DISTRIBUTION OF URANIUM, THORIUM, AND ISOTOPIC COMPOSITION OF URANIUM IN SOIL SAMPLES OF SOUTH SERBIA: EVIDENCE OF DEPLETED URANIUM

by

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Inductively coupled plasma mass spectrometry and thermal ionization mass spectrometry were used to measure concentration of uranium and thorium as well as isotopic composition of uranium respectively in soil samples collected around south Serbia. An analytical method was established for a routine sample preparation procedure for uranium and thorium. Uranium was chemically separated and purified from soil samples by anion exchange resin and UTEVA extraction chromatography and its isotopic composition was measured using a thermal ionization mass spectrometry. There was a little deviation of U/Th ratio from the average values in some soil samples. Presence of ^{236}U as well as depleted uranium was observed in ^{235}U/^{238}U ratio measurement in the same soil sample.

Key words: TIMS, ICP-MS, soil, uranium isotopes, depleted uranium

INTRODUCTION

Anthropogenic processes (mining, milling, industries, and automobiles) including modern trends in agriculture, contaminated the soil and water affecting the biogeochemical cycle of many elements. This resulted in the degradation of soil-water system causing damage to the environment and ecosystem. In addition to this, since depleted uranium (DU) was used in 1999 Balkan conflict, there has been a concern about the possible consequences of its use for the people and environment of this region [1]. Therefore, management of fresh water resources is of utmost importance in the 21st century for sustainable development. In this context, isotope geochemistry is a very useful tracer tool, not only to establish the origin of pollutants and their relative contributions from various (natural and anthropogenic) sources, but also the effect on the soil-water system. Isotope studies can be carried out by application of thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS), and results of such studies are very useful and precise in delineating the source(s) of contaminants, tracing the flow-path of ground water and aid in planning better management of freshwater resources.

There are three series of radioactive decays starting from ^{238}U ($T_{1/2} = 4.468\quad{}^{9}$ years), ^{235}U ($T_{1/2} = 7.038\ 10^{8}$ years), and ^{232}Th ($T_{1/2} = 1.41\ 10^{10}$ years). In the course of the disintegration series of the parental nuclide ^{238}U, daughter nuclides ^{234}U ($T_{1/2} = 2.45\ 10^{5}$ years) and ^{230}Th ($T_{1/2} = 7.54\ 10^{4}$ years) are produced as intermediate members [2]. Thus, from the viewpoint of environmental and earth science, uranium and thorium are extremely important elements. Besides, ^{235}U is of special significance as a source material for nuclear reactors. Thus, the ^{234}U/^{238}U ratio serves as an indicator for radioactive equilibrium or disequilibrium in natural samples, while ^{235}U/^{238}U ratio deserves serious attention in relation with the enrichment or depletion of ^{235}U in nature. DU is a by-product of the process in which fuel for nuclear reactors and nuclear weapons is made. DU

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contains reduced amounts of the isotopes of ^{234}U and ^{235}U. Needless to say, the isotopic measurement with higher precision provides us with more valuable information. Usually, in practice, the alpha counting system has been used to measure the isotopic ratios of uranium (for ^{238}U, ^{234}U, and to a lesser extent ^{235}U). The measurement of the ratio of ^{234}U radioactivity to ^{238}U activity involves uncertainties of 20 to 40% in seawater samples [3], and takes more than a week by alpha counting measurement for the amounts of 100 to 200 ng of uranium [4]. Moreover, it is not possible to determine ^{236}U at environmental levels using alpha spectrometry.

Sample preparation procedures are critical analytical steps which influence the quality of final results. The representative of the examined samples, a digestion procedure which ensures the quantitative conversion of uranium and thorium into a suitable complex and elimination of matrix effects are essential while measuring uranium isotopes, especially in the analysis of environmental materials. Special procedures for the purification of reagents and reaction vessels are required in order to reduce the blank below the limits of detection of the most sensitive detection techniques, such as ICP-MS or TIMS.

The results and distribution of uranium and thorium using ICP-MS as well as uranium isotope ratios (^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U) using TIMS in soil samples will be discussed in this paper. TIMS shows the highest precision and accuracy [5, 6] and is capable of detecting depleted uranium in soil samples affected due to conflicts.

MATERIALS AND METHODS

Sampling of soils

The study area is located in south Serbia as shown in fig 1. Seven surface (0-5 cm) soil samples were collected around Reljan and Bratoselce Konz in the vicinity of penetrator holes (tab. 1). Sampling points were decided on the basis of penetrators recovered from the area. A reference material supplied by Geological Survey of Japan JLK-1 is a sediment sample taken at lake Biwa (35°14 42 N, 136°03 14 E), 3.8 km off Takashima, Shiga prefecture, with water depth of 63 m. The sample came from the top sediment from zero down to 20 cm. After removing stones, the soils were oven-dried at 80 °C to constant weight and ground into powder.

Soil and sediment samples were digested with HNO_3, HF, and $HClO_4$ in PTFE pressure decomposition vessels. A microwave unit (MLS 1200 mega, Italy) was used for heating the samples. After digestion, samples were evaporated to dryness on a hot plate and the residue was dissolved in 5% HNO_3 to yield a sample solution.

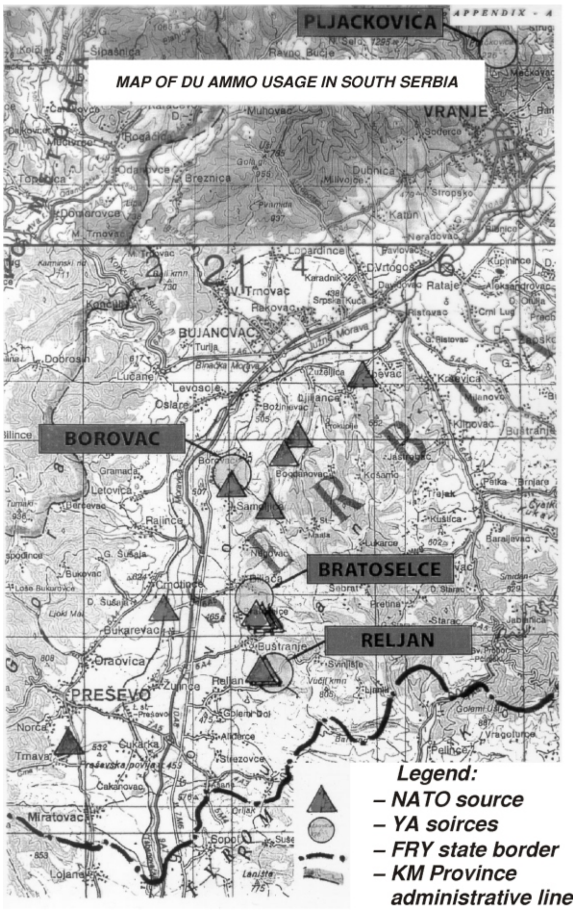

Figure 1. Map showing sampling area

Instrumental

ICP-MS (Helwett Packard – 4500) was used for the determination of ^{238}U and ^{232}Th in soil samples which yielded detection limits of 0.01-0.003 g/L. The parameters for data acquisition and optimization conditions are reported elsewhere [7]. Under these analytical conditions, the oxide formation level of Ce was found to be 0.4-2.0% (CeO^+/Ce^+). An internal standard, Rh, was used to assess any changes in analytical

Table 1. Location of soil samples around Reljan and Bratoselce

Sample ID	Location	Altitude	Dose rate [Sv/h]
Rel 1	42	636	0.13
Brat 1		561	0.15
Brat 2		561	0.13
Brat 3		582	0.15
Brat 4		576	0.16
Brat 5		580	0.15
Brat 6		580	0.13

signals during measurement. Standard solutions were prepared from SPEX multi-element Plasma standards (SPEX Industries, Inc.,) and used to derive calibration curves. Standard reference materials were used to validate the analytical procedure. Sediment sample, JLK-1, was used for soil analysis. The precision calculated using three independent runs was better than 5% RSD with a comparable accuracy. Analytical errors for measured values were less than 10% of the certified values.

The isotope ratios of uranium were measured on a single focusing VG Sector 54-30 thermal ionization mass spectrometer (TIMS) at National Institute of Radiological Sciences. The instrument is equipped with new bucket type nine Faraday collectors and a Daly ion-counting system detector positioned behind axial Faraday and WARP filter. Signals from the Daly detector are received by an EG&G Ortec 9302 amplifier/discriminator and EG&G Ortec 996 ion counter/timer.

Chemical separation

The determination of uranium by TIMS requires pure uranium isolates. The current method of chemical separation used here is based upon two separation columns. Most of the techniques for the purification of uranium have used anion exchange chromatography, solvent extraction and more recently extraction chromatography. We have used a combination of anion exchange and extraction chromatography with a little modification of the earlier methods [8, 9]. The first column was prepared by using pre-cleaned anion exchange resins (Dowex 1X-8, 200-400 mesh, Cl^- form) and packed into 2 cm i.d. Pyrex columns up to a height of 6 cm and the second UTEVA resin (Eichrom industries Inc.) in pre-packed columns with 2 ml resin and 100-150 m particle size material. The UTEVA resin contains diamyl amylphosphonate (DAAP) as a specific extractant. Both columns were conditioned by passing 15 ml of 7M HNO_3. The sample was transferred to the anion exchange column and the eluent was subsequently passed onto the UTEVA column. Both columns were washed with 10 ml of 7M HNO_3 followed by 20 ml of 3M HNO_3.

The uranium was eluted from UTEVA column using 5 ml of 0.02M HCl. The concentration of eluent was adjusted to 9M HCl. The resulting solution was loaded onto an anion exchange column preconditioned with 9M HCl and washed with 10 ml of 9M HCl. Finally, uranium was eluted with 10 ml of 0.02M HCl and the eluent was evaporated to dryness in a Teflon beaker. U recovery from the samples is about 90~95%.

Mass spectrometry

A triple filament assembly was used for the thermal ionization of uranium isotopes. The filament material was 5-pass zone refined rhenium ribbon (H. Cross, 99.999%) with 0.003 cm thickness and 0.07 cm width. Triple Re filaments were prepared by degassing for 1 h with a 4 A current under a vacuum better than 5 10^{-6} mbar. Pure isolates were dissolved in nitric acid and mounted, by evaporation, on the side filament of a triple filament. In case of triple filament assembly, the central filament is very hot and it ionizes and causes the side filaments to evaporate. Since the sample is not directly ionized it was noticed that mass fractionation is slower than that for a single filament [10]. The central filament was heated to produce ^{187}Re ion current of 0.2 V and then side filaments were heated to produce ion current of 0.03 V for ^{235}U. Uranium masses 234, 235, 236, and 238 were measured dynamically using Daly-ion counting and Faraday cup collectors with mass jumps. $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ isotope ratios were determined by static data collection on the Daly-ion counting and Faraday cup collectors. All ratios were taken as the grand mean of 7 blocks of 10 measurements over a period of 80 minutes. The vacuum during data acquisition was better than 2 10^{-8} mbar in the flight tube as well as ion source. Accuracy and precision of uranium isotope ratios measurement depends on the linearity of the detection system and mass fractionation of the isotopes during the run. The advantage of WARP filter is the enhanced transmission (100%) of U^+ ion, abundance sensitivity of 10 ppb at 1 amu with respect to ^{238}U and the suppression of tailing effect of adjacent strong ion.

RESULTS AND DISCUSSION

The results of the concentrations of uranium and thorium measured by ICP-MS in different soil samples are summarized in tab. 2. We have studied

Table 2. ICP-MS determination of uranium and thorium in south Serbia soil samples

Sample ID	Uranium [ppm]	Thorium [ppm]	U/Th ratio
JKL	3.58±0.02	20.1±0.38	0.18
Rel 1	2.30±0.07	15.03±0.72	0.15
Brat 1	5.86±0.11	9.26±0.13	0.63
Brat 2	4.22±0.16	9.32±0.28	0.45
Brat 3	5.97±0.14	11.74±0.44	0.51
Brat 4	5.14±0.18	11.04±0.34	0.46
Brat 5	5.36±0.16	11.41±0.23	0.47
Brat 6	4.81±0.17	11.56±0.24	0.42

the total concentration of uranium and thorium collected from selected soil samples around Reljan and Bratoselce Konz area. The mean concentration of uranium varied from 2.30 0.07 to 5.97 0.14 ppm (1 ppm = 10^{-6}) whereas for thorium it varied from 9.26 0.13 to 15.03 0.72 ppm. It was not possible to examine contamination due to uranium from natural uranium concentration. In considering possible contamination from the data of total uranium concentration, it is quite obvious to use thorium data for comparison. Wedepohl reported U/Th ratio as 0.20 and used mean concentration of uranium and thorium in the earth's crust of 1.7 ppm and 8.5 ppm respectively [11]. If we compare our data, certified reference material, JLK-1 is close to 0.2 whereas south Serbian samples are relatively higher than 0.20. There was a larger variation with ratios and excess uranium might be due to the inherent natural content of uranium or anthropogenic activities or it may be attributed to penetrators used during Balkan conflict.

We have carried out the isotopic measurement of uranium from same soil samples with the objective to detect any variability the presence and potential source of anthropogenic uranium might have caused. A representative duplicate set of samples from standard and contaminated area is given in tab. 3. Isotope ratios for samples Rel 1, Brat 3, and Brat 5 fall in the range expected for natural uranium. However, samples collected from Brat 1 and Brat 4 site do show a spread in uranium isotope ratio well outside the 99.7% confidence limit. This shows the heterogeneity in the distribution of isotopically depleted and/or enriched material within the soil. From duplicate runs of each sample, one can confirm that such deviations from natural ratios were readily reproducible at statistical levels predicted by standard measurements.

When we use ^{234}U/^{238}U ratio and express it as activity ratio, it varies from the lowest *i. e.* 0.8065 to the unity, showing a decrease in the natural abundance of ^{234}U in the samples. The lowest was noticed in case of Brat 1. In case of secular equilibrium, with a half-life of 4.47 10^{9} years, ^{238}U would be in secular equilibrium with all its daughters, including ^{234}U, with half-life of 2.45 10^{5} years. Therefore, ^{234}U/^{238}U atomic abundance ratio would be 2.45 10^{5}/4.47 10^{9} = = 54.8 10^{-6} (or 54.8 ppm) which is the expected ratio [12]. At the same point, depletion of ^{235}U has been found to be 0.83%. This indicates that depletion of ^{235}U is present in soil samples of Bratoselce Konz. However, we have noticed some points near to Brat 1 which is close to normal value of ^{235}U/^{238}U ratio (0.00725). Another effect is the remarkable enhancement of ^{236}U in the depleted soil sample. This is judged to be sudden introduction of ^{236}U due to the bombardment of penetrators. It is worthwhile to note that ^{236}U is considerably enhanced in Brat 1, Brat 2, Brat 4, and Brat 6. Although its production is lower, ^{236}U/^{238}U indicates anthropogenic activities or a neutron burst, ^{235}U (n,) ^{236}U on the bombardment. However, in some papers the presence of ^{236}U was noted in penetrators [13] and also in soil samples [14]. We have used NBS U010 as a certified reference material to check the measurement of ^{234}U, ^{235}U, ^{236}U, and ^{238}U simultaneously.

Table 3. Uranium isotopic composition measured by TIMS in south Serbia soil samples

Sample ID	^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U
JKL	0.0000549	0.0072548	ND
Rel 1	0.0000544	0.0071127	ND
Brat 1	0.0000442	0.0060617	5.7 10^{-6}
Brat 2	0.0000534	0.0071194	2.86 10^{-8}
Brat 3	0.0000548	0.0072067	ND
Brat 4	0.0000488	0.0064564	2.7 10^{-6}
Brat 5	0.0000544	0.0072007	ND
Brat 6	0.0000539	0.0071101	6.1 10^{-7}
NBS U010	0.0000546	0.0101400	6.87 10^{-5}

CONCLUSIONS

We have developed a procedure to measure ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U to accuracy better than 0.2% at two standard deviation. This method should be applicable to a wide range of environmental and geological problems which are limited by sample size or for which higher precision is required. This method was used to determine more precisely the ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U ratio in south Serbian soil samples and limit the variability of this ratio. Results obtained here are of preliminary nature. However, systematic studies are necessary in order to ascertain the behavior of DU in soil water interaction in the south Serbian soils. In addition to this, human uptake of this uranium material could be a possible pathway to indicate presence of ^{236}U/^{238}U atom ratio in hair, blood or urine of subjects.

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РАСПОДЕЛА УРАНИЈУМА, ТОРИЈУМА И ИЗОТОПСКОГ САСТАВА УРАНИЈУМА У УЗОРЦИМА ЗЕМЉИШТА ИЗ ЈУЖНЕ СРБИЈЕ: ДОКАЗ ЗА ОСИРОМАШЕНИ УРАНИЈУМ

Индукованом куплованом масеном спектрометријом и термалном јонизационом масеном спектрометријом измерене су концентрације уранијума и торијума као и изотопског састава уранијума земљишта сакупљеног у подручју јужне Србије. Успостављена је аналитичка метода за рутински поступак припремања узорака уранијума и торијума. Уранијум је хемијским путем издвајан и пречишћаван из узорака земљишта помоћу хроматографских метода, анјонском изменом смола и UTEVA екстракцијом и изотопски однос уранијумских фракција измерен је помоћу термалне јонизационе масене спектрометрије. Постоји извесно одступање у односу на просечне вредности односа уранијума и торијума (U/Th) у неколико анализираних узорака земљишта. Присуство ^{236}U као и осиромашеног уранијума утврђено је приликом одређивања односа ^{235}U/^{238}U у истим узорцима земљишта.