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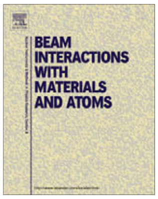

Determination of the isotopic ratio $^{236}U/^{238}U$ in Austrian water samples

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ABSTRACT

^{236}U with a half life of 2.3×10^7 years is naturally produced in ultra-trace amounts ($^{236}U/^{238}U < 10^{-10}$) in ores, soils and rocks, while a huge amount has been produced in nuclear power plants and possibly nuclear weapons tests by man. Thus, anthropogenic uranium may cause a significant measurement background for geological applications of natural ^{236}U. To investigate this background, water samples from rivers, creeks and wells were collected in the alpine region of Forstau (Salzburg, Austria) and from surrounding areas. Thin sources for alpha spectrometry were prepared by anion exchange and co-precipitation with NdF_3 to determine the ^{238}U concentration. These filters were reprocessed for the analysis of the isotopic ratio $^{236}U/^{238}U$ by AMS. The special aim was the characterization of the $^{236}U/^{238}U$ ratio in natural waters and the investigation of contributions from anthropogenic sources. Our measurements of ^{236}U in Austrian water samples from wells, rivers and creeks show the first data on the spreading of anthropogenic ^{236}U in the general environment far from local contamination sources.

1. Introduction

^{236}U with a half life of 2.3×10^7 years is continuously produced via thermal neutron capture on the isotope ^{235}U which is present in uranium ores, soils and rocks. Natural production results from neutrons produced by (α,n)-reactions on lighter nuclides, spontaneous fission of ^{238}U, induced fission of ^{235}U and at the earth's surface from cosmic rays [1,2]. The natural ratio in river water is expected to be between 1×10^{-14} and 1×10^{-13} [3]. Additionally, a huge amount ($\sim 10^6$ kg, [3]) has been produced by man in nuclear power plants. However, the extend to which this has been dispersed into the general environment is as yet unclear. Our main aim was to probe for the first time whether anthropogenic ^{236}U, which up to now has only been detected near known contaminated sites [4–6], is present also in the "typical" environment. The northern foothills of the Alps in Austria was one of the regions in western Europe which was most heavily affected by fallout from the Chernobyl accident, with ^{137}Cs depositions of 50 kBq/m^2 or even higher [7]. The deposition shows a strong regional variation of up to 1:100, controlled by the rainfall pattern. The mean inventory of ^{137}Cs from global fallout was 2.3 kBq/m^2 at the time of the Chernobyl accident. Well and rivulet water from this area were chosen for our first investigations and were expected to provide data on the average ^{236}U contamination throughout their feeding area because uranium generally shows good water solubility. Measurements on river sediments from the Garigliano river (Southern Italy) had not shown ^{236}U levels above the laboratory background in a previous investigation [8]. Compared to ore samples [2] with a large uranium content, the measurement of these low-concentration natural samples depends strongly on sensitivity and background, and the samples require a more complex preparation procedure.

Mineral waters which stem from very deep aquifers generally show a high amount of natural radionuclides compared to surface water and water from shallower wells; to date artificial nuclides have not been found in these very old, deeply stored waters [9]. An example of this water type is well water from inside the Badgastein radon healing gallery (Salzburg, Austria), which was also investigated here.

2. Materials and methods

Water samples were collected in different regions of Austria as shown in Fig. 1. These were mainly in Salzburg and Styria but also in Lower and Upper Austria from rivers, creeks and wells. A uranium mine existed more than 20 years ago near the sampling site in Forstau (Salzburg), and studies have shown that in this area relatively higher uranium concentrations can be found in river and spring waters [10]. We collected samples in this region from a well (Fahlhaus) and from a river (Forstaubach).

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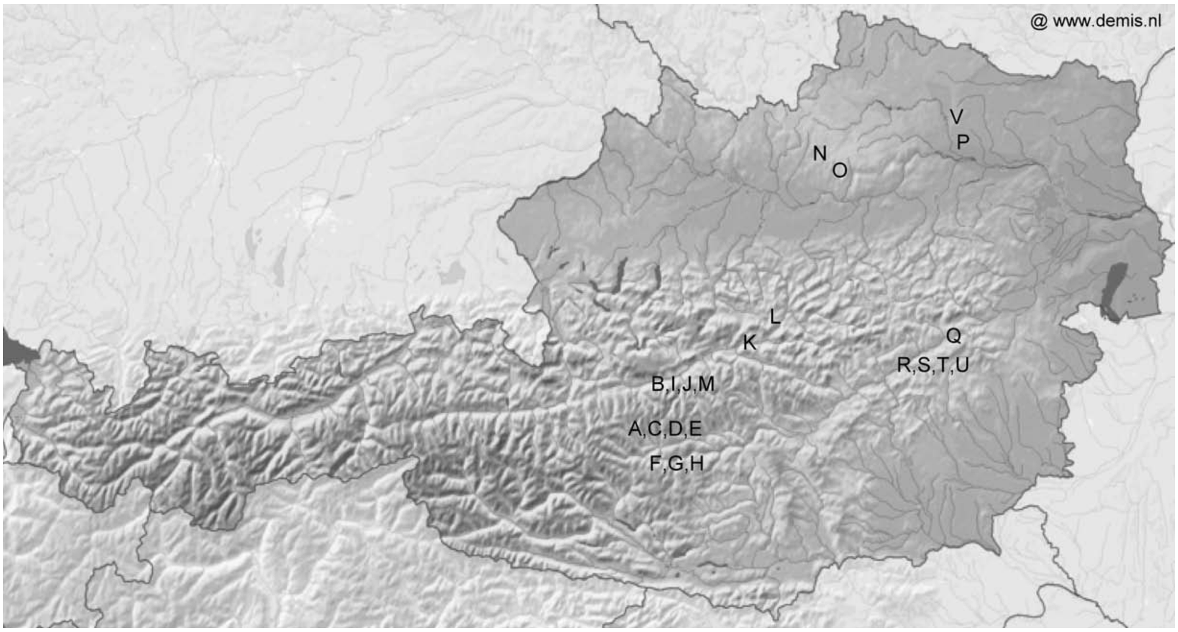

Fig. 1. Sampling sites (a description of the alphabetic character is given in Table 2).

2.1. Sample preparation and measurements

Water samples of 1.5 L and up to 5 L were collected and acidified with an appropriate amount of 7.2 M HNO_3, and a ^{232}U spike (NIST SRM 4324B, 1.443 ± 0.009 Bq/mL, reference date September 30, 2006) was added. Two different resins (Dowex 1x2, Dow Chemical Co. and UTEVA, Eichrom Technologies, LLC) were used for uranium separation.

2.2. Separation by Dowex 1x2

After adding 20 μL of the ^{232}U tracer the water samples were evaporated to dryness and fumed three times with conc. HNO_3 and three times with conc. HCl. In some cases after the HNO_3 fuming step it was also necessary to fume the samples with conc. HF because of the presence of large amounts of silica acid. Where the HF step was necessary the samples were fumed several times with H_3BO_3 ($c = 5$ g/100 mL), then with HNO_3/H_2O_2 and finally with conc. HCl. The residue was dissolved in 80 mL 8 M HCl, loaded onto the column (Dowex 1x2, 100–200 mesh, Cl^- form) and washed twice with 25 mL 8 M HCl to remove Th and Ca. Uranium was eluted with 90 mL 0.1 M HCl [11].

2.3. Separation by UTEVA

The procedure for the determination of uranium in water using UTEVA available from Eichrom Technologies, LLC [12] was modified to our needs. After adding the ^{232}U spike the water sample was evaporated to maximally 200 mL, 0.5 mL of 1.25 M $Ca(NO_3)_2$ was added and the sample heated until boiling. Phenolphthalein indicator and 200 μL of 3.2 M $(NH_4)_2HPO_4$ were added followed by conc. NH_4OH to reach the phenolphthalein end point and formation of $Ca_3(PO_4)_2$ (pH 8–10). The sample was heated for 30 min and the precipitate was allowed to settle over night. If it was not possible to decant most of the supernatant, the solution was transferred stepwise to a 50 mL centrifuge tube and centrifuged 30 min at 4000 rpm (the relative centrifugal force (RCF) is 1646). The precipitate was washed three times with Millipore water (approximately twice the volume of the precipitate) and was centrifuged for another 20 min at 4000 rpm. It was then dissolved in 10 mL conc. HNO_3, transferred to a 100 mL beaker, 4 mL H_2O_2 was added and the solution evaporated to dryness. This step was repeated with another 10 mL conc. HNO_3. The residue was dissolved in 15 mL 3 M HNO_3–1 M $Al(NO_3)_3$ and any insoluble residua centrifuged off (20 min at 4000 rpm). A column filled with 0.5 g of UTEVA (100–150 μm) was conditioned with 3 M HNO_3 before the sample was transferred to the column. The beaker was rinsed with 5 mL and then three times with 10 mL of 3 M HNO_3. To convert the resin to the chloride form 10 mL of 9 M HCl was loaded onto the column, and after adding (three times) 10 mL 5 M HCl–0.05 M oxalic acid to remove Np, Pu and Th, uranium was eluted with 30 mL of 0.01 M HCl.

2.4. Microprecipitation

The uranium fraction was evaporated to dryness, fumed three times with 5 mL conc. HNO_3 and 2 mL H_2O_2 and three times with 5 mL conc. HCl. The residue was taken up in 20 mL 1 M HCl and 50 μL of Nd^{3+} solution ($c = 1$ mg/mL), 100 μL of 15 % $TiCl_3$ solution (for uranium reduction) and 5 mL 40% HF were added [13,14]. After 1 h the solution was filtered through a cellulose nitrate membrane filter (Whatman®, 0.1 μm pore size) and the NdF_3 precipitate washed three times with 2 mL 4% HF and twice with 2 mL Millipore water.

2.5. Alpha measurement

Alpha spectrometry was performed using a PIPS (Passivated Implanted Planar Silicon) Detector, Model 7401 VR, Canberra/Packard with an active area of 450 mm^2. The counting time was 252000 s and for these measurements, the detection limits, calculated according to Currie [15], were 0.3 mBq/sample for ^{238}U. The software Genie 2.1 (Canberra, USA) was used to evaluate the spectra.

2.6. AMS measurement

For the AMS measurement the filters already analyzed by alpha spectrometry were reprocessed according to Srncik et al. [16]. The procedure consists of re-dissolving the precipitate with HNO_3, coprecipitation with iron hydroxide, and combustion to oxides which

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are pressed into an aluminium sample holder either with or without silver as binder. The VERA setup as used for actinide measurements is described in Vockenhuber et al. [17]. Molecular UO$^-$ ions are extracted from the solid sample in the caesium sputter source. The low-energy mass spectrometer selects ^{236}U^{16}O$^-$. Gas stripping at 3 MV terminal voltage efficiently removes any molecular isobars (especially ^{235}UH$^-$). The stripping yield achieved is about 5% for U^{5+}. The ions of interest and any interfering ions which pass all beam filters are identified with a high resolution time-of-flight system with 2.8 m flight path, a time resolution of 0.7 ns (FWHM) for ^{238}U at 18 MeV and a transmission of 30%. The energy is then measured in an ionization chamber.

Table 1
Isotopic ratio of ^{236}U/^{238}U from the Badgastein Water.

Sample	^{236}U/^{238}U
GastW0.1L	$(1.06 \pm 0.19) \times 10^{-9}$
GastW0.3L	$(7.11 \pm 1.22) \times 10^{-10}$
GastW1L	$(3.03 \pm 0.40) \times 10^{-11}$
GastW3L	$(2.42 \pm 0.21) \times 10^{-11}$

3. Results and discussion

Initially we measured four different volumes (0.1 L, 0.3 L, 1 L and 3 L) of water from the radon gallery in Badgastein (Salzburg, Austria) because it is the well with the highest known content of

Table 2
The isotopic ratio of ^{236}U/^{238}U by AMS in Austrian water samples. The measurement uncertainties are given in $\pm\sigma$.

Map position	Sample	^{236}U/^{238}U	Volume (L)	Chem. yield (%)	^{238}U (µg/L)
A	Brandgrabenbach	$(6.29 \pm 1.19) \times 10^{-8}$	1.5	97 ± 13	0.18
B	Forstaubach	$(6.99 \pm 0.92) \times 10^{-8}$	1.5	81 ± 7	0.39
C	Gengitschhütte	$(2.12 \pm 1.46) \times 10^{-8}$	1.5	56 ± 5	–
D	Kerngrabenbach	$(4.37 \pm 0.13) \times 10^{-8}$	1.5	86 ± 8	2.7
E	Liegnitz	–	1.5	61 ± 6	0.019
F	Purngrabenbach	$(5.76 \pm 0.85) \times 10^{-8}$	1.5	60 ± 8	0.53
G	Taurach Süd	$(4.04 \pm 0.25) \times 10^{-8}$	1.5	43 ± 4	0.83
H	Reitbach	$(1.14 \pm 0.37) \times 10^{-8}$	1.5	82 ± 11	0.14
I	Fahlhaus	$(5.95 \pm 1.27) \times 10^{-9}$	4.424	86 ± 11	5.46
J	Preuneggbach	$(5.36 \pm 1.12) \times 10^{-9}$	4.887	73 ± 6	1.90
K	Enns/Weißenbach	$(1.51 \pm 0.07) \times 10^{-7}$	4.959	67 ± 6	0.56
L	Marienwaldweg	$(2.84 \pm 0.36) \times 10^{-8}$	4.887	55 ± 5	0.51
M	Enns/Warterdorf	$(4.65 \pm 2.28) \times 10^{-9}$	4.917	28 ± 3	1.41
N	Irxwasser	$(4.57 \pm 0.39) \times 10^{-5}$	4.392	58 ± 5	0.23
O	Augenbründl	$(2.75 \pm 0.42) \times 10^{-7}$	4.314	49 ± 7	0.19
P	Kamp	$(7.02 \pm 1.28) \times 10^{-8}$	4.997	23 ± 2	0.40
Q	Kaltenbach	$(1.86 \pm 0.14) \times 10^{-7}$	2.431	53 ± 5	0.91
R	Feistritz	$(5.65 \pm 1.81) \times 10^{-7}$	1.431	77 ± 7	0.19
S	Tributary to Reithbach	$(5.72 \pm 0.30) \times 10^{-8}$	5.398	49 ± 4	1.11
T	Reithbach	$(9.98 \pm 1.23) \times 10^{-9}$	5.29	93 ± 8	0.80
U	Small tributary to Reithbach	$(3.58 \pm 0.21) \times 10^{-8}$	1.496	88 ± 12	4.48
V	Kamegg4	$(1.24 \pm 0.04) \times 10^{-7}$	5.416	25 ± 3	6.85

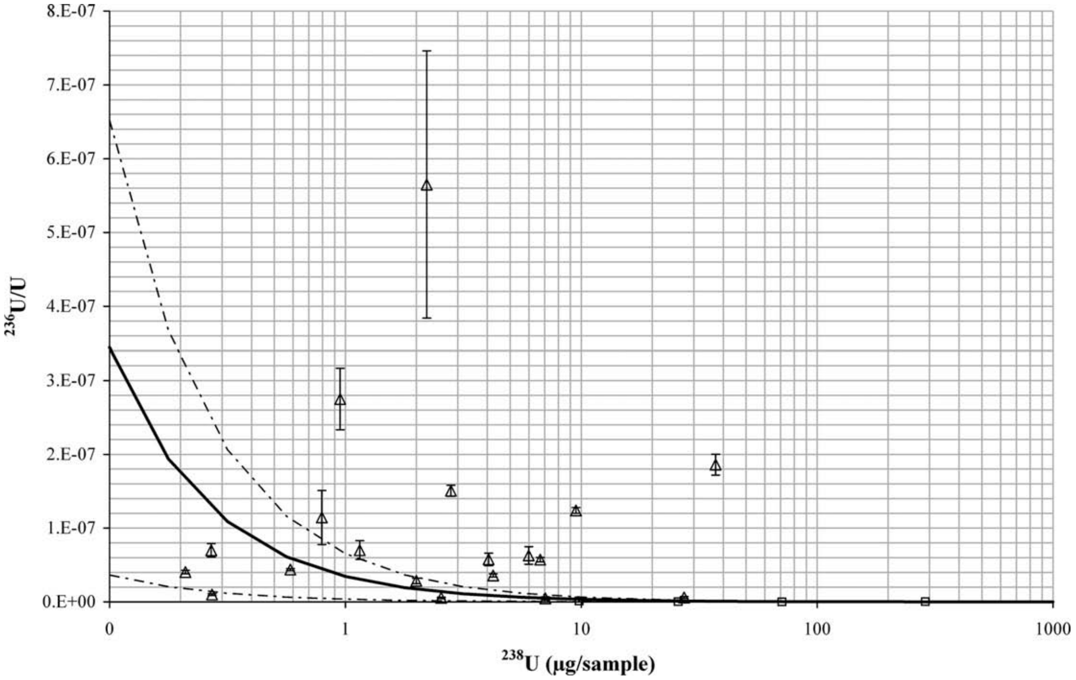

Fig. 2. The isotopic ratio ^{236}U/U determined by AMS versus the total amount of ^{238}U determined by alpha spectrometry. The open squares show the Gasteiner water and the open triangles represent all other water samples. The black line indicates the background whereas the uncertainty is shown by a dashed line. The error bars of the mass (x-direction) are smaller than the point size. The uncertainty of the blank correction is not included in the error bars of the points. One sample [Irxwasser, $(4.57 \pm 0.39) \times 10^{-5}$] is too high to be shown in the plot.

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^{238}U in Austria (∼88 μg/L), and the clearly pre-anthropogenic ^{236}U/^{238}U isotopic ratio is already known from previous measurements (∼6.6×10^{-12} [3]). The obtained values are shown in Table 1 to be between 10^{-11} and 10^{-9}; they do not agree with the previously reported, clearly lower value. We attribute this to differences between the sample preparation procedures in the past and now: no spike was added to the earlier samples and they had not passed through a neodymium co-precipitation step. A much simpler separation with Dowex 1x8 had been performed, which the high uranium concentration in Badgastein water makes possible, but this is not applicable for the low-concentration and large volume samples which are the target of this project. The previously used laboratory is no longer available, and all laboratory ware and reagents have been changed. To assess whether the ^{232}U spike contains ^{236}U, a 20 μL spike solution was co-precipitated with iron hydroxide and measured by AMS. The result obtained corresponds to $(9 \pm 8) \times 10^7$ atoms of ^{236}U, whereas a sputter target prepared from directly combusted pure iron gave no ^{236}U counts. The value for the spike is unexpectedly high, but too low to explain the high isotopic ratios obtained for the new Badgastein samples, thus an additional background contribution during later steps of the sample preparation exists. Further investigations will be performed to reduce the background, but, as discussed in the results section below, the present level is sufficiently low for investigations of anthropogenically influenced surface water.

The results of the isotopic ratio ^{236}U/^{238}U measured by AMS are given in Table 2 and Fig. 2. All ratios are higher than the natural ratio ($<10^{-10}$). If we subtract the laboratory background of about 10^8 ^{236}U atoms per sample (black line in Fig. 2), several of the samples show a ^{236}U content significantly above our background line estimated from the Badgastein water (Fig. 2); especially remarkable is the value of Irxwasser with an atomic ratio of $(4.57 \pm 0.03) \times 10^{-5}$. Two especially small samples show a ^{236}U/^{238}U value lower than the background; we attribute this to a bad reproducibility of the background. Generally, no correlation is visible between the ^{236}U and the ^{238}U concentration, which is in agreement with the assumption that the (anthropogenic) ^{236}U and the (natural) ^{238}U originate from different sources.

4. Conclusion

Our measurements of ^{236}U in water samples from wells and rivulets in Austria have yielded the first data on the dispersion of anthropogenic ^{236}U in the general environment far from local contamination sources, and demonstrate that AMS can reach the required sensitivity levels, which are generally too low for other methods. The ^{238}U concentrations range from 0.019 μg/L (Liegnitz, Salzburg) up to 6.85 μg/L (Kamegg4, Lower Austria), while the ^{236}U levels range from 4.14×10^6 atoms/L to 2.14×10^9 atoms/L.

Several samples show ^{236}U/^{238}U ratios considerably higher than the natural ratio. We think that we see in Austria an almost omnipresent ^{236}U contamination from global fallout and/or from Chernobyl. The absence of a second anthropogenic isotope of uranium (as it exists e.g. in the case of Cs or Pu) makes the assessment of the source for a single sample difficult. Our small first data set does not yet allow us to determine whether the ^{236}U contamination is correlated with the spatial pattern of ^{137}Cs fallout from Chernobyl.

The unexpectedly high laboratory background of around 10^8 atoms ^{236}U per sample is perhaps a further indication of the widespread distribution of anthropogenic uranium, which was undetectable before the development of suitable AMS methods. Screening of all used laboratory ware and reagents for ^{236}U contamination will be necessary to reduce the background to the levels required for the much lower natural isotopic ratios. Further measurements will be performed to obtain a general overview of the environmental distribution of anthropogenic ^{236}U, and to identify its main sources.

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