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Assessment on Radioactive Uranium Contamination of Paddy Soil in Uranium Mine at Southeast China by ICP-MS

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Plasma mass spectrometry was applied to measure the level of radioactive uranium in 151 paddy soil samples collected from a uranium mine in southeast China and the uranium contamination was assessed. The results showed that the average uranium content in the paddy soil in the active mining region was 7.88 and 11.44 times the soil background value of the Jiangxi Province and of China nationwide, respectively and was 14.50 times that of the control zone; the average uranium content in the paddy soil in unworked mine region was 1.93 and 1.33 times the soil background value of the Jiangxi Province and of China nationwide, respectively and was 2.44 times that of control zone. The coefficient of variation of uranium content in the active mining region was as high as 201.18 %, suggesting strong impact of anthropogenic disturbance factors. The uranium level in the paddy soil in the active mining region was 2.63 times that in the unworked mine region, suggesting that mining activity was an important factor contributing to aggravated uranium contamination in the mine area. The levels of uranium contamination of paddy soil samples collected from different regions were active mining region > unworked mine region > control zone; there was severe or moderate uranium contamination in the active mining region, mild or no uranium contamination in the unworked mine region and no uranium contamination in the control zone.

Keywords: Paddy soil, Contamination assessment, Uranium contamination, Uranium mine.

INTRODUCTION

After the founding of the P.R. China, the national uranium mining and metallurgy industry developed rapidly. More than 200 uranium deposits of different sizes have been found, of which 85 % are located in Hunan, Jiangxi, Guangdong and other regions[1]. On the one hand, uranium mining is of great significance for the development of China's national defense and nuclear power industry. On the other hand, uranium mining and metallurgy will produce large amounts of solid and liquid wastes rich in uranium and other radionuclides. Currently the solid and liquid wastes are rarely disposed properly and are often simply dumped in open space or discharged in the nearest site available. The content of natural radionuclides in these tailings or liquid waste is relatively high. In particular, the radionuclide uranium is rather chemically active and can easily be oxidized into uranyl complexes under natural conditions and migrate to other areas; once the environment changes, these uranyl complexes are easily reduced, precipitated and thus accumulate. Studies have demonstrated that harmful elements in soils contaminated by heavy metals or radionuclides can accumulate in river sediments, soils and migrate to organisms[2-6]. The uranium mine examined in the present study is located in hills in the southeast China with subtropical monsoon climate and is the largest uranium mine in China, with a mining history of more than 50 years. In the mining area the agricultural activity is mainly rice cultivation. This subtropical hilly region is humid and rainy, with developed surface water system and rugged terrain; the natural conditions can easily form an environment suitable for uranium oxidation and migration and uranium is prone to migration, conversion and accumulation in paddy soils, leading to radioactive contamination of the mining area.

At present, quantitative investigations on the radioactive contamination of the mining area caused by mining of uranium deposits are still relatively less. Related studies have mainly focused on environmental radioactivity levels and radiation dose[7-11] and there have been only a small number of studies exploring the radionuclide content in rice and whether it is affected by the radionuclide[12]. Rice paddy soil is the most important factor that influences the accumulation of radionuclide in rice. Yet currently there are few literatures on radionuclide contamination of paddy soil and we did not find a single research on uranium and paddy soil contamination. In the present study, a certain uranium mining area in southeast China was examined to accurately measure the uranium content in paddy soil (topsoil in rice field), in order to evaluate whether paddy soil in the mining area was contaminated by uranium and the degree of the contamination. This is of important significance for protecting ecological safety and the health of the citizens in the mining area.

EXPERIMENTAL

According to geological and topographical conditions as well as the condition of deposit mining, the uranium mine was divided into active mining region and unworked mine region for collection of paddy soil samples. Composite sampling was applied; the sampling depth was 0-25 cm; for each sample collection, after the center collection spot was set, five samples were collected from five spots evenly distributed on a circle of 5 meter radius and then mixed together to count as one sample. The GPS coordinates of the center was recorded as the position of the sampling point and the sample was placed in a labeled bag. A total of 151 paddy soil samples were collected, including 142 from the mine (117 active mining regions and 25 unworked mine regions). In addition, 9 paddy soil samples were collected from the countryside of the same prefecture-level city 60 km away from the uranium mine (where water, atmospheric and other relatively factors are different from that in the mining area) as control. All sample analyses were performed by the analytic test center of Beijing Research Institute of Uranium Geology.

ELEMENT XR high-resolution inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Fisher Scientific, U.S.); all vessels were soaked in 20 % nitric acid and then rinses with high-purity water before use. All single element standard solutions were purchased from the National Research Center for Certified Reference Materials (China); metal-oxide-semiconductor (MOS) grade HNO_3.

Working condition of the equipments: After optimization, the working conditions of the ICP-MS were: cooling air flow rate: 15 L^{-1} min; auxiliary gas flow rate: 0.86 L^{-1} min; carrier gas flow rate: 1.012 L^{-1} min; power: 1400 W.

Sample preparation and experimental methods: The collected field soil samples were let dry naturally in the laboratory before subjected to crushing to remove gravels, plant roots and other impurities; then preliminary grinding was applied and the samples were filtered through a 60 mesh sieve and sent for testing; right best testing, with quartering an appropriate amount of sample was triturated and filtered through a 200 mesh sieve. The sample was dried at 60 °C for 4 h, then 0.0500 g sample was accurately weighed and placed in a sealed Teflon dissolution tank. A small amount of water was added to wet the sample and the tank was gently shaken before 3 mL hydrofluoric acid, 1 mL nitric acid and 1 mL perchloric acid were added. The dedicated dissolution tank lid was put on and the tank was placed on low-temperature guarded hot plate for over 24 h at 200 °C for sample dissolution. The tank lid was then taken off and the tank was heated on the hot plate till the sample nearly dried. Depending on the completeness of the digestion, 3 mL hydrofluoric acid, 1 mL nitric acid and 1 mL perchloric acid may be added again to repeat the above digestion process. After the sample was evaporated to near dryness, 3 mL 1:1 nitric acid was added and the lid was put back on and the sample was let sit for a while to dissolve soluble residues. Then 1 % nitric acid was used to exact the sample to a 50 mL volumetric flask, homogenized by shaking. Online internal standard (Rh) method was applied to use the ICP-MS for measurements.

RESULTS AND DISCUSSION

Analysis of uranium content in paddy soils: Table-1 shows the uranium contents in paddy soils collected from different regions and the corresponding coefficients of variation. It can be seen that among the 117 samples collected from active mining region, the minimum value of uranium content was 2.87 mg kg^{-1}, maximum 416 mg kg^{-1}; the mean was 34.66 mg kg^{-1}, 14.50 times the average uranium content in paddy soils collected from the control zone, 7.88 and 11.44 times the soil background value of Jiangxi Province[13] and that of China nationwide[14], respectively and 5.93 times the average uranium content in paddy soils collected from unworked mine region (5.84 mg kg^{-1}). Among the above 117 samples, 112 samples had uranium content higher than the soil background value of Jiangxi Province, accounting for 95.73 % of all samples; 78 samples had uranium content over two times the soil background value of Jiangxi Province, accounting for 66.67 % of all samples. Similarly, 114 samples had uranium content higher than the soil background value of China nationwide, accounting for 97.44 % of all samples; 92 samples had uranium content over two times the soil background value of China nationwide, accounting for 78.63 % of all samples. This suggested that in the vast majority of the soils in the rice field (paddy soil) of the active mining region had excessive uranium levels and two thirds had severely excessive uranium levels.

For paddy soil samples collected from the unworked mine region, the minimum value of uranium content was 3.04 mg kg^{-1}, maximum 8.08 mg kg^{-1}; the mean was 5.84 mg kg^{-1}, 2.44 times the average uranium content in the paddy soil samples collected from the control zone and 1.33 and 1.93 times the

TABLE-1
URANIUM CONTENT AND ITS COEFFICIENT OF VARIATION IN PADDY SOILS OF DIFFERENT REGIONS

Region	Average content (mg kg^{-1})	Maximum value (mg kg^{-1})	Minimum value (mg kg^{-1})	Standard deviation	Coefficient of variation (%)	Background value of soils in Jiangxi Province	Background value of soils in China
Active mining region	34.66	416.00	2.87	69.72	201.18	4.40	3.03
Unworked mine region	5.84	8.08	3.04	1.36	23.36		
Control zone	2.39	3.07	2.10	0.30	12.39		

TABLE-2
GRADING CRITERIA USING SINGLE-FACTOR INDEX

Pi value	Pi ≤ 1	1 < Pi ≤ 2	2 < Pi ≤ 3	Pi > 3
Degree of contamination	Not contaminated	Mildly contaminated	Moderately contaminated	Severely contaminated

TABLE-3
GRADING CRITERIA USING GEO-ACCUMULATION INDEX

Ii value	< 0	0 ≤ Ii < 1	1 ≤ Ii < 2	2 ≤ Ii < 3	3 ≤ Ii < 4	4 ≤ Ii < 5	Ii ≤ 5
Grade of contamination	0	1	2	3	4	5	6
Degree of contamination	Not contaminated	Mildly contaminated	Close to moderately contaminated	Moderately contaminated	Close to severely contaminated	Severely contaminated	Extremely severely contaminated

soil background value of Jiangxi Province and that of China nationwide, respectively. The mean uranium level in paddy soil samples collected from the unworked mine region was far lower than that of the active mining region, only 16.85 % of the latter. Among the 25 samples collected from the unworked mine region, 21 samples had uranium content higher than the soil background value of Jiangxi Province, accounting for 84 % of all samples; no sample had uranium content over two times the soil background value of Jiangxi Province. All samples had uranium content higher than the soil background value of China nationwide; 10 samples had uranium content over two times the soil background value of China nationwide, accounting for accounting for 40 % of all samples. This result showed that although the majority of paddy soils in the unworked mine region exceeded the soil background values of Jiangxi Province and of China nationwide, the severity of the excessiveness was far less than that in the active mining region.

The coefficient of variation of uranium level in paddy soils of the active mining region was 201.18 %, far higher than that of the unworked mine region and the control zone. This suggested that the uranium level in paddy soils of the active mining region was largely influenced by the mining process and the impact of anthropogenic disturbance factors was very strong[15].

Assessment on uranium contamination of paddy soils: Single-factor index method and geo-accumulation index method were applied to assess the degree of uranium contamination of soils in the rice field (paddy soil) in the mining area.

Single-factor index method: Single factor index method is a general method used in China for pollution assessment of heavy metals and the expression is Pi = Ci/Si.

where, Pi is the pollution index of the pollutant i in the soil and the grading criteria is as shown in Table-2; Ci is the measured content of pollutant i in the soil, mg kg^{-1}; Si is the evaluation reference value of pollutant i in the soil, mg kg^{-1}. In the present paper, the soil background value of Jiangxi Province was used as the evaluation reference value to apply the single-factor index method to assess uranium contamination in three different regions: the active mining region, the unworked mine region and the control zone. The result is summarized in Table-4.

As illustrated in Table-4, the degrees of uranium contamination of paddy soils collected from the different sampling region, as determined using the single-factor index method, were active mining region > unworked mine region > control zone. In the active mining region, the single-factor evaluation value was 7.88, far higher than the threshold of severe pollution (2.63 times the threshold of severe pollution) and the pollution was severe; in the unworked mine region, the single-factor evaluation value was 1.33 and the pollution was mild; in the control zone, the single-factor evaluation value was 0.54 and the region was not polluted.

Geo-accumulation index method: The geo-accumulation index method was proposed by Muller from the University of Heidelberg, Germany[12] in 1969. It is one of the most widely applied methods for assessing the degree of soil contamination. This method takes into account not only anthropogenic pollution factors and environmental geochemical background values, but also possible changes in the background values caused by natural diagenesis. It can rather directly reflect the degree of enrichment of exogenous contaminants in the sediment and the data are of relatively high comparability. The expression is Ii = Log2 (Ci/kBi), k = 1.5. Where, Ii is the geo-accumulation index of pollutant element i and the grading criteria are shown in Table-3; Bi is the local background value of pollutant element i in the soil and the unit was mg kg^{-1}; k is the background value coefficient due to changes between different soils or rocks and typically is set to 1.5. The calculated Ii values are shown in Table-4.

TABLE-4
CONTAMINATION ASSESSMENT RESULTS ON RADIOACTIVE URANIUM IN PADDY SOILS

Region	Single-factor index method	Geo-accumulation index method
Active mining region	7.88	2.39
Unworked mine region	1.33	-0.18
Control zone	0.54	-1.47

The degrees of uranium contamination of paddy soils collected from the different sampling region, as determined using geo-accumulation index method, were active mining region > unworked mine region > control zone. The geo-accumulation index of the active mining region was 2.39, suggesting moderate contamination; the geo-accumulation index of the unworked mine region and that of the control zone were both below zero, suggesting that these two regions were not contaminated.

The average uranium content in the paddy soil in the active mining region was 7.88 and 11.44 times the background value in the Jiangxi Province and in China nationwide, respectively and was 14.50 times that of the control zone; the average uranium content in the paddy soil in unworked mine region was 1.93 and 1.33 times the background value in the Jiangxi Province and in China nationwide, respectively and was 2.44 times that of control zone.

In both the active mining region and the unworked mine region, the uranium content in paddy soils was excessive, but the degree was more severe in the active mining region than in the unworked mine region, the average uranium content of the former being 2.63 times that of the latter.

The coefficient of variation of uranium content in the paddy soils in the active mining region was as high as 201.18 %, suggesting strong impact of anthropogenic disturbance factors. The uranium content in the paddy soil in the active mining region was far higher than that in the unworked mine region, suggesting that the mining activity was an important cause of aggravated uranium contamination of the paddy soil in the mining area.

With both single-factor index method and geo-accumulation index method, it was found that degrees of uranium contamination of paddy soils collected from the different sampling region were active mining region > unworked mine region > control zone. The active mining region suffered from severe or moderate uranium contamination and the unworked region suffered from mild or no uranium contamination, while the control zone was not contaminated.

The uranium content in the paddy soils of the unworked mine region was also generally higher than the reference value might be related to relatively high background uranium value of soil parent material in the mining area or the relatively high uranium content in the surface water of the mining area. Further investigations are needed to determine the specific cause.

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