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Variation in the uranium isotopic ratios ^{234}U/^{238}U, ^{238}U/total-U and ^{234}U/total-U in Indian soil samples: Application to environmental monitoring

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ABSTRACT The uranium isotopes ^{238}U, ^{235}U and ^{234}U are found naturally in the environment. ^{238}U and ^{235}U are parent nuclides of two independent decay series of isotopes, while ^{234}U is a member of the ^{238}U decay chain. When decay series occur in a closed system the series tends to reach, with time, the state of secular equilibrium in which the activities of all series members are equal to the activity of its first nuclide. The activity ratio ^{234}U/^{238}U in natural uranium may vary as a consequence of decay chain disequilibrium due to alpha recoil and biogeochemical processes. A study based on measurement of uranium concentration and ^{234}U/^{238}U activity ratios in soil samples collected from Nalgonda district, Andhra Pradesh, India, a proposed mining site, was carried out to find the spatial distribution of uranium and the state of secular equilibrium of ^{234}U/^{238}U to examine the possibility of applying uranium concentration and uranium isotopic activity ratios to detect any hydrogeochemical changes in the environment during/post-operation. Soil samples were collected and analyzed for uranium concentration using the conventional UV fluorimetric method, showing a uranium concentration in the range of 0.7 ± 0.2 ppm to 7.9 ± 0.4 ppm with an average of 3.4 ppm, and ^{234}U/^{238}U activity ratios were estimated using the alpha spectrometry technique, showing an activity ratio in the range of 0.92 ± 0.11 to 1.02 ± 0.11. The ^{234}U/^{238}U activity ratio obtained indicated that these two uranium isotopes are in the state of secular radioactive equilibrium. The percent activity ratio of ^{238}U/total U and ^{234}U /total U is observed to vary from 47.94 ± 4.83 to 50.76 ± 4.87 and 45.80 ± 3.83 to 49.14 ± 3.99, respectively.

Keywords: uranium / alpha spectrometer / electroplating / activity

1. Introduction

The uranium (^{238}U), thorium (^{232}Th) and actinium (^{235}U) natural series are composed of radioactive nuclides with different physical and chemical properties and with half-lives varying from a few seconds to more than 10^9 years. When

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decay series occur in a closed system for physical and chemical exchange with the environment, the series tends to reach, with time, the state of secular equilibrium. In this state, the activities of all series members are equal to the activity of its first nuclide.

In nature, however, many processes lead to geological environments open to element exchanges. Such processes can occur continuously in time such as slow soil matrix dissolution by surface and groundwater, mineral precipitation, adsorption on mineral surfaces, dissolution and the recoil following alpha decay.

In recent years, the methods based on radioactive disequilibria have been applied to the study of different geological processes during the recent Quaternary, such as sedimentation in marine and continental environments (Legeleux *et al.*, 1994; Burnett and Veeh, 1992), soil formation and evolution (Mathieu *et al.*, 1995; Lowson *et al.*, 1986), groundwater dynamics (Lievert *et al.*, 1994; Ivanovich *et al.*, 1991), and magma genesis (Macdougall, 1995; Heath *et al.*, 1998; Condomines *et al.*, 1988, 1995; Chabaux and Allegre, 1994; Asmeron and Edwards, 1995). Furthermore, geochronological methods based on radioactive disequilibria have been applied in dating sedimentary and volcanic rocks younger than 300,000 years (Ivanovich *et al.*, 1992; Condomines *et al.*, 1988).

The uranium isotopes ^{238}U, ^{235}U and ^{234}U are found naturally in the environment. ^{238}U constitutes 99.27 mass percent of all uranium. The amount of natural uranium in nature varies from less than a nanogram per gram in biological material to a few percent in uranium-containing minerals. In most soils the uranium concentration is a few ppm. Natural uranium principally consists of three isotopes, primordial ^{238}U ($t_{1/2} = 4.47 \times 10^9$ y) and ^{235}U ($t_{1/2} = 7.04 \times 10^8$ y), which are parent nuclides of two independent decay series of isotopes before terminating in the stable, non-radioactive lead isotopes ^{206}Pb and ^{207}Pb, respectively, and ^{234}U ($t_{1/2} = 2.45 \times 10^5$ years), which is a member of the ^{238}U decay chain. The natural abundances of the three primary uranium isotopes ^{234}U, ^{235}U and ^{238}U as well as specific activity and relative weights are summarized in Table I (Bleise *et al.*, 2003).

TABLE I
Characteristics of uranium isotopes in natural uranium.

Isotope	Half-life (years)	Relative mass (%)	Radioactivity (%)	Decay energy (MeV)	Specific activity (Bq.g^{-1})
^{234}U	2.445×10^5	0.0053	48.9	4.8 α	231.3×10^6
^{235}U	7.04×10^8	0.711	2.2	4.4 α 0.18 i	80.01×10^3
^{238}U	4.47×10^9	99.275	48.9	4.2 α	12.44×10^3

For natural uranium, the ^{235}U/^{238}U activity ratio has a constant value of 0.046, while the ^{234}U/^{238}U activity ratio is variable. The variation in the ^{234}U/^{238}U ratio is due to natural causes in many waters (Riotte and Chabaux, 1999; Plater *et al.*, 1992), soil (Lowson and Short, 1988; Lowson *et al.*, 1986; Hansen and Stout, 1968; Stuckless *et al.*, 1977; Rosholt *et al.*, 1966), sediment and uranium ores of different geographical origin (Richter *et al.*, 1999). The mechanism of such variation is preferential leaching of ^{234}U compared with ^{238}U from the solid phase, caused by radiation damage of the crystal lattice upon alpha decay of ^{238}U, oxidation of insoluble tetravalent ^{234}U to soluble hexavalent ^{234}U during decay, and alpha recoil of ^{234}Th (and its daughter ^{234}U) into the solution phase.

^{234}U/^{238}U activity ratios in water reportedly vary from 0.5 to 40 (Gilkeson and Cowart, 1987; Osmond and Cowart, 1976), while those in soil typically range from 0.5 to 1.2 (Goldstein *et al.*, 1997; Osmond and Cowart, 1976).

Since the natural radioactive series have several alpha-emitting radionuclides, alpha spectrometry is one of the methods used to determine the isotope activity ratio. There are many published methods describing both the chemical separation and source preparation for alpha particle measurements. In the case of uranium and thorium, solvent extraction and ion exchange chromatography are the usual techniques for chemical separation and purification. There are also many methods for alpha particle spectrometry source preparation but electrodeposition carried out from aqueous solution seems to be the most frequently used technique for actinides.

Determination of uranium in soil/sediment is generally performed by acid leaching from the host matrix. From the leach solution uranium is selectively separated from other transuranics and quantitatively estimated by alpha spectrometry.

2. Material and methods

2.1. Study area

The study area is situated in a tropical region where the climate is characterized by a very hot summer, mild winter and low rainfall. This area experiences an arid to semiarid climate. This area has a hot climate during the summer (March–May) with the temperature ranging from 30 to 46.5 °C, and in winter (November–January) it varies between 16 and 29 °C. The average annual rainfall in this area is about 1000 mm, occurring mostly during the southwest monsoon (June–September). There are several small hillocks in this area with height ranging from 100 to 200 m. The Lambapur Peddagattu area where the uranium minerals
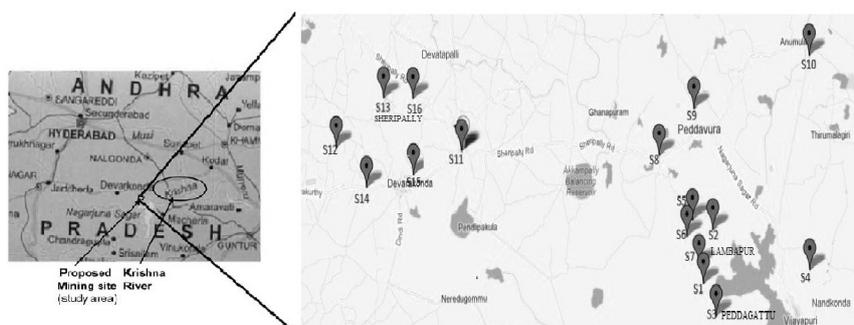
Figure 1 – *Map showing sampling locations in the Peddagattu, Lambapur and Sheripally areas.*

occur are flat-topped hills with an elevation of about 300 m msl. To understand the uranium isotopic activity ratio and spatial distribution of uranium in the proposed mining area, surface soil samples were collected from 16 locations covering Lambapur, Peddagattu and Sherilpally (Fig. 1).

2.2. Soil sampling

Samples of surface soil were collected as per the protocols of the IAEA Technical Report Series 295 (IAEA, 1989). The sampling sites are shown in Figure 1. Following removal of the surface vegetation, soil samples were collected using a spade. Soil samples were sampled to a depth of 10–15 cm. Between 2 and 3 kg (dry mass equivalent) of soil were collected at each site. Soil samples were sealed in plastic bags for transportation to the laboratory, where they were dried at 40 °C, ground to pass through a 300-micron sieve and stored in airtight containers.

2.3. Uranium concentration analysis

Soil samples were ashed at 600 °C for 6 hours or more to destroy organic components. Next, samples were acid-digested in a hot 1:1 $HF:HNO_3$ mixture for 6 hours, evaporated to near dryness and treated with $HClO_4$ to remove any remaining organics. Residues were evaporated again and further digested with concentrated HNO_3, after which they were evaporated once more before being re-dissolved in 4 M HNO_3 followed by solvent extraction with ethyl acetate in the presence of aluminum nitrate as a salting-out agent. The extracted uranium was evaporated to dryness and digested with concentrated HNO_3. The residue was dissolved in dilute HNO_3 and a suitable aliquot was taken for the conventional UV fluorimetry technique for uranium estimation.
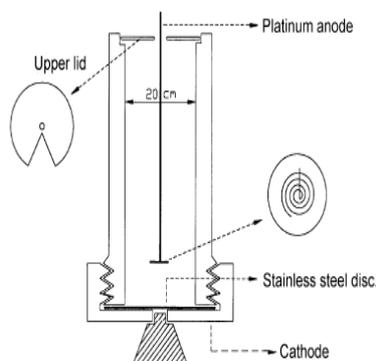
Figure 2 – *Schematic diagram of electrodeposition cell.*

2.4. Uranium isotope analysis

The activities of ^{234}U and ^{238}U in soil samples were determined by alpha spectrometry. The method employed is consistent with others reported in the literature (Goldstein *et al.*, 1997; Yamamoto *et al.*, 2002; Jia Guogang *et al.*, 2004; Vera Tome *et al.*, 1994). Soil samples were ashed at 600 °C for 6 hours or more to destroy organic components. Next, samples were acid-digested in a hot 1:1 HCl:HNO$_3$ mixture for 6 hours, evaporated to near dryness and treated with HClO$_4$ to remove any remaining organics. Residues were evaporated again and further digested with concentrated HF for 8 hours, after which they were evaporated once more before being re-dissolved in 4 M HNO$_3$. The U and Th present in the sample solutions were co-precipitated with Fe(OH)$_3$ by adding ammonia solution (35%, added as supplied) with the precipitate then separated from the solution by centrifugation and decanting. Precipitates were rinsed with deionized water, re-centrifuged and dissolved in concentrated HCl. Samples were then evaporated to near dryness, dissolved in 8M HCl and subjected to solvent extraction with di-isopropyl ether to remove Fe. Following this, sample solutions were passed through glass columns containing chloride-form anion-exchange resin (Dowex, 1 × 8, 100-200 mesh, pre-conditioned with ~50 mL 8 M HCl) for U/Th separation. After rinsing with 5 × 10 mL 8M HCl to ensure all Th had been flushed, U adhering to the resin was eluted with 100 mL 0.1 M HCl. The eluted samples were then evaporated to near dryness and electrodeposited onto stainless steel planchettes for counting by alpha spectrometry. The counting time varied depending on sample activity.

2.5. Preparation of electrodeposition

The electroplating solution used in this study was prepared as follows: 43 g ammonium oxalate, 53 g ammonium sulfate, 18 g hydroxylammonium sulfate and

2 g diethyltriaminopentaacetic acid (DTPA) were dissolved in 1 L H_2O and then the pH was exactly adjusted to 1.8 with sulfuric acid. The electroplating cell was made of Teflon. Figure 2 describes the cell used in the study.

The effective area of electrodeposition was 3.14 cm^2. The anode was a polished platinum spiral wire. The upper lid, from which a small segment was cut out, was used not only to prevent release of the electrolyte outward but also to check visually the volume of the electrolyte inside the cell during the electrodeposition procedure.

2.6. Electrodeposition procedure

1. Added the U fraction obtained after the separation and cleaning procedure to a 50-mL crystallizing dish, and then evaporated it on a sand bath slowly to near dryness;
2. rinsed the crystallizing dish with a 3-mL electroplating solution and transferred the rinsing solution into an electrodeposition cell;
3. washed the crystallizing dish twice with a 3-mL electroplating solution and transferred it into the cell;
4. adjusted the distance between the two electrodes to about 5 mm;
5. turned on power for 2 hours and then adjusted the current to 950 mA;
6. added about 1 mL conc. NH_4OH to the cell before the end of electrodeposition;
7. rinsed the stainless steel plate with water and alcohol, and flamed it for 30 seconds in the flame of a Bunsen burner.

2.7. Alpha spectrometry

The alpha spectrometer (Eurisys Mesures, Model 7184) includes an ion-implanted silicon detector (CANBERRA, size: 600 mm^2; alpha resolution: 18.2 keV FWHM at 5.486 MeV of ^{241}Am) in a vacuum chamber (Edwards, Model E2M1.5), a detector bias supplier, a preamplifier, a linear amplifier, and a multichannel pulse height analyzer. During the measurement, the pressure of the chamber was maintained at less than 0.2 Torr.

3. Results and discussion

Typical alpha spectra of standard natural uranium and uranium in soil samples are presented in Figures 3 and 4, respectively.

The activity ratio of $^{234}U/^{238}U$ is observed to vary between 0.92 ± 0.11 and 1.02 ± 0.11 (Fig. 5). The observed isotopic activity ratios of $^{234}U/^{238}U$ in soil
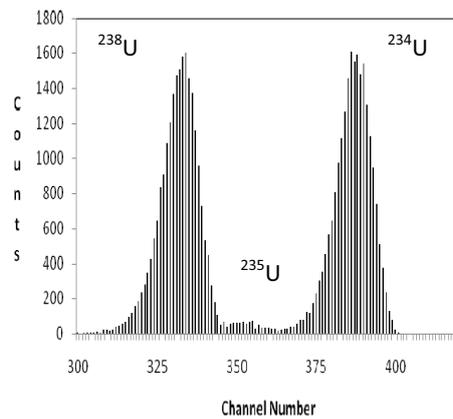
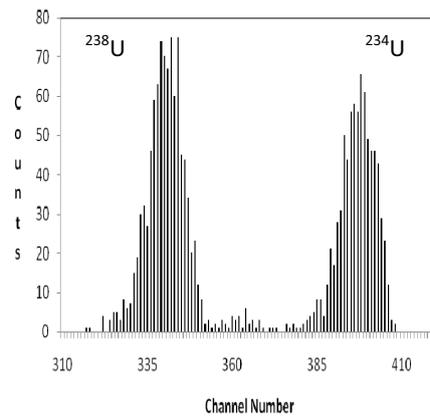**Figure 3 – *A typical alpha spectrum of standard natural uranium.***

Figure 4 – *A typical alpha spectrum of uranium in soil samples.*

samples are comparable to 0.8-1.2, as reported elsewhere (Goldstein *et al.*, 1997; Fisenne, 1996).

Any deviation in the isotopic activity ratio of ^{234}U/^{238}U due to hydrogeochemical changes in the environment during operation/post-operation will also lead to variation in the inherent percent activity ratios of ^{238}U/total U and ^{234}U/total U. Hence, the observations in the study area were also expressed in percent activity ratio of ^{238}U/total U and that of ^{234}U /total U for feasibility of
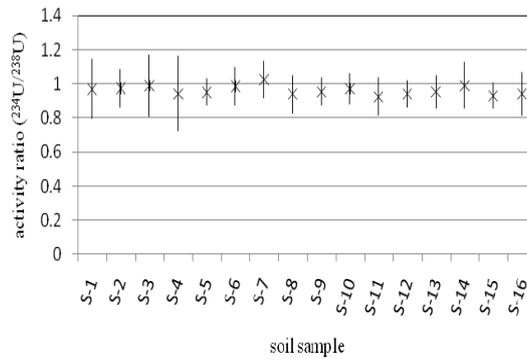
Figure 5 – *Activity ratio of $^{234}U/^{238}U$ in soil samples.*

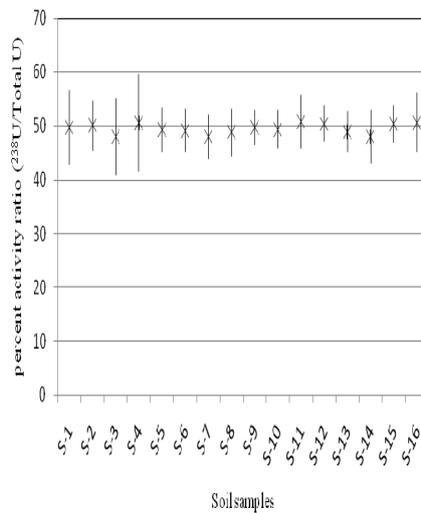**Figure 6 –** *Percent activity ratio of $^{238}U/total\ U$ in soil samples.*

future studies. The percent activity ratio of $^{238}U/total\ U$ is observed to vary between 47.94 ± 4.83 and 50.76 ± 4.87 (Fig. 6). The percent activity ratio of $^{234}U/total\ U$ is observed to vary from 45.80 ± 3.83 to 49.14 ± 3.99 (Fig. 7).

The observed percent radioactivity of ^{238}U and ^{234}U isotopes in natural uranium is comparable with the 48.9 and 48.9, respectively, reported elsewhere
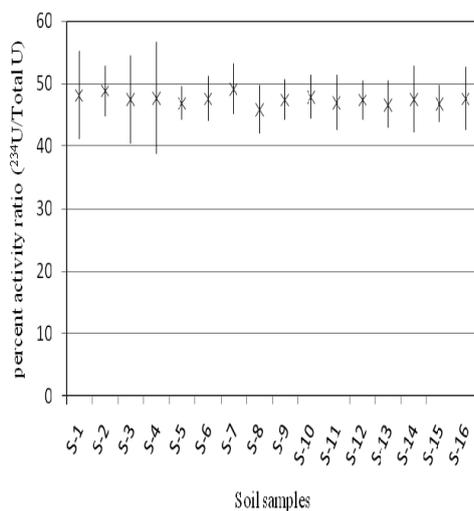
Figure 7 – *Percent activity ratio of ^{234}U/ total U in soil samples.*

TABLE II
Uranium concentration in soil samples.

Peddagattu and Lambapur area		Sheripally area	
sample	uranium (ppm)	sample	uranium (ppm)
S1	1.9 ± 0.2	S11	6.2 ± 0.4
S2	5.6 ± 0.3	S12	4.4 ± 0.3
S3	3.1 ± 0.2	S13	2.3 ± 0.2
S4	2.1 ± 0.2	S14	5.1 ± 0.3
S5	7.9 ± 0.4	S15	6.8 ± 0.4
S6	2.4 ± 0.2	S16	6.1 ± 0.3
S7	3.5 ± 0.2		
S8	1.7 ± 0.2		
S9	0.7 ± 0.2		
S10	3.9 ± 0.3		

(Bleise *et al.*, 2003). The uncertainties associated with the activity ratio correspond only to the statistical counting error in the alpha spectrum.Uranium concentrations in soil samples of the study area are observed to be in the range of 0.7 ± 0.2 ppm to 7.9 ± 0.4 ppm with an average of 3.4 ppm. Uranium concentrations in soil samples of the study area are shown in Table II.

The uranium concentration in groundwater in the study area and a part of Nalgonda district, Andhra Pradesh, India, has been reported to be in the range of 0.2 ppb to 68 ppb with a mean of 18.5 ppb (Brindha *et al.*, 2011). The uranium concentration in groundwater changes depending on lithology, degree of weathering and rainfall recharge.

4. Conclusion

Spatial distribution and isotopic ratios (^{234}U/^{238}U, ^{238}U/total U and ^{234}U/total U) of uranium in Indian soil in the Lambapur, Peddagattu and Sherilpally areas in Nalgonda Distict, Andhra Padesh, a proposed uranium mining site, were measured using alpha spectrometry. Uranium concentrations in soil samples were observed in the range of 0.7 ± 0.2 ppm to 7.9 ± 0.4 ppm with an average of 3.4 ppm. The ^{234}U/^{238}U isotopic activity ratio varied from 0.92 ± 0.11 to 1.02 ± 0.11. Soil samples in the study area exhibited secular equilibrium between ^{234}U and ^{238}U. The percent activity ratio of ^{238}U/total U and ^{234}U/total U varied between 47.94 ± 4.83 to 50.76 ± 4.87, and 45.80 ± 3.83 to 49.14 ± 3.99, respectively. The observed percent activity of ^{238}U and ^{234}U to total uranium activity indicated the presence of natural uranium in the soil in the study area. The pre-operational environmental monitoring results will be utilized to correlate the results with those during the operational/post-operational phase environmental monitoring.

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