$^{236}U/^{238}U$ and $^{240}Pu/^{239}Pu$ isotopic ratios in small (2 L) sea and river water samples

R. Eigl [a,*], M. Srncik [a], P. Steier [b], G. Wallner [a]

[a] *Department of Inorganic Chemistry, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria*
[b] *VERA Laboratory, Faculty of Physics − Isotope Research, University of Vienna, Währinger Straße 17, A-1090 Vienna, Austria*

ABSTRACT

Accelerator Mass Spectrometry (AMS) and alpha spectrometry were used to determine uranium (^{236}U, ^{238}U, ^{234}U) and plutonium isotopes (^{239}Pu, ^{240}Pu) in sea and river water samples. Plutonium was separated by Dowex® 1 × 8 resin and UTEVA® resin was used for uranium purification. The measured $^{236}U/^{238}U$ isotopic ratios for surface water from the Atlantic Ocean, the Pacific Ocean and the Black Sea were in the order of 10^{-9}, while values for river water were in the order of 10^{-8}. These contaminations may be attributed to global fallout. A sample of the reference material IAEA-443, collected from the Irish Sea, showed, in accordance to the reference value, a ratio that was 10^3 times higher due to effluents from the reprocessing plant at Sellafield. These results underline the good suitability of $^{236}U/^{238}U$ as a tracer for hydrology and oceanography, and show that relatively small water samples are sufficient for the determination of ^{236}U by AMS, which is not the case for plutonium with present techniques. The plutonium concentrations in our water samples could only be measured with large uncertainties and were in the order of 10^{-3} mBq/L (with the exception of the Irish Sea sample).

1. Introduction

1.1. Uranium

Naturally occurring uranium consists mainly of the primordial nuclides ^{238}U and ^{235}U as well as of ^{234}U, which is part of the ^{238}U−^{226}Ra decay series. The natural abundances of those uranium isotopes are approximately 99.3% ^{238}U, 0.72% ^{235}U and 0.005% ^{234}U. ^{236}U, an α-emitter with a half-life of 2.3×10^7 years, occurs in nature only in ultra-trace amounts. The global inventory of natural ^{236}U is estimated to be only 30 kg ^{236}U in the upper layers of land surface and less than 0.5 kg in the oceans. The anthropogenic inventory, on the other hand, is expected to be in the order of 10^6 kg, based on the assumption that the total uranium mined till 2003 produces 2.2×10^9 kg and assuming that 50% of ^{235}U were actually used up in reactors (Steier et al., 2008). The estimated natural $^{236}U/^{238}U$ atom ratios in the pre-anthropogenic environment range from 10^{-14} to 10^{-10} (Steier et al., 2008), but so far only the highest of these ratios, found in uranium ore, have been verified on real samples (Srncik et al., 2011c).

^{236}U can be formed by various ways, induced either by thermal or fast neutrons. In nature, the thermal neutron capture process $^{235}U(n, \gamma)U^{236}$ is enabled by neutrons produced from (α,n)-reactions on lighter nuclei such as Na and Mg and from spontaneous fission of ^{238}U. The thermal neutron capture cross section of the $^{235}U(n,\gamma)^{236}U$ reaction is 95 b, which is about 1/6 of the fission cross section (586 b) (Mironov et al., 2002). Thermal neutrons derived from cosmic rays can also induce production of ^{236}U on the earth's surface (Fabryka-Martin, 1988; Wilcken et al., 2008). ^{236}U from the atmospheric weapons tests originates mostly from $^{238}U(n,3n)^{236}U$ reactions with fast neutrons and a minor contribution results from $^{235}U(n,\gamma)^{236}U$ reactions (Sakaguchi et al., 2009). However, a much greater amount of ^{236}U is produced in nuclear reactors, also via the thermal neutron capture on ^{235}U (Mironov et al., 2002).

Based on the fact that already small amounts of irradiated uranium can significantly change the $^{236}U/^{238}U$ isotopic ratio, ^{236}U can figure as a useful tracer of environmental processes, because it carries a key signature to differentiate uranium sources (Lee et al., 2008). So far, no widespread survey has been completed because levels are too low for routine detection by techniques other than Accelerator Mass Spectrometry (AMS) (Buchholz et al., 2007; Hotchkis et al., 2000; Marsden et al., 2001; Quinto et al., 2009; Zhao et al., 1997). In the past, measurements could identify ^{236}U only in the vicinity of known contaminated sites (Sellafield, Chernobyl,

* Corresponding author. Tel.: +43 1 4277 52623; fax: +43 1 4277 52620.
  E-mail address: rosmarie_eigl@yahoo.de (R. Eigl).

etc.), but during the last years suitable methods have been established and the Vienna Environmental Research Accelerator (VERA) was especially adapted for this isotope (Steier et al., 2009; Srncik et al., 2010, 2011a).

Uranium behaves as a conservative element in the ocean, with a residence time of several 10^5 years (Dunk et al., 2002). This makes anthropogenic ^{236}U a promising candidate as isotopic tracer in oceanography. So far, little data has been published on the global distribution of ^{236}U in the sea. Two oceanic depth profiles of ^{236}U sampled in the western equatorial Atlantic Ocean were presented by Christl et al. (2012). The $^{236}U/^{238}U$ ratios decrease from about 10^{-9} at the surface down to about 10^{-10} in a depth of 4250 m. Similar values of a few times 10^{-9} are observed for surface water of the Japan Sea (Sakaguchi et al., 2012), corresponding to 10^7 atoms $^{236}U/L$ water. Both previous studies (Christl et al., 2012; Sakaguchi et al., 2012) use sample volumes of about 20 L. However, AMS of ^{236}U reaches overall detection efficiency in the order of 10^{-4}, suggesting that a reasonable measurement precision may be reached with less than 1 L of water. Such a small sample size would greatly simplify routine application, and render ^{236}U superior to other isotopic tracers, especially to the well established ^{137}Cs (Hirose et al., 2005). In order to verify that much smaller sample sizes are realistic, we performed our measurements with samples of only 2 L water (i.e. 6 μg of uranium). Therefore, our work, which focuses primarily on the chemical preparation of samples, is part of the effort to establish ^{236}U as an oceanographic tracer.

1.2. Plutonium

While ^{239}Pu occurs naturally only in ultra-trace amounts, it is produced in large quantities from nuclear fuel during reactor activity (Lee et al., 2001). As plutonium is formed by neutron irradiation, the $^{240}Pu/^{239}Pu$ ratio is a function of the neutron flux and the duration of irradiation and thus a characteristic fingerprint of the source. The assessment of isotopic ratios enables one to reconstruct the history of the neutron exposure to a sample (Hrnecek et al., 2005). The mean $^{240}Pu/^{239}Pu$ atom ratio for global fallout from atmospheric weapons testing is found to be 0.178 ± 0.023 (Perkins and Thomas, 1980), whereas $^{240}Pu/^{239}Pu$ ratios from the Chernobyl accident are characterized by a significantly higher value of 0.38 ± 0.07 (Lindahl et al., 2010).

The amount of plutonium found in sea water is very low with activity concentrations in the range of $(0.8–9.2) \times 10^{-3}$ mBq/L for the Pacific Ocean, for instance (Hirose et al., 2007). This is due to the fact that plutonium attaches to particles and settles to the seafloor. Therefore it was necessary to improve the sensitivity of the analysis methods for plutonium isotopes and in recent years, various high-capacity analytical procedures such as high resolution inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS) and AMS were established as methods for the detection of plutonium (Lee et al., 2001). We included plutonium in our study, because it is a well established environmental tracer that can be extracted by procedures similar to those used for ^{236}U extraction and it is essentially of the same origin (global fallout). However, the low number of atoms expected in our small samples prohibited detection by α-spectroscopy, and reliable assessment was even difficult with AMS.

2. Materials and methods

2.1. Samples

Water samples were collected from rivers and oceans, as shown in Table 1. In order to obtain samples from the whole world within reasonable time and affordable cost, we decided to take our water

Table 1
Sample locations.

Sample	Origin	N [°]	E [°]
La Palma	Atlantic Ocean	28.718	−17.992
Rio Negro	Rio Negro	−3.061	−60.414
Danube	Danube	45.175	29.107
Hawaii	Pacific Ocean	19.557	−155.966
Irish Sea	Irish Sea	54.40	−3.55
Black Sea	Black Sea	44.430	28.769

samples on the side of conferences and private travels of the scientists involved. Samples were collected in PE canisters used for distilled water or bottles used for drinking water, which were bought in local shops near the sampling sites and emptied. Canisters were repeatedly rinsed with the sampling water before collecting the actual samples. The Atlantic ocean water samples were taken on Nov 20, 2007 near La Palma, one of the Canary islands (Spain), about 3 km east of Playa de la Veta (28°43′19″ N, 17°58′50″ W) from board of a rented boat. Pacific water samples were taken at 19°33′26″ N, 155°57′57″ W from the rocky coast near Kahaluu-Keauhou on Big Island, Hawaii (USA), on June 5, 2009. The Black Sea sample was collected 10 m off the gravel beach near Vadu, Romania (44°26′24″ N, 28°46′44″ E) on May 6, 2008. The Irish Sea water measured was the reference material IAEA-381 (Povinec et al., 2002), later recertified as IAEA-443 (IAEA, 2009).

River water samples from the Danube were sampled at 45°10′29″ N, 29°06′41″ E, near Maliuc (Romania), close to the mouth into the Black Sea, on May 4, 2008, from the reinforced river bank. Rio Negro water was sampled from 2°59′46″ S, 60°29′06″ W from a rented boat in the middle of the river on December 14, 2008. The samples were shipped back to Vienna by mail.

2.2. Experimental

Prior to sample preparation, the samples were acidified with 5 mL of HNO_3 per liter of sample inside the original containers, stored for at least 24 h, and then split in order to prepare two different sub-samples for alpha spectrometry and AMS, respectively. Empty canisters were rinsed with diluted HNO_3 and the solution was added to the sample.

2.2.1. Sample preparation for alpha spectrometry
For the determination of the ^{238}U and ^{234}U content by α-spectrometry, 20 μL of ^{232}U spike solution (NIST SRM 4324B, 28.9 ± 1.8 mBq/20 μL, reference date September 30, 2005) were added to 1 L of the acidified water samples. After addition of 10 mL Fe^{3+}-solution (1 mg Fe^{3+}/mL), the samples were heated for 2 h at 70–80 °C. Then, the pH was adjusted to pH = 8–9 with NH_4OH solution, which results in $Fe(OH)_3$ precipitation. The next day, the supernatant was decanted and the solution centrifuged (RCF 1340/12 min). The precipitate was dissolved in 5 mL HNO_3, evaporated to dryness and redissolved in 10 mL 3 M HNO_3.

A column filled with 0.5 g UTEVA® (100–150 μm) resin was conditioned with 3 M HNO_3. The sample solution was brought on the column and the beaker was rinsed with 20 mL 3 M HNO_3. Then 5 mL 9 M HCl and 20 mL 5 M HCl were used to remove Th, Pu and Np. Uranium was eluted using 30 mL 0.01 M HCl (Eichrom Technologies, 2001).

The sample solution was evaporated to dryness and fumed 3 times with 5 mL HNO_3 and 0.5 mL 30% H_2O_2 solution and then 3×5 mL concentrated HCl. The residue was taken up in 20 mL 1 M HCl and for the micro-precipitation, 50 μL of 1 mg/mL Nd^{3+} solution, 6–8 drops of 15% $TiCl_3$ solution and 5 mL 40% HF were added (Hindman, 1983). The solution was allowed to stand for half an

hour, then shaken and allowed to stand for another 30 min. After the sample solution had slowly passed through a cellulose nitrate membrane filter (Whatman®, 0.1 μm pore size), the vial was washed using three times 2 mL 4% HF and twice 2 mL Millipore® water. The air-dried filter was mounted on a sample holder and measured by alpha spectrometry (Srncik et al., 2010).

2.2.2. Sample preparation for AMS

Due to the low concentrations of ^{236}U and Pu isotopes in water samples, special strategies were adopted to ensure the purity of the employed chemicals in AMS sample preparation. HNO_3 was distilled for purification using an acid distillation unit made of quartz glass and the solution was always prepared freshly in order to avoid any contamination from storage. In the course of 8 h, about 250 mL of HNO_3 were purified. Concentrated HCl and 9 M HCl were passed through columns filled with UTEVA® resin. Required dilutions were prepared from 9 M HCl, because the resin's performance is best at this molarity (Horwitz et al., 1995). By applying this strategy, about 200 mL of purified HCl were obtained within 6 h.

In the preparation of AMS samples, 20 μL of a ^{233}U/^{242}Pu spike solution (IRMM-058, 0008/0087, $(4.76 \pm 0.05) \times 10^{10}$ atoms ^{233}U per g and $(2.69 \pm 0.03) \times 10^{11}$ atoms ^{242}Pu per g) were added to 2 L of the acidified (pH = 2) water samples and co-precipitation with $Fe(OH)_3$ was done in the same way as described in the sample preparation for alpha spectrometry.

The residue was dissolved in 20 mL 1 M HNO_3, 100 mg Mohr's salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, 20 mL concentrated HNO_3 and 0.5 g $NaNO_2$ were added and the solution was heated gently until the formation of nitrous gases stopped.

For the purification of plutonium, a column filled with 6 g Dowex® 1 × 8 resin was conditioned using 40 mL 8 M HNO_3. The sample solution was loaded onto the column, the beaker rinsed using 4 times 10 mL 8 M HNO_3 and these fractions were combined for further uranium purification. Concentrated HCl (50 mL) was used to remove Fe, Am, Th and Ca from the column. Plutonium was eluted using 50 mL of a 0.1 M NH_4I–9 M HCl solution and the plutonium fraction was evaporated to dryness and fumed using 3 times 5 mL HNO_3/0.5 mL 30% H_2O_2 and afterwards 3 × 5 mL HCl. For the AMS target preparation, the residue was taken up in 2 mL concentrated HCl. After addition of 7 mL H_2O and 1 mL Fe^{3+} solution (1 mg Fe^{3+}/mL), 25% NH_3 solution was added drop by drop till the forming of $Fe(OH)_3$ precipitate. After the pH had been reduced to pH = 8–9 by heating on a water bath, the precipitate was centrifuged for 15 min (RCF 1340). The supernatant was decanted and the precipitate dried at 100 °C for 2 h in an electric oven. The samples were transferred to small quartz cups for calcination at 800 °C for 2 h in a muffle furnace (Srncik et al., 2011b). The resulting oxides were pressed into small sample holders made of aluminium.

The uranium fraction was loaded onto a column filled with 0.5 g UTEVA® resin, as described for the sample preparation for alpha spectrometry, and the targets for AMS were prepared in the same way as those for plutonium determination.

2.3. Alpha measurement

Alpha spectrometry was done using a PIPS (Passivated Implanted Planar Silicon) detector (7401 VR, Canberra/Packard) with an active area of 450 mm². The counting time was 300,000 s and the software Genie 2.1 (Canberra, USA) was used for the evaluation of the spectra.

2.4. AMS measurement

AMS measurements were performed using the VERA (Vienna Environmental Research Accelerator) facility. The measurement time was 2,600 s. The AMS technique for the detection of actinides is described in Steier et al. (2009). The facility uses a +3 MV tandem accelerator and oxygen as stripper gas to remove molecular isobars (e.g. ^{235}UH⁻). The stripping yields are about 5% for the charge state U^{5+}. After separation by the high-energy mass spectrometer, the particle energy is measured in an ionization chamber, which allows the separation of background ions with lower charge states. The overall efficiency of the instrument in the configuration used for this measurement is about 3×10^{-4} and the abundance sensitivity for ^{236}U is ^{236}U/^{238}U = 10^{-12}. Better abundance sensitivity could be reached by using the installed time-of-flight (ToF) detector, but at the cost of a 5 times lower efficiency. For the small samples with relatively high isotopic ratios in this work, the ToF detector was therefore not used.

3. Results and discussion

3.1. Uranium isotopes

Results for the activity concentrations of ^{234}U and ^{238}U nuclides, the concentration of ^{238}U and the ^{234}U/^{238}U activity ratios measured by alpha-spectrometry are given in Table 2. The ^{238}U concentration, ^{236}U/^{238}U isotopic ratios, ^{236}U activity concentration in mBq/L and ^{236}U isotopes in atoms/L measured by AMS are shown in Table 3. In sea water samples, values for the ^{238}U concentration varied between (3.9 ± 0.6) μg/L (La Palma) and (1.9 ± 0.3) μg/L (Black Sea), which corresponds to activity concentrations of (47 ± 4) mBq/L and (23 ± 1) mBq/L for ^{238}U and (51 ± 4) mBq/L and (27 ± 2) mBq/L for ^{234}U. These results agree well with data in literature that suggests a uranium concentration of approximately 3 μg/L in sea water (Kester et al., 1967). Measurements by alpha spectrometry and AMS were consistent, with the exception of water from the Black Sea. In alpha measurements, a significantly lower concentration of (1.9 ± 0.3) μg/L was found for this sample, which could be explained by uranium precipitation in the sediment (Anderson et al., 1989). The ^{238}U concentration of Black Sea water determined by AMS measurements was higher (3.2 ± 0.4) μg/L. In this case, however, we think that our alpha measurements were a more robust means in the determination of ^{238}U concentrations and regard the uranium content measured by alpha spectrometry as more reliable.

River water showed lower uranium concentration, with (0.8 ± 0.2) μg ^{238}U/L for water from the Danube, reflecting activity concentrations of (10.0 ± 1.3) mBq/L for ^{238}U and (13.5 ± 1.5) mBq/L for ^{234}U. Water from Rio Negro showed even lower uranium content. We were not able to measure it by alpha measurement and the AMS determination suggests that the ^{238}U concentration (which can be roughly estimated from the ^{238}U current) was lower than the detection limit of our alpha spectrometer (0.3 mBq for both ^{234}U and ^{238}U). This low concentration may have been caused by sedimentation or by problems in the process of sampling and sample preparation. The water from Rio Negro was collected two years prior to processing and had not been acidified at the time of

Table 2
Results for U isotopes measured by alpha spectrometry, the measurement uncertainties are given in $\pm 1\sigma$.

Sample	^{234}U [mBq/L]	^{238}U [mBq/L]	^{238}U [μg/L]	^{234}U/^{238}U
La Palma	51.0 ± 3.8	47.4 ± 3.5	3.9 ± 0.6	1.08 ± 0.07
Rio Negro	<0.3	<0.3	<0.02	
Danube	13.5 ± 1.5	10.0 ± 1.3	0.8 ± 0.2	1.36 ± 0.02
Hawaii	37.3 ± 2.6	35.5 ± 2.3	2.9 ± 0.4	1.05 ± 0.05
Irish Sea	32.8 ± 2.8	30.1 ± 2.6	2.5 ± 0.5	1.09 ± 0.04
Black Sea	26.5 ± 1.7	22.8 ± 1.3	1.9 ± 0.3	1.16 ± 0.04

Table 3
Results for the mass concentration of ^{238}U, ^{236}U/^{238}U isotopic ratios, ^{236}U activity concentration and ^{236}U atoms/L, measured by AMS. The measurement uncertainties are given in $\pm 1\sigma$.

Sample	^{238}U [μg/L]	^{236}U/^{238}U	^{236}U [mBq/L]	^{236}U [atoms/L]
La Palma	3.35 ± 0.35	$(1.87 \pm 0.56) \times 10^{-9}$	$(1.5 \pm 0.5) \times 10^{-5}$	$(1.6 \pm 0.5) \times 10^{7}$
Rio Negro	0.07 ± 0.004	$(2.73 \pm 0.33) \times 10^{-8}$	$(4.9 \pm 0.6) \times 10^{-6}$	$(5.2 \pm 0.7) \times 10^{6}$
Danube	0.90 ± 0.14	$(1.08 \pm 0.26) \times 10^{-8}$	$(2.3 \pm 0.7) \times 10^{-5}$	$(2.5 \pm 0.7) \times 10^{7}$
Hawaii	2.56 ± 0.16	$(5.74 \pm 0.31) \times 10^{-9}$	$(3.5 \pm 0.3) \times 10^{-5}$	$(3.8 \pm 0.3) \times 10^{7}$
Irish Sea	2.73 ± 0.26	$(2.04 \pm 0.02) \times 10^{-6}$	0.013 ± 0.001	$(1.4 \pm 0.1) \times 10^{10}$
Black Sea	3.19 ± 0.36	$(3.63 \pm 0.49) \times 10^{-9}$	$(2.8 \pm 0.4) \times 10^{-5}$	$(3.0 \pm 0.5) \times 10^{7}$
Blank	0.20 ± 0.04	$<(5 \pm 1.0) \times 10^{-12}$	$<(2.4 \pm 0.5) \times 10^{-9}$	$<(2.6 \pm 0.5) \times 10^{3}$
Irish Sea (Povinec et al., 2002)		$(2.45 \pm 0.09) \times 10^{-6}$ (mass ratio)	0.0192 ± 0.0006	$(2.0 \pm 0.06) \times 10^{10}$ (calculated)
Irish Sea (Lee et al., 2008)		$(2.47 \pm 0.19) \times 10^{-6}$	0.0193 ± 0.0029	$(2.1 \pm 0.3) \times 10^{10}$ (calculated)

sampling. To reduce any loss of uranium, the sample container was rinsed subsequently with diluted HNO_3 and the rinsing solution was added to the sample. The low uranium values could also be due to the fact that Rio Negro water was very muddy and that suspended particles (which might contain uranium bound in complexes) were filtered off.

The ^{236}U/^{238}U isotopic ratios measured by AMS are depicted in Table 3. The chemical blank value of the ^{236}U/^{238}U ratio was determined by using 2 L deionized Milli-Q (18 MΩ cm) water (millipore, USA) as a "sample" and was found to be $<(5 \pm 1) \times 10^{-12}$. The results for the isotopic composition of uranium showed that all samples were affected by anthropogenic nuclear activity, which is indicated by a ^{236}U/^{238}U atomic ratio of 10^{-9} or higher. Sea water samples – apart from the Irish Sea – were characterized by a ^{236}U/^{238}U ratio in the order of 10^{-9}, whereas in river water from the Danube $(1.08 \pm 0.26) \times 10^{-8}$ and the Rio Negro $(2.73 \pm 0.33) \times 10^{-8}$, higher ratios were detected. This is probably due to the surface run-off of land-deposited ^{236}U, which is collected in rivers and then again diluted by the huge amount of uranium dissolved in ocean water. The origin of elevated ^{236}U/^{238}U ratios is likely to be global fallout. The outstanding ^{236}U/^{238}U ratio of $(2.04 \pm 0.02) \times 10^{-6}$ in water from the Irish Sea is a clear indicator for the influence of the Sellafield reprocessing plant. This value is about 17% lower than in the findings of (Povinec et al., 2002) and (Lee et al., 2008) who measured the same material before. The deviation probably results from detector dead time issues caused by the exceptionally high count rate, and from the fact that we dared only one short measurement to avoid contamination of the ion source.

For most samples (2 exceptions), a precision of about 15% was reached for the ^{236}U/U ratios. We think that the precision can be further improved if we could attain higher chemical yields in our sample preparation (between 25 and 67% in this work). We also plan to reduce the iron mass in the sputter target in order to completely sputter the extracted uranium, and to extend the measurement duration. Generally, the ^{236}U concentrations measured in ocean water is in the order of 10^7 atoms per kg, thus at the instrumental sensitivity of 3×10^{-4} of our AMS setup, the detection of 3000 counts of ^{236}U is feasible from 1 L of water.

3.2. Plutonium isotopes

Results for plutonium activity concentrations, the isotopic ratio ^{240}Pu/^{239}Pu and ^{239}Pu atoms/L are given in Table 4. The chemical blank produced one count for ^{239}Pu and no counts for ^{240}Pu in 2,600 s. For most of our samples, measured ^{240}Pu/^{239}Pu ratios seemed to coincide with the typical value for global fallout $(0.178 \pm 0.025$ (Perkins and Thomas, 1980)), but due to low count rates, uncertainties are significant (again with the exception of the sample from the Irish Sea). While in water from the Black Sea, a contamination by Chernobyl-associated radionuclides (Ketterer et al., 2010) might be expected, our sample showed surprisingly low plutonium count rates and the large uncertainty of the ^{240}Pu/^{239}Pu isotopic ratio (0.25 ± 0.15) does not allow a differentiation between Chernobyl $(^{240}$Pu/^{239}Pu $= 0.45–0.52$ in fuel particles (Oughton et al., 2001)) and global fallout origin. In this case, larger water samples would be needed to achieve significant results. For water from the Irish Sea, a ^{240}Pu/^{239}Pu isotopic ratio of 0.184 ± 0.003 was found, which is 16% lower than the value found by Povinec et al. (2002). Values for the ^{239}Pu and ^{240}Pu activity concentrations are in the range of 10^{-3} mBq/L, except for water from the Irish Sea, which showed an activity concentration of 16.2 ± 0.3 mBq/L, which is 18% higher than the certified value by Povinec et al. (2002), but agrees well with the findings of Lee et al. (2001). They published a mean value of 15.0 ± 0.1 mBq/kg for ^{239,240}Pu isotopes measured by various methods and a higher value of 16.0 ± 0.1 mBq/kg in AMS measurements.

Even though our plutonium results (with the exception of the sample from the Irish Sea) showed large uncertainties, we also give the activity ratios and atomic ratios of ^{236}U/^{239}Pu and ^{236}U/^{239,240}Pu in Table 5. The values for the Irish Sea sample can be compared with the ratios derived from the data measured by Povinec et al. (2002). Our values for the activity ratios ^{236}U/^{239,240}Pu and ^{236}U/^{239}Pu were calculated as 0.00082 ± 0.00008 and 0.00137 ± 0.00013, respectively, and are in satisfying agreement with the above cited findings of 0.00143 ± 0.00013 and 0.00237 ± 0.00043. The atomic ratio ^{236}U/^{239}Pu for all of our water samples were in the range of 1–12, clearly higher than the values of 0.05–0.50 (Ketterer et al., 2007)

Table 4
Results for ^{240}Pu/^{239}Pu isotopic ratios, activity concentrations of Pu isotopes and ^{239}Pu atoms/L, measured by AMS. The measurement uncertainties are given in $\pm 1\sigma$.

Sample	^{240}Pu/^{239}Pu	^{239,240}Pu [mBq/L]	^{239}Pu [mBq/L]	^{240}Pu [mBq/L]	^{239}Pu [atoms/L]
La Palma	0.12 ± 0.05	$(9.8 \pm 4.7) \times 10^{-3}$	$(6.8 \pm 4.1) \times 10^{-3}$	$(3.0 \pm 2.2) \times 10^{-3}$	$(7.5 \pm 4.5) \times 10^{6}$
Rio Negro	0.09 ± 0.04	$(6.5 \pm 1.6) \times 10^{-3}$	$(4.9 \pm 1.4) \times 10^{-3}$	$(1.6 \pm 0.9) \times 10^{-3}$	$(5.3 \pm 1.5) \times 10^{6}$
Danube	0.11 ± 0.07	$(2.7 \pm 0.7) \times 10^{-3}$	$(1.9 \pm 0.5) \times 10^{-3}$	$(0.7 \pm 0.5) \times 10^{-3}$	$(2.1 \pm 0.5) \times 10^{6}$
Hawaii	0.19 ± 0.22	$(1.0 \pm 6.8) \times 10^{-3}$	$(6.1 \pm 3.8) \times 10^{-3}$	$(4.3 \pm 5.6) \times 10^{-3}$	$(6.7 \pm 4.2) \times 10^{6}$
Irish Sea	0.184 ± 0.003	16.2 ± 0.3	9.6 ± 0.2	6.5 ± 0.2	$(1.1 \pm 0.02) \times 10^{10}$
Black Sea	0.25 ± 0.16	$(4.6 \pm 1.0) \times 10^{-3}$	$(2.4 \pm 0.8) \times 10^{-3}$	$(2.2 \pm 1.6) \times 10^{-3}$	$(2.6 \pm 0.9) \times 10^{6}$
Irish Sea (Povinec et al., 2002)	0.22 ± 0.03 (mass ratio)	13.7 ± 1.2	8.1 ± 1.0	6.6 ± 0.4	$(8.9 \pm 1.1) \times 10^{9}$ (calculated)
Irish Sea (Lee et al., 2001)	0.24 ± 0.03	15.0 ± 0.1 (mean) 16.0 ± 0.1 (AMS)	8.2 ± 0.3	7.1 ± 0.5	$(9.0 \pm 0.3) \times 10^{9}$ (calculated)

Table 5
Activity and atom ratios of ^{236}U and Pu isotopes.

Sample	Activity ratio ^{236}U/^{239}Pu	Activity ratio ^{236}U/^{239,240}Pu	Atom ratio ^{236}U/^{239}Pu
La Palma	0.0022 ± 0.0015	0.0015 ± 0.0009	2.1 ± 1.4
Rio Negro	0.0010 ± 0.0003	0.0008 ± 0.0002	1.0 ± 0.3
Danube	0.0122 ± 0.0046	0.0087 ± 0.0034	12.0 ± 4.4
Hawaii	0.0057 ± 0.0036	0.0034 ± 0.0022	5.6 ± 3.5
Irish Sea	0.00137 ± 0.00013	0.00082 ± 0.00008	1.3 ± 0.1
Black Sea	0.0117 ± 0.0044	0.0061 ± 0.0026	11.3 ± 4.3
Irish Sea, Povinec et al. (calculated)	0.00237 ± 0.00043	0.00143 ± 0.00013	2.3 ± 0.3

and 0.235 ± 0.014 (Sakaguchi et al., 2009), published for sediment samples. This reflects the higher sedimentation rate of plutonium compared to uranium in water.

4. Conclusions

Our results underline the good suitability of ^{236}U as a tracer of environmental processes. Even with small samples of only 2 L volume, a precision of 15% was achieved in the majority of measurements and we are convinced that this can be improved in future by refined procedures. In sea water samples from around the globe, we found ^{236}U/^{238}U isotopic ratios in the order of 10^{-9} (with the exception of a certified sample from the Irish Sea which showed a ratio of $(2.04 \pm 0.02) \times 10^{-6}$, in reasonable agreement with the reference value).

The potential of ^{236}U as oceanographic tracer comes to light in the direct comparison with plutonium. Even though plutonium isotopes are already established as tracers for the contamination caused by human nuclear activity, most research focused either on the detection of plutonium in sediment and biota or requires the employment of huge water samples, because plutonium is quickly scavenged from the water column. Plutonium levels and isotopic ratios could only be measured with large uncertainties. ^{239,240}Pu activity concentrations were found in the range of $(3-10) \times 10^{-3}$ mBq/L (Irish Sea 16 mBq/L) and ^{240}Pu/^{239}Pu isotopic ratios were between 0.09 and 0.25, indicating global fallout as the contamination source.

In order to obtain smaller uncertainties in the determination of the plutonium isotopes, further improvements of the sample preparation techniques and also of the AMS facility are required.

Acknowledgement

References

Anderson, R.F., Fleisher, M.Q., LeHurey, A.P., 1989. Concentration, oxidation state, and particulate flux of uranium in the Black Sea. Geochim. Cosmochim. Acta 53 (9), 2215–2224.

Buchholz, B.A., Brown, T.A., Hamilton, T.F., Hutcheon, I.D., Marchetti, A.A., Martinelli, R.E., Ramon, E.C., Tumey, S.J., Williams, R.W., 2007. Investigating uranium isotopic distributions in environmental samples using AMS and MC-ICPMS. Nucl. Instrum. Methods Phys. Res. Sect. B 259, 733–738.

Christl, M., Lachner, J., Vockenhuber, C., Lechtenfeld, O., Stimac, I., van der Loeff, M.R., Synal, H.-A., 2012. A depth profile of uranium-236 in the Atlantic Ocean. Geochim. Cosmochim. Acta 77, 98–107.

Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium budget for the Holocene. Chem. Geol. 190 (1–4), 45–67.

Eichrom Technologies, Inc.: Uranium in water, Analytical Procedures, 30th of April 2001, ACWO2, Rev. 1.3.

Fabryka-Martin, J.T., 1988. Production of Radionuclides in the Earth and their Hydrogeologic Significance, with Emphasis on Chlorine-36 and Iodine-129, University of Arizona, Ph. D. dissertation.

Hindman, D.F., 1983. Neodymium fluoride mounting for spectrometric determination of uranium, plutonium and americium. Anal. Chem. 55, 2460–2461.

Hirose, K., Aoyama, M., Igarashi, Y., Komura, K., 2005. Extremely low background measurements of ^{137}Cs in seawater samples using an underground facility (Ogoya). J. Radioanal. Nucl. Chem. 263 (2), 349–353.

Hirose, K., Aoyama, M., Kim, C.S., 2007. Plutonium in seawater of the Pacific Ocean. J. Radioanal. Nucl. Chem. 274 (3), 635–638.

Hotchkis, M.A.C., Child, D., Fink, D., Jacobsen, G.E., Lee, P.J., Mino, N., Smith, A.M., Tuniz, C., 2000. Measurement of ^{236}U in environmental media. Nucl. Instrum. Methods Phys. Res. Sect. B 172, 659–665.

Horwitz, E.P., Dietz, M.L., Chiarizia, R., Diamond, H., Maxwell, S.L., Nelson, M.R., 1995. Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions. Anal. Chim. Acta 310, 63–78.

Hrnecek, E., Steier, P., Wallner, A., 2005. Determination of plutonium in environmental samples by AMS and alpha spectrometry. Appl. Radiat. Isot. 63, 633–638.

IAEA, 2009. Interlaboratory Comparison. Radionuclides in Irish Sea Water. IAEA-443. IAEA/AQ/010, Vienna, Austria.

Kester, D.R., Duedall, I.W., Connors, D.N., Pytkowicz, R.M., 1967. Preparation of artificial sea water. Limnol. Oceanogr. 12 (1), 176–179.

Ketterer, M.E., Groves, A.D., Strick, B.J., 2007. ^{236}U Inventories, ^{236}U/^{238}U, and ^{236}U/^{239}Pu: The Stratospheric Fallout. Goldschmidt 2007 atoms to planets, Cologne, Germany.

Ketterer, M.E., Gulin, S.B., MacLellan, G.D., Hartsock, W.J., 2010. Fluvial transport of Chernobyl plutonium (Pu) to the Black Sea: evidence from ^{240}Pu/^{239}Pu atom ratios in Danube Delta sediments. Open Chem. Biomed. Methods J. 3, 197–201.

Lee, S.H., Gastaud, J., La Rosa, J.J., Liong Wee Kwong, L., Povinec, P.P., Wyse, E., Fifield, L.K., Hausladen, P.A., Di Tada, L.M., Santos, G.M., 2001. Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. J. Radioanal. Nucl. Chem. 248 (3), 757–764.

Lee, S.H., Povinec, P.P., Wyse, E., Hotchkis, M.A.C., 2008. Ultra-low level determination of ^{236}U in IAEA marine reference materials by ICPMS and AMS. Appl. Radiat. Isot. 66, 823–828.

Lindahl, P., Lee, S.-H., Worsfold, P., Keith-Roach, M., 2010. Plutonium isotopes as tracers for ocean processes: a review. Mar. Environ. Res. 69, 73–84.

Marsden, O.J., Livens, F.R., Day, J.P., Fifield, L.K., Goodall, P.S., 2001. Determination of U-236 in sediment samples by accelerator mass spectrometry. Analyst 126, 633–636.

Mironov, V.P., Matusevich, J.L., Kudrjashov, V.P., Boulyga, S.F., Becker, J.S., 2002. Determination of irradiated reactor uranium in soil samples in Belarus using ^{236}U as irradiated uranium tracer. J. Environ. Monit. 4, 997–1002.

Oughton, D., Day, P., Fifield, K., 2001. Plutonium measurements using accelerator mass spectrometry: methodology and applications. In: Kudo, A. (Ed.), Plutonium in the Environment, vol. 1. Elsevier Science Ltd., pp. 47–62.

Perkins, R.W., Thomas, C.W., 1980. Worldwide fallout. US DOE/TIC-22800. In: Hanson, W.C. (Ed.), Transuranic Elements in the Environment. Office of Health and Environmental Research, pp. 53–82.

Povinec, P.P., Badie, C., Baeza, A., Barci-Funel, G., Bergan, T.D., Bojanowski, R., Burnett, W., Eikenberg, J., Fifield, L.K., Serradell, V., Gastaud, J., Goroncy, I., Herrmann, J., Hotchkis, M.A.C., Ikaheimonen, T.K., Jakobsen, E., Kalimbadjan, J., La Rosa, J.J., Lee, S.H., Liong Wee Kwong, L., Lueng, W.M., Nielson, S.P., Noureddine, A., Pham, M.K., Rohou, J.-N., Sanchez-Cabeza, J.A., Suomela, J., Suplinska, M., Wyse, E., 2002. Certified reference material for radionuclides in seawater IAEA-381 (Irish Sea Water). Radioanal. Nucl. Chem. 251 (3), 369–374.

Quinto, F., Steier, P., Wallner, G., Wallner, A., Srncik, M., Bichler, M., Kutschera, W., Terrasi, F., Petraglia, A., Sabbarese, C., 2009. The first use of ^{236}U in the general environment and near a shutdown nuclear power plant. Appl. Radiat. Isot 67, 1775–1780.

Sakaguchi, A., Kawai, K., Steier, P., Quinto, F., Mino, K., Tomita, J., Hoshi, M., Whitehead, N., Yamamoto, M., 2009. First results on ^{236}U levels in global fallout. Sci. Total Environ. 407, 4238–4242.

Sakaguchi, A., Kadokura, A., Steier, P., Takahashi, Y., Shizuma, K., Hoshi, M., Nakakuki, T., Yamamoto, M., 2012. Uranium-236 as a new oceanic tracer: first depth profile in the Japan Sea and comparison with ceasium-137. Earth Planet. Sci. Lett. 333–334, 165–170.

Srncik, M., Steier, P., Wallner, G., 2010. Determination of the isotopic ratio ^{236}U/^{238}U in Austrian water samples. Nucl. Instrum. Methods Phys. Res. B 268, 1146–1149.

Srncik, M., Steier, P., Wallner, G., 2011a. Depth profile of ^{236}U/^{238}U in soil samples in La Palma, Canary Islands. J. Environ. Radioact. 102, 614–619.

Srncik, M., Hrnecek, E., Steier, P., Wallner, G., 2011b. Determination of U, Pu and Am isotopes in Irish Sea sediment by a combination of AMS and radiometric methods. J. Environ. Radioact. 102, 331–335.

Srncik, M., Mayer, K., Hrnecek, E., Wallenius, M., Varga, Z., Steier, P., Wallner, G., 2011c. Investigation of the ^{236}U/^{238}U isotope abundance ratio in uranium ores and yellow cake samples. Radiochim. Acta 99 (6), 335–339.

Steier, P., Bichler, M., Fifield, L.K., Golser, R., Kutschera, W., Priller, A., Quinto, F., Richter, S., Srncik, M., Terrasi, F., Wacker, L., Wallner, A., Wallner, G., Wilcken, K.M., Wild, E.M., 2008. Natural and anthropogenic ^{236}U in environmental samples. Nucl. Instrum. Methods Phys. Res. Sect. B 266, 2246–2250.

Steier, P., Dellinger, F., Forstner, O., Golser, R., Knie, K., Kutschera, W., Priller, A., Quinto, F., Srncik, M., Terrasi, F., Vockenhuber, C., Wallner, A., Wallner, G., Wild, E.M., 2009. Analysis and application of heavy isotopes in the environment. Nucl. Instrum. Methods Phys. Res. Sect. B 268, 1045–1049.

Wilcken, K.M., Fifield, L.K., Barrows, T.T., Tims, S.G., Gladkis, L.G., 2008. Nucleogenic ^{36}Cl, ^{236}U and ^{239}Pu in uranium ores. Nucl. Instrum. Methods Phys. Res. Sect. B 266, 3614–3624.

Zhao, X.-L., Kilius, L.R., Litherland, A.E., Beasley, T., 1997. AMS measurement of environmental U-236. Preliminary results and perspectives. Nucl. Instrum. Methods Phys. Res. Sect. B 126, 297–300.