001).

Previous research indicated that application of chemical fertilizers can decrease arable land soil pH levels (Guo *et al*., 2010; Lesturgez *et al*., 2006). Due to the soil productivity was relatively lower in Hainan arable land (Cheng *et al*., 2007), the consumption volumes of chemical fertilizers increased significantly in recent years in Hainan, which will attribute the acidification of arable land soil (Qi *et al*., 2009). Therefore, application of lime or alkaline fertilizers in arable land soil of Se-rich area can promote the accumulation of Se in polished rice while restrict the intake of Cd in rice crops.

CONCLUSION

The content of Se in arable land soils was higher than average level of Hainan and China as well. The concentration of Cd was lower than the agriculture land-use threshold of China. The distribution of Se and Cd was primarily determined by processes of diagenesis and mineralization.

Se and Cd were more inclined to accumulate in stalk than polished rice. The contents of these two elements in polished rice were closely related to that in stalk. As the contents of Se and Cd in stalk reached certain contents, the concentrations in polished rice increased slowly when concentrations of stalks increased.

Soil acidification will affect the development of Se-rice rice. It will threaten public health for the BAF of Cd in polished rice increased significantly with the decrease of soil pH. Thus, application of lime or alkaline fertilizers in arable land soil of Se-rich area can promote the accumulation of Se in polished rice but reduced the intake of Cd in rice crops.

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