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Determination of Selenium Concentration of Rice in China and Effect of Fertilization of Selenite and Selenate on Selenium Content of Rice

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A method of hydride generation atomic fluorescence spectrometry was applied to the determination of the selenium concentration of regular polished rice in China and selenium-enriched polished rice obtained by foliar application of selenium-enriched fertilizer in the forms of selenite and selenate. The average selenium content of regular rice was 0.025 ± 0.011 μg g^{-1}. On the basis of a daily dietary rice intake of 300−500 g suggested by the China Nutrition Society, the total selenium intake from regular rice was calculated to be 7.5−12.5 μg per person per day for an adult. The selenium contents of rice were significantly increased to 0.471−0.640 μg g^{-1} by foliar application of selenium-enriched fertilizer at rate of 20 g of Se ha^{-1} in the forms of sodium selenite and sodium selenate. The selenium content of rice by application of a fertilizer of selenate was 35.9% higher than that by a fertilizer of selenite, which showed that Se-enriched fertilizer in selenate exhibited greater efficiency in increasing Se content in rice products. The Se-enriched rice products can increase daily Se intake on average by 100−200 μg of Se per day by the consumption of 400 g of rice products if the Se level of rice products is controlled at 0.3−0.5 μg of Se g^{-1}. Because rice is a staple food in China, selenium-enriched rice obtained by bioenrichment of selenium to increase the Se content of rice could be a good selenium source for the population in selenium-deficient regions.

KEYWORDS: Rice; selenium content; daily dietary selenium intake; selenium-enriched rice

INTRODUCTION

Selenium is an essential trace element for human health and has received considerable attention for its possible role as an effective, naturally occurring, anticarcinogenic agent (*1*). Epidemiological studies reveal that selenium intake correlates inversely with death from various types of cancer (*2*). Enriching food with selenium appears to be an effective way for providing selenium to humans for cancer prevention (*3*−*7*). A Recommended Dietary Allowance (RDA) of 55 μg day^{-1} for men and women has been determined on the basis of the maximization of glutathione (GSH-Px) enzyme activity (*8*). Publication of the cancer-protective benefits of selenium has resulted in many people seeking to increase their selenium intake. However, selenium concentration of a particular food may be variable and dependent on the geographic origin of the raw agricultural product with regard to the soil in which the agricultural crop was grown (*9*, *10*). Selenium deficiency is still a very serious nutritional and health problem in China. The total human selenium intake was reported by the China Nutrition Society (CNS), to be only 26−32 μg day^{-1}, with some regions below 10 μg day^{-1} (*11*−*13*). The selenium supply is below the recommended daily intake. In these areas an endemic, often-fatal cardiomyopathy affects the population (*14*).

Supplementation of fertilizer with selenium is a safe and effective means of increasing the selenium intake of both animals and humans that is feasible in countries with relatively uniform geochemical conditions (*15*−*21*). Food system-based approaches are discussed for preventing selenium deficiency by enhancing intakes of selenium-enriched agricultural products and for reducing cancer risk by enhancing intakes of forms of the element that support antitumorigenic selenium metabolites. Plant-based selenium has been accepted as safe and effective for human selenium intake (*22*). In our previous study, we demonstrated that Se-enriched tea leaves were a safe and effective selenium source to enhance human selenium intake (*23*). China has one of the highest rice products consumptions in the world, and rice is the major foodstuff. However, the selenium content of rice products was lower, and the mainly rice-based diet contributed an inadequate amount of selenium for Chinese inhabitants (*24*).

The objectives of this study were to determine the selenium content in rice products of different cultivars grown mainly in China and the influence of foliar application of Se-enriched fertilizer with sodium selenate or selenite on increasing the

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Table 1. Selenium Concentrations of Rice Products of Different Species Cultured Mainly in China

sample location (province)	no. of samples	Se content[a] (μg g^{-1})
Beijing	3	0.035 ± 0.012
Fujian	4	0.021 ± 0.005
Guangdong	3	0.039 ± 0.018
Hebei	2	0.021 ± 0.008
Heilongjiang	3	0.034 ± 0.007
Hubei (regular areas)	2	0.028 ± 0.005
Hubei (Enshi)	2	0.226 ± 0.120
Jiangsu	9	0.019 ± 0.005
Jiangxi	2	0.028 ± 0.006
Liaoning	3	0.014 ± 0.004
Shanghai	6	0.029 ± 0.011
Shandong	2	0.038 ± 0.008

[a] Values are means of determinations ± standard deviation.

selenium content of rice products to enhance human selenium intake.

MATERIALS AND METHODS

Apparatus. Selenium determination was conducted with the method of hydride generation atomic fluorescence spectrometry (AFS). An atomic fluorescence spectrometer (AFS-610, produced by Beijing Rayleigh Analytical Instrument Corp.) was used with a hollow cathode lamp current of 80 mA. All measurements were performed in peak height mode. The digested samples were autosampled and determined by AFS.

Reagents. All solutions were prepared with deionized water. Nitric acid, hydrochloric acid, and perchloric acid of guaranteed reagent grade and potassium hydroxide, potassium tetrahydroborate, and potassium ferricyanide of analytical reagent grade were also used.

Standard Solution of Selenium. The standard solution of selenium with a concentration of 1 μg of Se mL^{-1} was prepared with guaranteed reagent grade element selenium dissolved in nitric acid and stored at 0 °C for making the standard curve in the selenium determination.

Regular Rice Samples. All regular rice samples were purchased from grocery stores in different provinces of China (**Table 1**). The polished rice samples were the representative and typical ones consumed by inhabitants in certain local areas. Samples were dried at 50 °C and then milled for selenium determination.

Selenium-Enriched Rice Samples. The plot experiment was conducted in Ganyu County, Jiangsu Province. The soil pH in this region is 7.18, and the total selenium content is 0.51 μg of Se g^{-1} of soil. There were two treatments (treatments A and B) and one control. Each plot was 4 × 7.5 m in triplicate. Treatment A was foliar spraying with 20 g of Se ha^{-1} with sodium selenite, and treatment B was the same dose of selenium with sodium selenate at 25 mg of Se L^{-1}. The sodium selenite and sodium selenate were combined with an organic carrier detailed by Hu et al. (*24*). The control was sprayed with water instead of selenium fertilizer.

The cultivar of rice was Premium No. 59 (Teyou 59). Foliar application of selenium fertilizer was conducted on August 21, 2001, when the rice was thoroughly tasseled, and the grain was hand harvested on September 28, 2001. After harvesting, the grain was dried at 50 °C, then ground into polished rice, and milled into powder for selenium determination.

Procedure. Around 1 g of powdered subsample of each sample was taken for analysis. The powdered subsample was put into a high-walled beaker and mineralized with 10 mL of a 4:1 (v/v) mixture of HNO_3 and $HClO_4$ at a constant 150 °C in a sand bath until the solution became colorless and clear.

For reduction of Se^{6+} to Se^{4+}, 5 mL of 6 mol L^{-1} HCl was added to the digested solution and heated in the same thermostatic bath until the solution became colorless and clear. Then, the digested sample was cooled and diluted to 25 mL with deionized water; 5 mL of the solution was put into a test tube, and 1 mL of concentrated HCl and 0.5 mL of 10% $K_3Fe(CN)_6$ (w/w) were added; then 1 mL of mixture was autosampled into a reaction vessel. Selenium was determined with an atomic fluorescence spectrometer.

Table 2. Effect of Fertilization of Selenate and Selenite on the Selenium Contents of Rice Products (Number of Samples $n = 3$)

Se treatment	application of Se (g of Se ha^{-1})	yield[a] (kg per plot)	Se content of rice[a] (μg g^{-1})
control	0	24.05 ± 2.16a	0.071 ± 0.002a
selenite fertilizer	20	24.54 ± 5.15a	0.471 ± 0.134b
selenate fertilizer	20	23.78 ± 0.45a	0.640 ± 0.191c

[a] Values are means of three determinations ± standard deviation. Values followed by a different letter in each column are significantly different ($P < 0.05$) from one anther.

Rice samples and blank were subjected to the same procedure. The data presented here were corrected for blank values, which were usually very low for this method.

Recovery and Accuracy. The recovery and accuracy of the Se measurements were determined using the procedure described above to determine the standard reference Se material (GBW 07603-GSV-2) manufactured by the National Institute of Mineral of China.

Statistical Analysis. Statistical analysis was performed using an SAS program for PCs (*SAS User's Guide*, version 6, 4th ed., SAS Institute, Cary, NC, 1990). Significant differences between individual treatments were determined using Duncan's multiple-range test ($P < 0.05$ as different).

RESULTS AND DISCUSSION

Recovery and Accuracy. The calculated analytical detection limit was 0.5 ng mL^{-1} under the instrumental conditions in the analyses of all samples. The certified and determined values of the reference material were 0.120 ± 0.020 and 0.121 ± 0.009 μg g^{-1}, respectively. The recovery was 101.05 ± 7.47%, which indicated that hydride generation AFS could be reliably used for rice selenium determination.

Concentrations of Regular Rice and Contributions of Selenium Intake to Chinese Inhabitants. The selenium concentrations of the regular rice, except the rice from Enshi County, Hubei Province, were <0.06 μg g^{-1}, some being <0.02 μg g^{-1} (**Table 2**). The average Se content in rice products of different cultivars cultured mainly in China was 0.025 ± 0.011 μg of Se g^{-1}, regarded as seriously low-selenium rice. Among these data, the selenium content of rice from Enshi, a naturally high selenium area in China, was 0.226 μg of Se g^{-1}, less than that determined [0.31−1.86 μg of Se g^{-1} (average of 0.605)] by Wang (*25*). Rice is the main food for inhabitants in China. However, the contribution to selenium intake for inhabitants from regular rice products was estimated to be ∼7.5−12.5 μg of Se per person per day if the mean consumption of an adult was 300−500 g of rice product as recommended by the (CNS), except for the population in Enshi, Hubei Province. Because cereal selenium was the main selenium source in the Chinese diet, lower Se in rice products may be responsible for the Se deficiency status of inhabitants in China.

Effect of Se-Enriched Fertilizer on the Selenium Contents of Rice Products. The Se contents of rice were significantly increased up to 0.471−0.640 μg g^{-1} by foliar application of selenium-enriched fertilizer with selenate or selenite compared with no selenium treatment (**Table 2**). There are no significant effects of selenium treatment on the crop yield and growth. However, the selenium content of rice by application of selenate was 35.9% higher than that by selenite, which showed that Se-enriched selenate fertilizer exhibited more efficiency in increasing the Se content in rice products.

Calculated Contribution of Se-Enriched Rice Products To Increase Se Intake. There are many Se-deficient areas in China. Table salt fortified with 15 mg of sodium selenite kg^{-1} was used as a daily Se supplement to reduce the incidence of primary liver cancer (*26*, *27*). This supplied an additional 35−50 μg of Se daily to individual diets. However, Ip et al. compared the efficacy of selenium-enriched yeast versus selenium-enriched garlic in the reduction of mammary tumors. The selenium-enriched garlic was as effective in the reduction of these tumors, regardless of whether induced by either of the two chemicals, as compared to selenium-enriched yeast. The primary form of selenium in enriched garlic is Se-methylselenocysteine, whereas the main form in enriched yeast is selenomethionine. The differences in efficacy are attributed to these different forms of selenium (*5*). Daily supplementation of 200 μg of Se was effective in cancer prevention in patients with carcinoma of the skin and in colon cancer in rats (*2*, *28*). Since the early 1980s, selenium as fertilizer has been extensively used to produce appropriate levels of selenium in feed/food crops, notably in Finland and New Zealand. An application of 10 g of Se ha^{-1} can raise the feed crop Se level sufficiently to meet the needs of livestock (*15*, *29*). A foliar spray of Se-enriched fertilizer can produce functional rice products with an optimum Se concentration acceptable for human health. The optimum Se content of rice products can be achieved by varying the concentration and amounts of Se-enriched fertilizer. When the Se level of rice products is controlled at 0.3−0.5 μg of Se g^{-1}, Se-enriched rice products can increase daily Se intake on average by 100−200 μg of Se by the mean consumption of 400 g of rice products. Because rice is a staple food in China, selenium-enriched rice obtained by bioenrichment of selenium to increase the Se content of rice is a good selenium source for the population in selenium-deficient regions.

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