Distribution and Translocation of Selenium from Soil to Grain and Its Speciation in Paddy Rice (*Oryza sativa* L.)

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Selenium, an essential micronutrient for humans, is insufficient in dietary intake for millions of people worldwide. Rice as the most popular staple food in the world is one of the dominant selenium (Se) sources for people. The distribution and translocation of Se from soil to grain were investigated in a Se-rich environment in this study. The Se levels in soils ranged widely from 0.5 to 47.7 mg kg⁻¹. Selenium concentration in rice bran was 1.94 times higher than that in corresponding polished rice. The total Se concentrations in the rice fractions were in the following order: straw > bran > whole grain > polished rice > husk. Significant linear relationships between different rice fractions were observed with each other, and Se in the soil has a linear relationship with different rice fractions as well. Se concentration in rice can easily be predicted by soil Se concentrations or any rice fractions and *vice versa* according to their linear relationships. In all rice samples for Se speciation, SeMet was the major Se species, followed by MeSeCys and SeCys. The average percentage for SeMet (82.9%) and MeSeCys (6.2%) was similar in the range of total Se from 2.2 to 8.4 mg kg⁻¹ tested. The percentage of SeCys decreased from 6.3 to 2.8%, although its concentration elevated with the increase in total Se in rice. This could be due to the fact that SeCys is the precursor for the formation of other organic Se compounds. The information obtained may have considerable significance for assessing translocation and accumulation of Se in plant.

Introduction

It is well-known that selenium (Se) as an essential trace element is important for humans and animals, playing a critical role in maintaining a healthy immune system and reducing cancer risks (1). In many regions of China and other

parts of the world the dietary Se intake on average is lower than the recommended level of 40 μg d⁻¹ set by the World Health Organization (WHO) (2–4). The total Se intake in some Se deficient areas of China is below 10 μg d⁻¹ (5). To minimize the occurrence of health problems, such as cancer and cardiovascular and viral diseases, which can be induced by selenium deficiency (6), increasing the Se concentration in foods is an excellent means of Se supply to humans. Cereals as the major foodstuff may offer the best opportunity to do so (7). Rice is the world's dominant staple food; for many in Asia it contributes 35–59% of consumed energy, while accounting for 69% of protein intake (8). Nevertheless, in some countries, Se is too low in rice to be sufficient for dietary Se requirement (9). Therefore Se fertilizers have been used to increase Se concentration in cereals, and Se fertilization is considered as an effective way of biofortification (5, 10–12). For better biofortification of crop plants with Se, it is essential to understand the patterns of Se transfer from soil to plant, and the translocation from root to grain, because Se accumulation in edible parts of crop plants is directly associated with Se in soil and its distribution within the plant (6). The distribution of Se in rice grain has been studied and indicated that Se was mainly accumulated in the outer regions of the wholegrain (9, 13). However, to date there have been few reports on Se distribution and translocation in the whole rice plant, e.g. straw, husk, bran, and polished rice. The relationships between the Se concentration in different parts of rice plants and that in corresponding soils where they are grown are still unclear. This information is crucial for understanding Se absorption by root, translocation, and accumulation within the rice plant and for predicting Se concentrations in the grain.

In addition to total Se concentration in plant food, it is believed that Se speciation is important in terms of its different health benefits (7). For example, monomethylselenol and its precursors methyl-selenocysteine (MeSeCys) have been identified to be the key anticarcinogenic Se species (14, 15). Se speciation in Se-enriched rice had been studied, and selenomethionine (SeMet) was confirmed to be the major Se species (16). Nevertheless, the percentages of major Se species in rice have rarely been investigated for plants grown in soils with a range of total soil Se. It is not clear if the percentage of various Se species changes with total Se concentrations in soils and rice plants.

In the present study, intact rice plants were collected in paddy fields from different regions in Enshi, China with a wide range of soil Se levels. Se concentrations in different fractions of rice grown in soils with a large variation of total Se were investigated. The relationships between the Se level in different parts of the rice plant and soil were explored to predict Se concentrations in wholegrain or polished rice according to Se in other fractions of rice or in soil. Se speciation in rice with various total Se concentrations was determined as well, and the percentage of different Se species was investigated.

Materials and Methods

Chemicals. Guaranteed reagent nitric acid (HNO₃) (70%) and hydrochloric acid (HCl) (36–38%) were obtained from Beijing Beihua Fine Chemicals Co. Ltd. (China). Perchloric acid (HClO₄) was from Shanghai Jinlu Chemicals Co. Ltd. (China). Indium (In) was obtained from Agilent (Japan). Two standard solutions were used; one multielement was obtained from Perkin-Elmer (USA) and the other Se standard (GBW080215) from the National Institute of Metrology (China). Calibrations from both stocks were run, as part of

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the stringent analytical control measures with each analytical sample batch. No significant difference was detected in Se levels between calibrations. Protease K was purchased from Merck and Lipase VII was from Sigma. All selenium standards for its speciation, e.g. selenocystine (SeCys), selenomethionine (SeMet), selenomethylselenocysteine (MeSeCys), Na_2SeO_3 (Se(IV)), and Na_2SeO_4 (Se(VI)) were purchased from Sigma.

Rice and Soil Sampling. Forty intact rice plants were directly collected from rice fields of 4 villages (Qianping, Hongtu, Huabei, Xintang, 10 samples for each) in Enshi district, Hubei province, which is known to be one of the most typical Se-rich areas in China (17).

Quadruplicate paired rice grain, shoot, and soil (0–12 cm depth/10–20 g) subsamples, based on strategies adapted from Williams et al. (18, 19), were obtained from each paddy site. Grain, shoot, and root/soil sections were separated by scissors in the field after collection and put in separate plastic bags. A section of shoot (first 10 cm of the culm to root base) was discarded to minimize errors associated with soil contamination. In each case the soil under the sampled plants (surrounding the root) was obtained directly.

Sample Preparation for Total Se. All plant materials (grain and straw) were washed with deionized water to remove soil and dust and air-dried at room temperature ($\sim 25^\circ\text{C}$). Grain was dehulled in a motorized dehusker (JLGJ4.5, TZYQ, Zhejiang, China). Parts of wholegrain were polished by a bench-type rice polisher (JNMJ3, TZYQ, Zhejiang, China). Four fractions of grain, i.e. husk, wholegrain, bran, and polished rice (white rice), were obtained. All of the plant samples including straw were dried at 70°C in the oven to constant weight, and then all the samples except for bran were milled to fine powder using a blender (Langjia, China).

Air-dried paddy soils were powdered in the mortar, passed through an 80-mesh sieve, and then further dried in the oven at 70°C until constant weight. GBW 07602 (GSV-1) rice flour was used as the standard reference material (SRM) for whole grain, bran, and polished rice; GBW 07603 (GSV-2) bush twigs and leaves was used as the SRM for rice straw, and GBW 07405 (GSS-5) soil was used as the SRM for soil samples.

Digestion and Total Se Analysis. For all plant material samples, the procedure of digestion was as described previously (20). Briefly, 0.2 g subsamples were weighed into separate 50 mL preacid-washed polyethylene centrifuge tubes, HNO_3 (2 mL) was added, and then the tubes were kept overnight at room temperature (25°C). For quality control, 3 samples of each SRM (GSV-2) for plant materials (i.e., straw and husk), 3 SRM of rice flour (GSV-1), and 3 blanks were prepared at the same time. All samples were microwave-assisted digested (MARS, Matthew Inc., USA) using the same temperature program reported (20). After digestion the samples were cooled and then diluted to 50 mL with Millipore ultrapure water. Soil samples (0.25 g) were weighed into 100-mL block digestion tubes. Aqua regia (5 mL) was added in each tube to stand overnight and then heated at 120°C for 12 h. Then perchloric acid (4 mL) was added to each tube, followed by heating at 140°C for 24 h. After cooling, the digests were filtered and diluted to 50 mL with ultrapure water (Millipore Milli Q). Two blanks and 2 samples of SRM for soil (GBW07405) were prepared and digested together with soil samples for quality control.

The samples were then analyzed for total Se contents using an ICP-MS 7500 (Agilent Technologies). Selenium isotopes Se^{77} , Se^{78} , and Se^{82} as well as indium (In) isotopes as internal standard were measured. All samples were randomized prior to analysis.

Quality Control. The median limit of detection (LOD) from 6 microwave-assisted sample runs was $0.011\ \mu\text{g L}^{-1}$, and recovery for rice flour and straw were 123 and 137%, respectively. The median LOD for block digested samples was $1.8\ \mu\text{g L}^{-1}$, and recovery for soil was 100%.

Enzymatic Hydrolysis for Se Speciation. A subset of polished rice samples with high total Se was chosen for Se speciation. Rice flour (0.2 g) was precisely weighed into a plastic centrifuge tube, and Protease K (20 mg), lipase VII (10 mg), and 5 mL of 30 mM Tris-HCl buffer solution (pH 7.5) were added and then incubated in the dark for 24 h at 37°C water bath. During enzymolysis, the sample slurries were constantly and gently homogenized, using a rotary shaker set at 60 rpm. Hydrolyzed samples were centrifuged at 3000 rpm for 30 min. The supernatants were finally passed through 5000-Da molecular weight cutoff filters and stored at -20°C for analysis.

Selenium Speciation by HPLC-ICP-MS. High performance liquid chromatography (HPLC, Agilent Technologies 1100 series) coupled with inductively coupled plasma mass spectrometry (ICP-MS, 7500, Agilent Technologies) was used for selenium speciation. Chromatographic separation consisted of a precolumn and a Hamilton PRP X-100 anion exchange column ($4.1\ \text{mm} \times 250\ \text{mm} \times 10\ \mu\text{m}$). The mobile phase was 5 mM ammonium citrate with pH 4.3 containing 2% of methanol with a flow rate at $1\ \text{mL min}^{-1}$. Quantitation was performed using peak area measurements of the chromatographic signals by monitoring the isotope ^{82}Se . Retention time for the Se species was determined using a species mix comprising standards of $50\ \mu\text{g L}^{-1}$ SeCys, MeSeCys, selenite, SeMet, and selenate.

Statistical Analysis. One-way analysis of variance (ANOVA) was used to identify significant differences ($p < 0.05$) between Se concentration in different parts of rice, corresponding soil, and speciation. Data analysis was carried out using SPSS software.

Results and Discussion

Total Se and Its Relationship between Different Fractions of Rice and Paddy Soil. The total soil Se concentrations in different sampling sites varied about 330-fold, from 0.5 to $47.7\ \text{mg kg}^{-1}$. The highest Se in soil ($47.7\ \text{mg kg}^{-1}$) was from Huabei village, Enshi district, which is one of the most typical Se-rich areas in China (7, 21). Selenite is the predominant form of available Se in the paddy soils (42, 43). The pH values of most soils in Enshi region are from acidic to neutral, about 4.5–6.5 (17, 21), under which condition Se exists predominantly as selenite in well-drained soils (7). Relatively low pH could increase the absorption and accumulation of Se in rice (42). Se concentrations in different fractions of rice plants were rather different. The highest Se concentration is the straw, followed by bran, whole grain, polished rice, and husk. The total Se in wholegrain varied from 0.084 to $9.67\ \text{mg kg}^{-1}$. The highest total Se ($9.67\ \text{mg kg}^{-1}$) was also from Huabei, and similarly elevated levels ($59.4\ \text{mg kg}^{-1}$ for soil and $9.2\ \text{mg kg}^{-1}$ for rice grain, respectively) have also been documented by other studies (22). China has a maximum food standard limit of $0.3\ \text{mg kg}^{-1}$ Se in cereal (23), and most of the rice samples (75%) from Enshi collected in this study were in excess of this food standard.

Whole grains collected in this study were polished, and $\sim 7\%$ of total wholegrain weight was removed as rice bran (20). Rice bran has been recognized as an extremely popular source for nutrition due to its high contents of lipid, protein, vitamin, minerals, and dietary fiber (24, 25). The Se concentrations in bran were higher than those in polished rice, 1.94 times on average according to all grain samples collected in this study. The percentage of polished rice Se to wholegrain Se was similar (83.7–96.6%), which was in agreement with the previously reported results (26). Se concentration in rice bran was a bit higher than that in corresponding endosperm. Similar results have also been obtained in other cereals, such as wheat grain (9, 13, 27). A recent study has shown that Se distribution in wheat grain is very similar to that of sulfur (S) (13). Lombi et al. showed that S distribution in rice wholegrain

FIGURE 1. The relationship of Se concentrations in whole grain and their corresponding polished rice.

FIGURE 2. The relationship of Se concentration in straw with corresponding Se in different rice fractions (wholegrain, bran, polished rice, husk): wholegrain, $R^2 = 0.89$; bran, $R^2 = 0.84$; polished rice, $R^2 = 0.91$; husk, $R^2 = 0.85$.

decreased from the outer parts of the grain to the interior of the endosperm (28). This is not unexpected as Se was absorbed into the plant and follows the sulfur assimilation pathway (7). In general, the pattern of total Se concentration in grain fractions followed the order: endosperm (polished rice) < whole grain < bran. Other studies have shown that Se concentrations in rice or wheat bran were higher than brown rice or wholegrain wheat (7, 29, 30). Within the range of Se concentrations in rice samples in this study (0.084–9.67 mg kg⁻¹), a significant linear relationship between the Se level of the wholegrain and polished rice was observed (Figure 1). Wholegrain versus bran fractions and polished rice versus bran fraction also displayed a significant positive correlation with R^2 of 0.97 and 0.96, respectively (Figures S1 and S2).

There were significant correlations between straw Se and corresponding whole grain, bran, polished rice, and husk. The R^2 values were up to 0.89, 0.84, 0.91, and 0.85, respectively (Figure 2). Highly linear correlations also existed between soil Se and Se in different rice fractions including straw, husk, and whole grain with R^2 values of 0.77, 0.84, and 0.88, respectively (Figure 3). All these linear relationships indicated that the concentrations of Se in rice can be predicted by Se concentrations in any part of rice plants (i.e., straw, husk, bran, whole grain) or Se in soil. It has been reported that Se concentrations in various parts of the rice plant were positively correlated with the available Se concentrations of the top layer of Se-deficient paddy soils (31). The available Se concentration was not detected here, but it is reasonable to assume that it increases with the increase in total Se in soil.

Se in husk was much lower than bran and whole grain (Figures 2 and 3). As can be seen from Figure 3, the trend lines observed for soil-straw and soil-wholegrain were almost the same, suggesting that within the range of soil Se concentrations in this study, the accumulation of Se in straw

FIGURE 3. The relationship of Se concentration in soil with corresponding Se in different rice fractions (straw, wholegrain, husk): straw, $R^2 = 0.77$; wholegrain, $R^2 = 0.84$; husk, $R^2 = 0.88$.

TABLE 1. Ratios of Se Concentration in Different Parts of Rice to Soil or Straw^a

ratio	average	range
straw Se/soil Se	0.32	0.16–0.71
wholegrain Se/soil Se	0.23	0.1–0.69
polished rice Se/soil Se	0.21	0.09–0.61
wholegrain Se/straw Se	0.75	0.28–1.59
polished rice Se/straw Se	0.69	0.25–1.37

^a The total Se concentration in rice were from 0.48 to 47.7 mg kg⁻¹.

and grain was almost the same, both of which were greater than that in husk. It seemed that grain accumulated more Se than the corresponding husk. The reason for higher Se accumulation in grain is still unclear. Se in the husk is probably derived from the xylem transport. Selenium was translocated from root to shoot (7, 29), probably up to the husk through xylem, similar to other nutrients (32). On the contrary, most nutrients are imported into seeds through hydrostatic pressure differences established along the phloem path from source leaves to developing seeds (30, 33). It is assumed that, like other nutrients, Se accumulation in the rice grain occurs primarily through the phloem. That is, during grain development, Se compounds accumulated in the husk, where they are transported into the developing rice seed via the phloem due to the hydrostatic pressure difference and incorporated with proteins or starch granules in rice seeds (13).

The ratio values of wholegrain Se/soil Se and wholegrain Se/straw Se were calculated as (Table 1). In the whole range of soil Se tested in this study, the Se transfer factor from soil to grain ranged from 0.1 to 0.69, and the average value was 0.23 (Table 1). The average transfer factor from soil Se to polished rice Se was 0.21. It was not surprising that this value was a bit lower than the whole grain ratio (the value 0.23), because the Se concentration in bran was higher than endosperm, and a little more Se was removed by milling. The highest transfer factor was for straw-soil Se, up to 0.32 (Table 1), because Se concentration in straw is the highest among all fractions of rice. The average transfer factor for straw Se to wholegrain Se was 0.75 ranging from 0.28 to 1.59. Similarly the transfer factor for straw Se to polished rice Se was 0.69, a little lower than wholegrain (Table 1). The transfer factors for straw Se to wholegrain Se were calculated here according to the published data (34), and the values of 0.46 and 0.71 were obtained, in agreement with our results. It was reported that corn growing in Yutangba, one of the villages of the Enshi region, exhibited a much higher transfer factor for Se. The average Se in corn was up to 8.07 mg kg⁻¹, 2 times

TABLE 2. Concentration of Se Speciation (mg kg^{-1}) and Extraction Efficiency

name	SeCys	MeSeCys	Se(IV)	SeMet	unknown	Se(VI)	sum of species	total Se (extracted)	total Se (digested)	analysis efficiency (%)	extraction efficiency (%)
XT2	0.063	0.049	0.083	0.811	0.000	0.000	1.006	1.376	2.182	73.1	63.1
XT5	0.077	0.090	0.020	1.226	0.000	0.000	1.412	1.845	3.380	76.5	54.6
HB1	0.084	0.132	0.079	1.690	0.000	0.070	2.055	2.039	3.522	100.8	57.9
HB10	0.112	0.198	0.127	2.704	0.128	0.191	3.461	4.692	6.787	73.8	69.1
XT10	0.175	0.324	0.000	3.577	0.300	0.069	4.444	5.591	8.324	79.5	67.2
HB7	0.127	0.226	0.188	3.888	0.059	0.000	4.489	5.498	8.440	81.6	65.1
average										82.4	62.8

higher than corresponding soils (4.06 mg kg^{-1}) when maize grown in the soil with Se was from 1.40 to 6.91 mg kg^{-1} (17). It seemed that more Se was transferred and accumulated in the corn, but the reason is still unclear.

Se had a linear transfer from soil to grain in the Enshi region with soil Se concentrations ranging from 0.48 to 47.7 mg kg^{-1} , which might be useful in predicting the efficiency of biofortification. Se fertilizers have been widely used in some countries, such as Finland to enhance Se concentration in cereals (5, 10–12). More recently, in order to enhance Se levels in meat and dairy products in the UK, commercial Se fertilizers are applied to pasture and forage crops (35). Since there is a narrow window for Se between essentiality and toxicity, it is important that the appropriate amount of Se fertilizers are applied for different crops and soils. The linear relationship between rice grain Se and soil Se could be used to deduce how much Se fertilizers should be applied in rice fields of other, Se-deficient regions to achieve the goal of sufficient Se in grains. However, the effect of other factors affecting Se uptake by plants should be taken into account, e.g. many physicochemical properties of the soil, such as pH and redox potential, the concentration of other ions, organic matter (36–38), and different Se chemical forms in soil (5–7, 13, 39, 40), and the actual relationship between soil and plant Se may vary from soil to soil and from crop to crop. The soils sampled in this study were underlain by Permian carbonaceous strata and have roughly similar basic soil properties (21). Rice growing in similar paddy soil exhibited comparable Se accumulation capacity, which might contribute to the strong linear relationship between soil Se and plant Se. Se fertilizers occur in different forms, e.g. selenate, selenite, and Se in an organic matrix. These forms all have different soil binding properties, which results in variable transfer to plants. Further studies are needed in the future to investigate the key factors for Se translocation from soil to plant, such as bioavailable Se and its speciation in paddy soil. To the best of our knowledge, this is the first report about Se translocation from soil to grain in a wide range of soil Se levels, and a strong linear relationship was observed with Se in the soil and corresponding rice grain.

Se Speciation in Plant Tissues. Various Se species have been identified in rice, and biological activity of Se is profoundly influenced by their chemical forms. In order to get more information about Se in rice, some of the samples were chosen for Se speciation (Table 2). The average extraction efficiency was 62.8% by calculating the ratio of extracted total Se to the digested total Se, and analysis efficiency was 82.4% by calculating the ratio of the summary of Se species to extracted total Se. As can be seen in Table 2, the total Se in rice ranged widely from 2.2 to 8.4 mg kg^{-1} . In all the speciated samples, most of the Se species in rice were organic Se, up to 95.3% of total Se on average, similar to other reports in which organic Se accounted for 94.5% (9). The inorganic Se was only 4.7% in the range of 1.4 to 9.2% . Of all the Se species, SeMet was the major Se species, up to 82.9% on average, followed by MeSeCys (6.2%) and SeCys (3.9%). Another report also suggested that SeMet was the

major Se species in rice in the Enshi region (38). Whereas results of Se speciation determined by X-ray absorption near edge structure (XANES) showed that 59% of total Se were identified as MeSeCys (9). This is probably due to the method limitations when different instruments were utilized for Se speciation (9). Microbeam techniques such as XANES could only provide an indication of the different species present in the sample but are unable to provide an accurate assessment of their proportion of each species in the whole samples (28, 41); this could well be the case for elements like Se that exhibit high spatial variability in terms of distribution and speciation in rice grain (9, 28) and have generally low concentration in the matrix.

In all the rice samples tested for Se speciation, with the increase in total Se concentration in rice the concentration of major Se species, i.e. SeMet, MeSeCys, and SeCys also increased accordingly. Perfect linear relationships were observed between the Se concentration of SeMet, MeSeCys, and SeCys with total Se (Figure 4). The values of R^2 were 0.99, 0.89, and 0.84 for SeMet, MeSeCys, and SeCys, respectively. In fact, the percentage of SeMet and MeSeCys did not change within the range of total Se (2.2 to 8.4 mg/kg). The average percentage for SeMet was 82.9% in the range of 78.1–86.6% and 6.2% from 4.8 to 7.3% MeSeCys. The SeCys concentration increased with the increase in total Se in rice, but the percentage decreased from 6.3 to 2.8% in the range of total Se from 2.2 to 8.4 mg kg^{-1} . One unknown Se species was observed in a relatively high Se rice sample (Table 2) and needed to be identified in further investigation. The mechanism of Se uptake and metabolism in plants has been summarized recently by Zhu et al. (7). The inorganic Se taken up in the plant is first transformed to SeCys, and then most other organic Se species are derived from SeCys by different enzymes. It looks like that SeCys is the key precursor for the formation of other organic Se species. The decrease in SeCys in relatively high Se rice might be due to the formation of unknown Se species.

FIGURE 4. The relationship of SeMet, MeSeCys, and SeCys with the total Se concentration in polished rice. The values of R^2 were 0.99, 0.89, and 0.84, respectively, for SeMet, MeSeCys, and SeCys.

In summary, the Se concentration from high to low in different rice fractions were rice straw > bran > wholegrain > polished rice > husk. The Se concentration in bran is 1.9 times higher than corresponding polished rice. This indicated that ~13% of wholegrain Se was removed by the milling process if 7% of wholegrain was polished as bran. Significant linear relationships were observed among the Se concentration in soil, straw, husk, bran, whole grain, and polished rice in the Enshi region, China. The transfer factors from soil to wholegrain and polished rice were 0.23 and 0.21, respectively. In all rice samples tested for the Se species, SeMet was the main Se species, followed by MeSeCys, and SeCys. The percentages for SeMet and MeSeCys did not change very much, but the percentage of SeCys decreased within the range of total Se. SeMet could protect keratinocytes against UV-induced oxidative damage (44), while also reducing genotoxicity induced doxorubicin and bleomycin-induced DNA damage on human lymphocytes (45, 46). The large predominance of selenomethionine shows that Se-enriched rice in Enshi can be a promising raw material for human diets in Se deficient area. Considering most of the rice samples (75%) from Enshi were in excess of the maximum food standard limit in China (0.3 mg kg⁻¹ Se in cereal), high Se rice must be diluted with Se deficient rice to keep the Se level in the human diet under the standard.

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Supporting Information Available

Table S1 and Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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