Isotopic composition of Uranium in soil and ground water samples collected around 30 km Chernobyl Exclusion Zone

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Abstract. Precise and accurate measurement of uranium isotope ratio is essential in environmental monitoring of any contamination in nuclear safeguards. ^{234}U, ^{235}U and ^{238}U are naturally occurring alpha-emitting long-lived radionuclides, which are taken up daily at low levels with food and drinking. IUPAC has established natural isotopic composition of $^{235}U/^{238}U$ to be 0.00725. Therefore, isotope ratio measurements are important to provide information on the origin of uranium. The isotope ratios of uranium, $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ were measured using a VG Sector 54 thermal ionization mass spectrometer (TIMS) as well as high resolution inductively coupled plasma mass spectrometry (ICP-MS) in soil samples as well as in some water samples collected in the exclusion zone of Chernobyl nuclear power plant. The isotopic composition of Chernobyl soil samples showed significant deviation from the natural uranium and presence of ^{236}U is quite noticeable. The $^{234}U/^{238}U$ activity ratio varies in the range 1.06 to 2.1 and 1.42 to 5.75 for soil and water samples, respectively. Enrichment of ^{235}U was also noticeable for soil as well as ground water samples.

1. INTRODUCTION

Actinides have extensively and inevitably entered into the environment due to nuclear accidents and atmospheric weapon testing. One such example is the Chernobyl nuclear power plant (CNPP) accident where, most of the radioactivity fallout descended in the vicinity of CNPP and adjoining areas of Ukraine and Belarus [1]. It thus becomes eminent to characterise and determine these elements for the purpose of environmental monitoring of large contaminated regions. The occurrence of natural radionuclides in the environment is an important part of the general study of radionuclide migration, and may even be used as an analogue of the possible behaviour of radionuclides in case of a nuclear accident. Especially, uranium isotopes are outstanding radioactive pollutants due to their long half-lives and high radiotoxicity. Due to difference in chemical characteristic of actinides, the migration of uranium differs from the migration of actinides e.g. plutonium. Hence, a systematic study of the radionuclides leached from fuel particles in soil, which require ultra sensitive isotope analytical methods for direct determination of spent reactor uranium. The data obtained is essential for the control and forecast of the radio-ecological situation in contaminated areas. Investigation of radionuclides in ground water provides useful information not only on their transport behaviour but also as guideline for ground water protection and remediation of nuclear sites. The leachability of radioactive elements has relevance in quantifying dissolved Ra as well as U and Rn, this is critically influenced by pH resulting from the reaction of water with radioactive material present in soil. There is a variation in U deposits from region to region due to fluvial sedimentary rocks, which are underlain by high-grade metamorphic rocks. In this paper, we have selected CNPP exclusion area as an excellent natural laboratory to study enrichment of uranium in soil and water samples.

Uranium comprises of three natural isotopes with long half-lives, ^{234}U, ^{235}U, and ^{238}U with average abundances of 0.0054%, 0.720% and 99.275%, respectively [2]. In natural system, ^{234}U present approximately in radioactive equilibrium with ^{238}U [3]. ^{236}U does occur in nature but only at ultra trace concentrations. Some ^{236}U has been found in exceptional natural samples e.g. Oklo reactor. Therefore, ^{236}U is a potential "fingerprint" for the presence of uranium originating from a nuclear reactor in the environment. Soil and sediments are the most suitable materials that would be likely to preserve any remains of anthropogenically altered uranium. The average world content of uranium is 1.7 ppm in soil [4].

To date, thermal ionization mass spectrometry has been accepted as a "benchmark" technique for its high precision and accuracy of isotope ratio measurements [5–7]. Recently, high resolution inductively coupled plasma mass spectrometry (HR-ICPMS) and multi-collector (MC-ICPMS) are used for high precision uranium isotopic measurements [8–10]. This paper presents precise measurement of ^{234}U/^{238}U, ^{235}U/^{238}U, ^{236}U/^{238}U ratios of uranium separated from soil samples as well as water samples collected around 30 km circumference of the CNNP exclusion zone to detect trace levels of nuclide contamination due to nuclear accident.

2. EXPERIMENTAL

2.1 Instrument

The isotope ratios of uranium were measured on a single focussing VG (Micromass) Sector 54 TIMS. It is equipped with nine Faraday cup collectors and a Daly ion-counting system detector positioned behind axial Faraday and wide aperture retardation potential (WARP) energy filter. Signals from the Daly detector are received by an EG & G Ortec 9302 amplifier/discriminator and EG & G Ortec 996 ion counter/timer. A sector field HR-ICP-MS (Finnigan Mat Element) was used to counter check concentration of uranium isotopes in water samples.

2.2 Reagents and standards

High purity water was obtained with a Millipore Milli-Q water purification system. High purity HCl, HNO_3, HF and $HClO_4$ were purchased from Tamapure chemical industries (Kawasaki, Japan). The strong anion exchange resin Dowex 1X-8 (200-400 mesh, Cl$^-$ form) was purchased from Bio-Rad Labs (Richmond, CA). It was soaked in 6M HNO_3 and subsequently washed with distilled water. Commercial extraction chromatographic resin, UTEVA was purchased from Eichrom Industries (Darien, IL) and consists of a neutral organophosphorus diamyl amyl phosphonate extractant adsorbed onto an inert polyacrylamide support. It was conditioned with 8M HNO_3.

2.3 Samples

To check the accuracy of the calibration, a standard reference material, NBS U010 was used. Isotopic composition of uranium from one uranium ore was analysed for comparison and to detect the presence of ^{236}U. Eight soil samples were chosen for this study: sediment reference material supplied by Geological Survey of Japan and seven surface soil samples from 30 km exclusion zone. Soil samples were collected according to "envelope" method using a cylindrical sampler to cut a diameter of 37 mm thick soil layers down to a depth of 20 cm. Twelve surface water samples were collected from the exclusion zone.

2.4 Chemical procedure

Soil samples were digested in PTFE pressure decomposition vessels by heating in a microwave unit (MLS 1200mega, Italy) using a mixture of HNO_3, HF and $HClO_4$ [11]. After complete digestion, samples were evaporated to dryness on a hot plate. Finally the residues were dissolved in 8M HNO_3 to yield the sample solution for chemical separation. The chemical separation of U is based on the method

developed by Croudace et al. [12]. Three columns were used for each soil or water sample. First column was prepared by using precleaned 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 1.0×0.5 cm internal diameter column containing Eichrom UTEVA resin. Both columns were conditioned by passing 15 ml of 8M HNO$_3$. The sample was transferred to anion exchange column and the eluent was subsequently passed onto the UTEVA column. Both columns were washed with 10 ml of 8M HNO$_3$ followed by 20 ml of 3M HNO$_3$.

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

2.5 Mass spectrometry

A triple filament assembly was used for the thermal ionization of uranium isotopes. Mass spectrometry analytical scheme in detail described elsewhere [7]. 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 $^{236}U/^{238}U$ ratios were determined using Daly-ion counting system and three Faraday cups with mass jumps. Accuracy and precision of uranium isotope ratio measurement depends on the linearity of the detection system and mass fractionation of the isotopes during the run.

3. RESULTS AND DISCUSSION

The reproducibility and accuracy of the TIMS method was verified by analyses of a certified standard reference material, NBSU010. The isotope ratio, $^{235}U/^{238}U$ was corrected for non-linearity of Daly detector. The $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios obtained were 0.0000546 ± 0.0000002, 0.010142 ± 0.00005 and 0.0000692 ± 0.0000005 against certified value of 0.0000546, 0.010140 and 0.0000687, respectively. The results are in good analytical agreement. Thus, the measurements of the isotopic ratio in the standards demonstrate that isotopic fractionation, if occurring in the system, is less than the uncertainty in the measurement.

The measured isotope ratios, $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$, of uranium ore Mistamisk (Labrador, Canada) were found to be 0.0000544 (46), 0.007255 (39) and 8.14518×10^9 (59) respectively. Analytical uncertainties refer to the least digit significant figures. The $^{235}U/^{238}U$ is comparable to well-known "normal terrestrial" ratio of about 0.00725. The instrument detection limit for the ratio $^{236}U/^{238}U$ was calculated as three times the standard uncertainty of the background rate divided by typical ^{238}U intensity ($^{238}U \cong 2 \times 10^{-11}$ A). This yields a value for the detection limit of $^{236}U/^{238}U$ to 1.2×10^{-10}.

A representative duplicate set of samples from standard and soil samples from Chernobyl exclusion zone is given in Table 1 with the objectives of detecting the presence and potential source of anthropogenic uranium. However, samples collected from Chernobyl exclusion zone do show a spread in uranium isotope ratio well outside the 99.7% confidence limit, having $^{235}U/^{238}U$ in the range of 0.008194. Enrichment of ^{234}U is also noticeable with $^{234}U/^{238}U$ ratio in case of Chernobyl sample. These results show the heterogeneity in the distribution of isotopically enriched material within the soil. Duplicate runs of each sample confirmed that such deviations from natural ratios were readily reproducible at statistical levels predicted by standard measurements. Another effect is the remarkable enhancement of ^{236}U in soil samples. The presence of ^{236}U indicates contamination of environmental samples with spent uranium from nuclear reactors [13]. Soil samples 6 and 7 closest to the Chernobyl nuclear reactor indicate a high value of $^{235}U/^{238}U$ and $^{236}U/^{238}U$. In principle, main sources of ^{236}U are ^{235}U (n,γ) ^{236}U reaction with a cross section of 95 barns for thermal neutrons vs. fission cross section of

**Table 1.** Isotope ratios of uranium measured from soil samples.

Sample Name	^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U
JLK-1 7	0.000055(51)	0.007254(32)	Not detectable
Chernobyl 1	0.000058(46)	0.007509(39)	0.000047(45)
Chernobyl 2	0.000056(48)	0.007363(49)	ND
Chernobyl 3	0.000090(56)	0.008794(43)	0.000533(65)
Chernobyl 4	0.000068(36)	0.008572(28)	0.000611(67)
Chernobyl 5	0.000083(57)	0.008503(53)	0.000307(57)
Chernobyl 6	0.000119(39)	0.010551(46)	0.000821(56)
Chernobyl 7	0.000102(42)	0.009224(49)	0.000746(64)

ND: Not detectable.

586 barns) [14] and to a lesser extent, the alpha decay of ^{240}Pu. In this case, it can be attributed to origin of nuclear fuel burn-up. A depth profile of ^{235}U/^{238}U isotope ratio has been shown in Figure 1. Top layer shows enrichment of U-235 due to spent reactor uranium. Whereas when we go to deeper level, it is close to normal terrestrial value. The highest level was noticed in the red forest area.

Soil conditions of exclusion zone are characterized by dominating soddy podzolic soils (36.4% of total surface). Soil forming rocks are alluvial and fluvioglacial sedimentations of sandy and consolidated sandy mechanic composition. These types are characterized with water penetration and consequently nutrients are removed or less due to atmospheric deposition. Soddy podzollic soil dominates in the territory with high level of soil waters. Such territories are covered by meadows. Swampy soils cover about 9.6% of the exclusion territory. Therefore, isotope ratio of U can play a major role when we carry out water analysis in the same area.

Uranium concentrations in natural waters vary from region to region due to the different rocks compositions, the aquifer, composition of water, distance from uraniferous areas and climatic and agricultural conditions. UNSCEAR reported that uranium in natural water in ranging from $< 1\,\mu$g L^{-1} to greater than $> 100\,\mu$g L^{-1} [15]. Goldstein et al. [16] reported that ^{234}U/^{238}U activity ratio in natural water samples range from 0.8 to 10, while atomic ratio ^{235}U/^{238}U is thought to have a quite uniform value of 0.00725. The water sample stations around 30 km exclusion zone have been described in Table 2. The isotope ratios ^{234}U/^{238}U and ^{235}U/^{238}U in natural water samples were analysed in duplicate to verify the accuracy using HR-ICP-MS and TIMS. The activity ratio ^{234}U/^{238}U has shown in Figure 2.
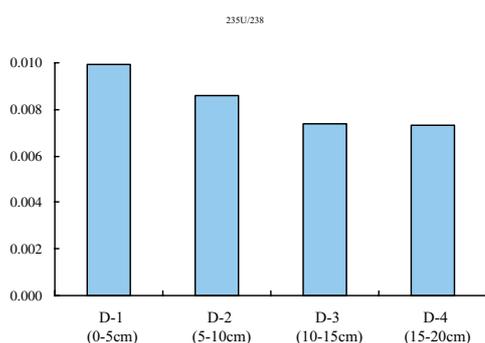
Figure 1. Depth profile of ^{235}U/^{238}U ratio.
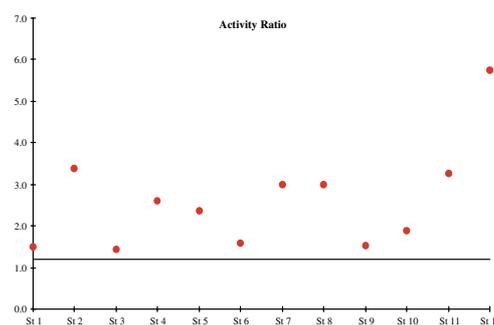
Figure 2. ^{234}U/^{238}U activity ratio in water samples.

A large variation is observed with activity ratio and was in the range of 1.42 to 5.75. The concentration of U-238 in water samples varied widely, from 0.17 to 27 Bq L^{-1}. The ^{235}U/^{238}U isotope ratio at St.7 and St.10 were found to 0.0078546 and 0.007645, respectively. Other stations were almost

Table 2. Description of water sample stations.

Sample	Description
St.1	The cooling pond
St.2	Pripyat creek
St.3	Semichody creek
St.4	Krasnesky creek
St.5	Peschane creek
St.6	Stream of Borschi
St.7	Drill near Red Forest
St.8	Drill 6-95 in Red Forest
St.9	Lake Glubokee
St.10	Drill near old base
St.11	Stream of Rodvino
St.12	Polder channel

close to normal value of 0.00725. The isotope ratio ^{235}U/^{238}U was measured in a natural standard supplied by Geological Society of Japan, JB-1 and an analytical error of $\pm 0.05\%$ was obtained between both TIMS and HR-ICP-MS techniques. Therefore, enrichment of U-235 in water samples can be due to anthropogenic contamination originated due to CNNP accident. One of the sites is in red forest area that was highly contaminated due to Chernobyl fall out.

4. CONCLUSION

The uranium isotope ratios in soil and water samples collected in CNPP exclusion area, indicates enrichment of U-235 in almost all soils and in a few water samples. However, ^{236}U in soil samples could be detected. The isotopic ratio ^{234}U/^{238}U in soil samples showed enrichment of U-234 along with U-235. In the case of water samples get enriched with U-235, attention is required from radiological protection viewpoint. Several such types of studies would to establish the migration of uranium isotopes in a hydrological environment.

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