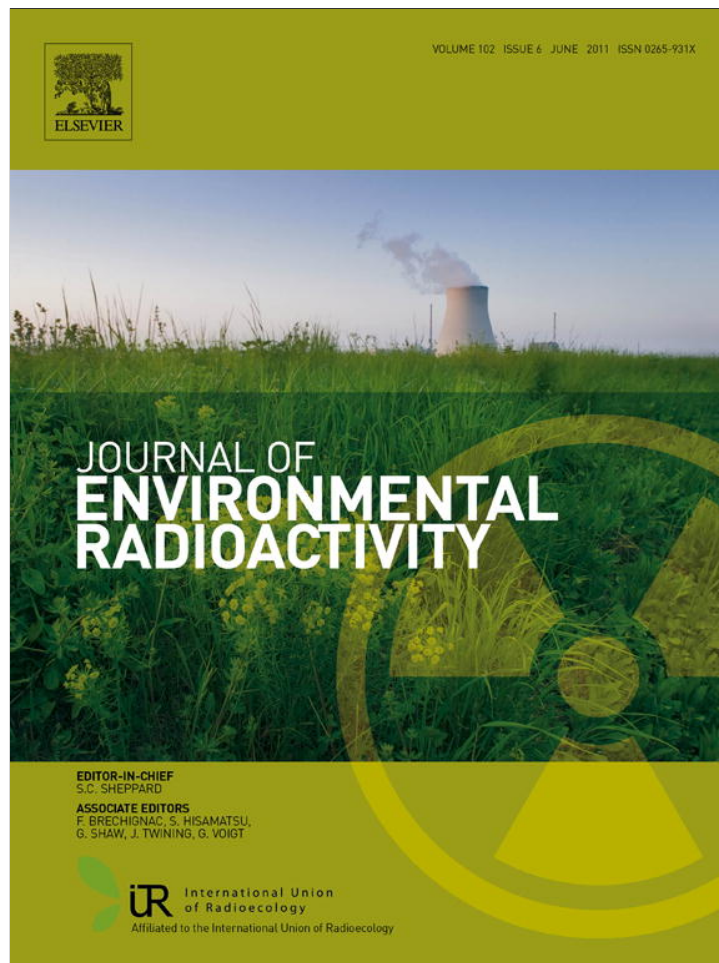


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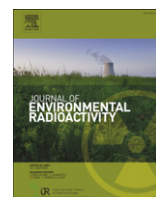
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## Journal of Environmental Radioactivity

journal homepage: [www.elsevier.com/locate/jenvrad](http://www.elsevier.com/locate/jenvrad)Depth profile of  $^{236}\text{U}/^{238}\text{U}$  in soil samples in La Palma, Canary IslandsM. Srncik<sup>a,\*</sup>, P. Steier<sup>b</sup>, G. Wallner<sup>a</sup><sup>a</sup> Department of Inorganic Chemistry, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria<sup>b</sup> VERA Institute, Faculty of Physics – Isotope Research, University of Vienna, Währinger Straße 17, A-1090 Vienna, Austria

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## ABSTRACT

The vertical distribution of the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio was investigated in soil samples from three different locations on La Palma (one of the seven Canary Islands, Spain). Additionally the  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio, as it is a well established tool for the source identification, was determined. The radiochemical procedure consisted of a U separation step by extraction chromatography using UTEVA<sup>®</sup> Resin (Eichrom Technologies, Inc.). Afterwards Pu was separated from Th and Np by anion exchange using Dowex 1x2 (Dow Chemical Co.). Furthermore a new chemical procedure with tandem columns to separate Pu and U from the matrix was tested. For the determination of the uranium and plutonium isotopes by alpha spectrometry thin sources were prepared by microprecipitation techniques. Additionally these fractions separated from the soil samples were measured by Accelerator Mass Spectrometry (AMS) to get information on the isotopic ratios  $^{236}\text{U}/^{238}\text{U}$ ,  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{236}\text{U}/^{239}\text{Pu}$ , respectively. The  $^{236}\text{U}$  concentrations [atoms/g] in each surface layer (~2 cm) were surprisingly high compared to deeper layers where values around two orders of magnitude smaller were found. Since the isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  indicated a global fallout signature we assume the same origin as the probable source for  $^{236}\text{U}$ . Our measured  $^{236}\text{U}/^{239}\text{Pu}$  value of around 0.2 is within the expected range for this contamination source.

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## 1. Introduction

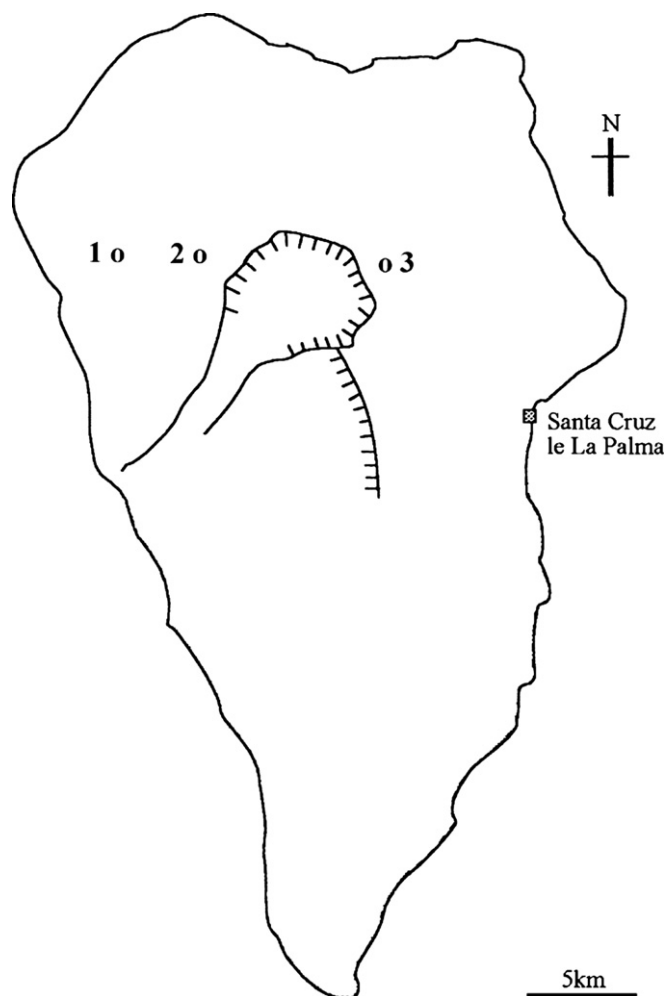
The major source of actinides (as e.g. plutonium) in the environment is global fallout which arose from about 541 atmospheric nuclear explosions (UNSCEAR Report, 1993). Other sources are nuclear reactor accidents (Chernobyl), discharges of radioactive waste (Sellafield, La Hague, Mayak) and accidents with nuclear devices (e.g. Palomares, Thule) (Salbu, 2001). Soil samples from three different locations on La Palma, Canary Islands, (see Fig. 1) were collected in November 2007 and in February 2009. The emphasis on this work was the vertical distribution of  $^{236}\text{U}/^{238}\text{U}$  in the soil and the measurement of Pu. In addition the determination of the  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratio in these samples was carried out.

$^{236}\text{U}$  with a half life of  $2.3 \times 10^7$  years is continuously produced by thermal neutron capture on  $^{235}\text{U}$  which is omnipresent in the environment. The natural  $^{236}\text{U}$  production results from neutrons produced by ( $\alpha$ , n)-reactions on lighter nuclides (e.g. Na and Mg), spontaneous fission of  $^{238}\text{U}$ , induced fission of  $^{235}\text{U}$  and at the earth's surface from cosmic rays (Wilcken et al., 2008). A  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio between  $1 \times 10^{-14}$  and  $5 \times 10^{-14}$  can be expected for typical crustal rocks with a uranium and thorium content of a few

ppm (Steier et al., 2008). On the other hand, significant releases to the environment can be expected as  $^{236}\text{U}$  is a by-product in nuclear power plants. This potentially enhances the very low natural isotopic ratio, but the environmental distribution of anthropogenic  $^{236}\text{U}$  is not well investigated yet. The present work is part of a larger effort to assess the dispersion of anthropogenic  $^{236}\text{U}$  in different compartments of the environment. The summit of La Palma Island is chosen since it allows relatively easy access to a site with clean tropospheric air, far away from anthropogenic emissions. It is thus well suited for studying fallout at minimum risk of local contamination. The climate of the Canary Islands (Herrera et al., 2001) is dominated by the direct influence of the trade wind belt, which blows mainly against the northern of the islands. La Palma (2312 m a.s.l.) is the second highest island of the Canary archipelago, and the most humid (~1000 mm/year at the sampling sites). The exceptional steep topography of La Palma leads to condensation directly from high-altitude clean air. Since the deposition of global fallout is controlled by precipitation, a sufficient amount of radionuclides is expected. On the other hand, the high mountain ranges of La Palma are easily accessible on good roads, since they host several European astronomical observatories.

Measurements of  $^{236}\text{U}$  became possible only recently by AMS on very few facilities, as e.g. VERA (Vienna Environmental Research Accelerator); plutonium isotopes, on the contrary, are comparably well studied as tracer for anthropogenic actinides with alpha

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**Fig. 1.** Modified map from La Palma (Moss et al., 1999). The numbers with the respective cycles indicate the sampling sites (1 represents IIC, IID and LP\_B1, LP\_B2, number 2 stands for IA, IB and 3 for LP\_A).

spectrometry and ICP-MS (Ketterer and Szechenyi, 2008) but also by AMS (Oughton et al., 2001). Although the environmental behaviour of U and Pu differs significantly, we consider plutonium as the best candidate for a methodical comparison. Also for Pu, AMS seems to have the best overall sensitivity (Fifield, 2008) but it can also be measured by other mass spectrometric techniques with partially higher detection efficiency (Steier et al., 2010). Recently soil samples from a site which was solely influenced by global fallout could be investigated for their  $^{236}\text{U}$  concentration. The amount ranged from  $10^8$ – $10^9$  atoms/g dry soil (Sakaguchi et al., 2009). A constant  $^{236}\text{U}/^{239}\text{Pu}$  ratio of  $\sim 0.2$  was found, which was interpreted as the original fingerprint of global fallout. In the general environment, however, differences in the mobility of Pu and U will lead to deviations from this ratio.

In this paper the combined procedure for the determination of U and Pu in soil samples is presented. Two column chromatography methods were applied: at the beginning the sample solution was passed through a column filled with UTEVA<sup>®</sup> Resin (Eichrom Technologies, Inc.) to separate U, and then the Pu fraction was purified with a second anion exchange step by using Dowex 1x2 (100–200 mesh, Dow Chemical Co.). The second method consisted of a double column system. The first column was filled with Dowex 1x8 and the second one with UTEVA<sup>®</sup> Resin. The UTEVA column was placed directly below the anion exchange column.

The advantage of this method is that no further purification (i.e. additional column chromatography steps) of the Pu fraction was necessary.

We present first  $^{236}\text{U}/^{238}\text{U}$  ratios from a clean air area as well as  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{236}\text{U}/^{239}\text{Pu}$  atomic ratios, from which the contamination source (namely global fallout) can be derived.

## 2. Materials and methods

The samples were collected at three different sites on the island La Palma in the Atlantic Ocean. Despite samples were taken close to roads or trails, we looked out for an intact and site-typical vegetation cover as indication for the absence of anthropogenic disturbance. From the first sampling location (N 28° 45.233'/W 17° 53.421', 2330 m a.s.l.) on the northern slope of Roque de los Muchachos two cores (IA and IB) were available which were separated into 2 cm layers and stored in plastic bags. The full length was 10 cm and 12 cm for IA and IB, respectively. At the second site several 100 m downhill (N 28° 46.191'/W 17° 54.224', 1970 m a.s.l.) again two cores with 8 cm length were collected (IIC and IID). IIC was separated into 2 cm layers whereas IID was taken as a bulk sample. Two years later two additional bulk samples (LP\_B1 and LP\_B2) were collected from the same site as IIC and IID: the depth of LP\_B1 ranged from 0 to 5 cm. LP\_B2 was sampled from an outcrop apparently exposed by road construction between 2007 and 2009. Approximately 10 cm of the vertical surface of the outcrop were removed, and then the material was taken from 15 to 40 cm below the horizontal surface. Additionally a third bulk sample (LP\_A) was collected on Pico de La Nieve (N 28° 43.717'/W 17° 49.636',  $\sim 2000$  m a.s.l.) with a depth down to 5 cm. In the time period between the two collection dates the sample procedure was improved. While the samples picked up in 2007 were prepared according to the chemical separation procedure A, the samples taken in 2009 were processed following the faster and more comfortable sample preparation B. The main difference of the second procedure is the usage of UTEVA<sup>®</sup> Resin coupled with Dowex 1x8 but few other changes are in the detail and therefore both sample treatments are described separately below. For spiking a stock solution of  $^{236}\text{Pu}$  was obtained from the University of Helsinki and calibrated against SRM 4334G ( $^{242}\text{Pu}$  solution) by alpha spectrometry. Furthermore a stock solution of SRM 4324B ( $^{232}\text{U}$  solution) was used. One reference sample (IAEA-135, Radionuclides in Irish Sea Sediment) was investigated with respect to Pu and U in order to check the validity of our results.

### 2.1. Chemical separation procedure A

After drying the samples by air, they were ashed in porcelain crucibles in an electric muffle furnace at 420 °C for 24 h. The radiochemical procedure applied to the analysis of U and Pu by alpha spectrometry followed the procedures given in (Eichrom Technologies, 2005; Hrnccek et al., 2002) with slight modifications which are discussed briefly below. Between 5 and 20 g soil were leached in 100 mL 65% HNO<sub>3</sub> and 25 mL 37% HCl. 0.5 g NaNO<sub>2</sub>,  $^{236}\text{Pu}$  and  $^{232}\text{U}$  tracer solutions were added. After boiling the mixture for 3 h, the sample was centrifuged for 30 min at 4000 rpm (relative centrifugal force (RCF) is 1646). The soil residue was leached twice with 20 mL 65% HNO<sub>3</sub> and 15 mL 48% HF for 1 h and was then rejected. The supernatant solutions were combined and evaporated to near dryness. The residue was fumed twice with 10 mL boric acid ( $c = 5$  g/100 mL), three times with 10 mL 65% HNO<sub>3</sub> and 4 mL 32% H<sub>2</sub>O<sub>2</sub>. The residue was taken up in 20 mL 3 M HNO<sub>3</sub> – 1 M Al(NO<sub>3</sub>)<sub>3</sub> and insoluble particles were removed by centrifugation.

### 2.1.1. Separation of uranium

0.5 g UTEVA<sup>®</sup> resin was pre-conditioned with 3 M HNO<sub>3</sub>, the sample solution was brought onto the column which was then washed with 35 mL 3 M HNO<sub>3</sub>. Pu was eluted with 10 mL 9 M HCl and 30 mL 5 M HCl – 0.05 M oxalic acid, and finally U was eluted with 30 mL 1 M HCl.

### 2.1.2. Purification of plutonium

The solution containing Pu was taken to dryness and fumed three times with 5 mL 65% HNO<sub>3</sub> and 2 mL 32% H<sub>2</sub>O<sub>2</sub>. The residue was taken up with 20 mL 1 M HNO<sub>3</sub> and 100 mg Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>6</sub>·H<sub>2</sub>O] were added to reduce Pu to trivalent state. Afterwards the solution was adjusted to 8 M HNO<sub>3</sub> by adding 20 mL 65% HNO<sub>3</sub>. Finally Pu was oxidized to tetravalent oxidation state by addition of 0.5 g NaNO<sub>2</sub>. The excess of nitrous acid was destroyed by gently boiling (NO<sub>x</sub> fumes). 6 g Dowex 1x2 were pre-conditioned with 8 M HNO<sub>3</sub> and then the sample solution was loaded onto the column which was subsequently washed with 50 mL 8 M HNO<sub>3</sub>. Th was removed with 30 mL 37% HCl and Pu was eluted with 50 mL 0.36 M HCl – 0.014 M HF.

The U and Pu fractions were evaporated until dryness and fumed three times with 5 mL 65% HNO<sub>3</sub> and 2 mL 32% H<sub>2</sub>O<sub>2</sub>. The U fraction was additionally fumed with 37% HCl (3x). Afterwards the Pu was dissolved in 20 mL 1 M HNO<sub>3</sub> and U in 20 mL 1 M HCl to carry out the microprecipitation (description see Section 2.3) for the alpha source preparation.

## 2.2. Chemical separation procedure B

The procedure described below (modified from Eichrom Technologies, 2005; Moreno et al., 1997; Warneke et al., 2002) was used for the bulk samples collected in 2009. Samples of 20 g were dried in an electric oven at 100 °C to constant weight and afterwards ashed in porcelain crucibles in an electric muffle furnace at 420 °C for 24 h. The sample was transferred to a Teflon beaker and was leached according to 2.1 "Chemical separation procedure A". Afterwards the combined solutions were evaporated till dryness, fumed three times with 10 mL boric acid ( $c = 5$  g/100 mL), with 10 mL 37% HCl (3x) and with 10 mL 65% HNO<sub>3</sub> (3x). The residue was dissolved in 8 M HNO<sub>3</sub> and a redox adjustment of Pu was carried out as described in Section 2.1. The insoluble part was removed by centrifugation (5 min at 4000 rpm). Two columns were prepared; the first one was filled with 6 g Dowex 1x8 (100–200 mesh, Dow Chemical Co.) and the second column with 0.5 g UTEVA<sup>®</sup> (Eichrom Technologies, Inc.). The UTEVA<sup>®</sup> column was placed directly under the anion exchange column and both were pre-conditioned with 8 M HNO<sub>3</sub>. The sample solution was transferred to the Dowex 1x8 column and the eluent passed directly onto the UTEVA<sup>®</sup> column. After washing with 60 mL 8 M HNO<sub>3</sub> the columns were separated. The Dowex 1x8 column was washed with 50 mL 37% HCl to remove Th, and Pu was finally eluted with 50 mL 0.1 M NH<sub>4</sub>I – 9 M HCl. The iodide reduced Pu(IV) to Pu(III) which does not form chloride complexes and was no longer retained by the column. The UTEVA<sup>®</sup> resin was washed with 40 mL 3 M HNO<sub>3</sub>, traces of Th and Np were eluted with 10 mL 9 M HCl and 30 mL 5 M HCl – 0.05 M oxalic acid. Finally U was eluted with 30 mL 1 M HCl. The U and Pu fractions were treated according to the last paragraph in Section 2.1.2.

### 2.3. Microprecipitation

To the plutonium fraction a tip of a spatula of Mohr's salt, 0.5 mL of a 25% NaNO<sub>2</sub> solution and 50 µL of a Nd<sup>3+</sup>-solution ( $c = 1$  mg/mL) were added.

To the U fraction 50 µL of a Nd<sup>3+</sup>-solution ( $c = 1$  mg/mL) were added and U was reduced to tetravalent oxidation state by addition of 100 µL 15% TiCl<sub>3</sub>-solution. Afterwards 5 mL 40% HF were added to both of the solutions. After 1 h the samples were filtered through a cellulose nitrate membrane filter (Whatman<sup>®</sup>, 0.1 µm pore size), washed three times with 2 mL 4% HF and twice with 2 mL Millipore water (18.2 MΩ cm).

### 2.4. Alpha measurement

Alpha spectrometry was performed with a PIPS (Passivated Implanted Planar Silicon) Detector, Model 7401 VR, Canberra/Packard with an active area of 450 mm<sup>2</sup>. The counting time was 252 000 s and 604 800 s for U and Pu, respectively. For these measurements, the detection limits calculated according to Currie (1968) were 1.12 mBq/sample for <sup>238</sup>U and 0.80 mBq/sample for <sup>239(40)</sup>Pu. The software Genie 2.1 (Canberra, USA) was used for the evaluation of the spectra.

### 2.5. AMS measurement

The filters already analysed by alpha spectrometry were reprocessed for the AMS measurement according to Srncik et al. (2008). The filters were dissolved in HNO<sub>3</sub>, the nuclides of interest were co-precipitated with iron hydroxide, and combusted to oxides which 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. (2003) and Steier et al. (2010).

PuO<sup>−</sup> at 50 keV was produced in a Cs-sputter source, mass analysed, accelerated to 3 MeV and stripped to positive charge state in a gas cell. By these means, all interfering molecular isobars are destroyed. The 5+ charge state is selected in a second, high energy mass spectrometer, after acceleration to 18 MeV. A combination of an ionization chamber and a time-of-flight measurement allow a unique identification of the isotope of interest. Significant background exists for <sup>240</sup>Pu<sup>5+</sup>, apparently from stable <sup>144</sup>Nd<sup>3+</sup>, which shares the same mass-to-charge ratio and thus cannot be suppressed by the mass spectrometer. In the present measurement, the residual Nd concentration in the sputter samples was, however, low enough and could therefore be separated in the energy-resolving detector.

The machine was tuned with <sup>238</sup>U<sup>16</sup>O<sup>−</sup> as a pilot beam, and the parameters were then scaled to the different rare radioisotopes which do not provide sufficient beam current for tuning. Alternating measurements of <sup>239</sup>Pu and <sup>240</sup>Pu were performed, with duration of several 100 s each. By these means, one tries to minimize the impact of source output variations on the measured count rate results. For <sup>236</sup>U, <sup>238</sup>U<sup>16</sup>O<sup>−</sup> can be measured once per second as a current before the accelerator, which renders source output variations negligible. Our in-house standard Vienna-KKU, <sup>236</sup>U/U =  $(6.98 \pm 0.32) \times 10^{-11}$  (Steier et al., 2008) was used to normalize the <sup>236</sup>U measurements. However, no standard is available for Pu; this introduces an additional uncertainty, which is however expected to be in the range of a few percent. Measurement times per sample ranged from 30 min to several hours, depending mainly on the machine time availability. Generally, the prepared samples last for several hours, and an efficiency of  $\sim 10^{-4}$  (counts in the detector per atom in sputter sample) is achieved if the samples are completely sputtered.

## 3. Results and discussion

The chemical separation A has been already applied in our laboratory but for sample preparation B the validity was checked by analysing an IAEA-135 reference material. The obtained result was

(225 ± 7) Bq/kg <sup>239(40)</sup>Pu; this value is in good agreement with the recommended value of (205–226) Bq/kg for <sup>239(40)</sup>Pu. The IAEA-135 standard was also measured for its <sup>236</sup>U/<sup>238</sup>U ratio by AMS. Our value of (1.48 ± 0.04) × 10<sup>-6</sup> agrees with Hotchkis et al. (2000) who determined (1.48 ± 0.37) × 10<sup>-6</sup> via AMS. Our result indicated a very good accuracy of the proposed method.

In Table 1 the results of the <sup>236</sup>U/<sup>238</sup>U isotopic ratios and <sup>236</sup>U [atoms/g] for all core layers and also for the bulk samples are shown. In each core (IA, IB and IID) the main amount of <sup>236</sup>U was found in the surface layer (between 10<sup>9</sup> and 10<sup>10</sup> atoms/g dry soil). With increasing depth the number of atoms per gram measured was in the range of 10<sup>7</sup>, except for the depth profile of IA. Here again an increase of two orders of magnitude was obtained for the deepest layer. As this value is so high and therefore implausible, we assume that a mistake during the sample collection occurred. According to the results that a relatively high value of <sup>236</sup>U atoms/g in each surface layer was found in contrast to the deeper layers (decrease by two orders of magnitude), it seems that the anthropogenic <sup>236</sup>U was not moving downwards. The layers below the “surface layer” show at all sites (IA, IB and IID) at least the same order of magnitude of <sup>236</sup>U atoms/g. The result of the respective sub-samples of LP\_B1 and LP\_B2 are consistent with the exception of LP\_B2\_2 which was below the blank value. The result of sample LP\_A\_2 is higher but agrees with LP\_A\_1 and LP\_A\_3 within 2σ. Both bulk samples LP\_B1 (0–5 cm) and LP\_B2 (15–40 cm) show a <sup>236</sup>U concentration in the range of 10<sup>8</sup> atoms/g dry soil. For the LP\_A bulk sample (0–5 cm depth) the results are one order of magnitude higher which reflects inhomogeneities in the <sup>236</sup>U distribution at different sample sites.

**Table 1**  
Results of the isotopic ratio <sup>236</sup>U/<sup>238</sup>U and <sup>236</sup>U [atoms/g] in soil samples from La Palma. The measurement uncertainties are given in ± 1σ.

Sample	Core, depth [cm]	<sup>236</sup> U/ <sup>238</sup> U	<sup>236</sup> U [atoms/g]
Depth profile – IA			
LP01a	IA, 2–6	(2.37 ± 0.07) × 10 <sup>-7</sup>	(9.69 ± 1.62) × 10 <sup>9</sup>
LP02a	IA, 6–8	(2.96 ± 0.20) × 10 <sup>-9</sup>	(6.08 ± 0.73) × 10 <sup>7</sup>
LP03	IA, 8–10	(1.23 ± 0.04) × 10 <sup>-7</sup>	(1.93 ± 0.31) × 10 <sup>9</sup>
Depth profile – IB			
LP04	IB, 0–2	(3.15 ± 0.09) × 10 <sup>-7</sup>	(8.76 ± 1.62) × 10 <sup>9</sup>
LP05a	IB, 2–4	(3.01 ± 0.09) × 10 <sup>-9</sup>	(3.91 ± 0.56) × 10 <sup>7</sup>
LP06	IB, 4–6	(3.90 ± 0.21) × 10 <sup>-9</sup>	(8.12 ± 1.24) × 10 <sup>7</sup>
LP07	IB, 6–8	(2.10 ± 0.23) × 10 <sup>-9</sup>	(4.95 ± 1.12) × 10 <sup>7</sup>
LP08a	IB, 8–10	(1.00 ± 0.11) × 10 <sup>-9</sup>	(1.43 ± 0.33) × 10 <sup>7</sup>
LP09	IB, 10–12	(2.13 ± 0.16) × 10 <sup>-9</sup>	(5.46 ± 0.89) × 10 <sup>7</sup>
Depth profile – IID			
LP10	IID, 0–2	(2.54 ± 0.08) × 10 <sup>-7</sup>	(2.82 ± 0.48) × 10 <sup>9</sup>
LP11	IID, 2–4	(4.93 ± 0.34) × 10 <sup>-9</sup>	(2.61 ± 0.48) × 10 <sup>7</sup>
LP12a	IID, 4–6	(3.25 ± 0.16) × 10 <sup>-9</sup>	(5.64 ± 0.96) × 10 <sup>7</sup>
LP13	IID, 6–8	(3.54 ± 0.33) × 10 <sup>-9</sup>	(2.85 ± 0.49) × 10 <sup>7</sup>
LP14	IID, 8–10	(3.52 ± 0.29) × 10 <sup>-9</sup>	(4.41 ± 0.96) × 10 <sup>7</sup>
IIC bulk sample			
LP15a	IIC, 0–8	(4.35 ± 0.24) × 10 <sup>-9</sup>	(5.75 ± 1.18) × 10 <sup>7</sup>
Sample	Depth [cm]	<sup>236</sup> U/ <sup>238</sup> U	<sup>236</sup> U [atoms/g]
LP_B1 bulk sample, again from IIC/IID			
LP_B1_1	0–5	(2.36 ± 0.07) × 10 <sup>-8</sup>	(4.44 ± 0.89) × 10 <sup>8</sup>
LP_B1_2	0–5	(2.45 ± 0.07) × 10 <sup>-8</sup>	(2.50 ± 0.41) × 10 <sup>8</sup>
LP_B1_3	0–5	(2.48 ± 0.07) × 10 <sup>-8</sup>	(3.22 ± 0.64) × 10 <sup>8</sup>
LP_B2 bulk sample, again from IIC/IID			
LP_B2_1	15–40	(4.85 ± 1.69) × 10 <sup>-9</sup>	(2.49 ± 0.92) × 10 <sup>8</sup>
LP_B2_2	15–40	–	–
LP_B2_3	15–40	(3.25 ± 1.54) × 10 <sup>-9</sup>	(1.78 ± 0.88) × 10 <sup>8</sup>
LP_A bulk sample			
LP_A_1	0–5	(4.21 ± 0.13) × 10 <sup>-8</sup>	(4.01 ± 0.48) × 10 <sup>9</sup>
LP_A_2	0–5	(3.41 ± 0.35) × 10 <sup>-8</sup>	(2.20 ± 0.43) × 10 <sup>9</sup>
LP_A_3	0–5	(1.31 ± 0.57) × 10 <sup>-8</sup>	(1.00 ± 0.46) × 10 <sup>9</sup>

The isotopic ratios <sup>236</sup>U/<sup>238</sup>U ranged from 10<sup>-7</sup> near the surface to 10<sup>-9</sup> with increasing depth. The obtained ratios of 10<sup>-9</sup> are not influenced by our blanks; this was proven by a blank correction. At the sample location LP\_B1, (0–5 cm) the level of few parts in 10<sup>-8</sup> was found and at LP\_B2 (15–40 cm) the isotopic ratio is one order of magnitude lower. The value for LP\_A is slightly higher than the bulk samples at the LP\_B site.

Table 2 shows the vertical distribution of <sup>239(40)</sup>Pu [Bq/kg] for each of the three sample locations (cores IA, IB and IID). At the sample site IA the surface layer (0–2 cm) got lost. The specific activities of <sup>239(40)</sup>Pu in layer LP01a (2–6 cm) and LP02a (6–8 cm) at location IA are similar [(0.32 ± 0.05) Bq/kg and (0.35 ± 0.06) Bq/kg, respectively]; in the deepest layer a decrease of one order of magnitude occurred. The highest specific activity at location IB of (0.46 ± 0.03) Bq/kg was found in the surface layer (0–2 cm). The values for LP05a (2–4 cm) and LP09 (10–12 cm) were below the limit of detection (<0.040 Bq/kg). At the sample location IID the highest value occurred in the layer between 2–4 cm and the decrease of the activity is less marked than at the other two locations. Also here two samples, LP12a (4–6 cm) and LP14 (8–10 cm), were below the detection limit (<0.080 Bq/kg).

The accumulated levels at site IB and IID were (36 ± 11) Bq <sup>239(40)</sup>Pu m<sup>-2</sup> and (22 ± 7) Bq <sup>239(40)</sup>Pu m<sup>-2</sup>, respectively. These <sup>239(40)</sup>Pu results are in the range of the expected value [(36 ± 3) Bq <sup>239(40)</sup>Pu m<sup>-2</sup>] for global fallout in the Northern Hemisphere at latitude 20°–30° N (Hardy et al., 1973).

Buesseler (1997) reports for the global fallout <sup>240</sup>Pu/<sup>239</sup>Pu isotopic ratio a typical interval of 0.175–0.19. According to Kelley et al. (1999) the average composition of fallout <sup>240</sup>Pu/<sup>239</sup>Pu for the north equatorial region (latitude, 30°N-0) is 0.178 with a standard deviation of 0.019 (2σ). The ratio for Chernobyl is 0.45–0.52 (Kutkov et al., 1995).

In the present work, for some samples the <sup>240</sup>Pu/<sup>239</sup>Pu ratio could not be determined (indicated by “–” in Table 3) due to relatively small <sup>239</sup>Pu and <sup>240</sup>Pu count rates. One reason was the low Pu chemical yield (the average was 24.3 ± 0.7) determined by alpha spectrometry which is attributed to difficulties during the leaching and fuming steps before the column separation step. Additionally, sometimes problems during the Fe(OH)<sub>3</sub> co-precipitation occurred which would further explain losses of Pu and therefore the low count rate by AMS. From Table 3 it can be seen that at the sample location IA only the first layer could be measured and is in agreement with global fallout, although the value was slightly higher.

**Table 2**  
Vertical distribution of <sup>239(40)</sup>Pu [Bq/kg] at the sample location IA, IB and IID and the measurement uncertainty is given in ± 1σ.

Sample	Depth [cm]	<sup>239(40)</sup> Pu [Bq/kg]
Depth profile – IA		
LP01a	IA, 2–6	0.322 ± 0.045
LP02a	IA, 6–8	0.350 ± 0.055
LP03	IA, 8–10	0.026 ± 0.007
Depth profile – IB		
LP04	IB, 0–2	0.458 ± 0.028
LP05a	IB, 2–4	–
LP06	IB, 4–6	0.088 ± 0.010
LP07	IB, 6–8	0.055 ± 0.011
LP08a	IB, 8–10	0.037 ± 0.013
LP09	IB, 10–12	–
Depth profile – IID		
LP10	IID, 0–2	0.296 ± 0.065
LP11	IID, 2–4	0.601 ± 0.100
LP12a	IID, 4–6	–
LP13	IID, 6–8	0.136 ± 0.025
LP14	IID, 8–10	–

The  $^{240}\text{Pu}$  count rates of both LP02a (6–8 cm) and LP03 (8–10 cm) were too low to determine the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio. The  $^{240}\text{Pu}/^{239}\text{Pu}$  results in all layers of location IB and IID showed a ratio indicating global fallout. The average isotopic ratio of bulk sample LP\_B1 was  $0.221 \pm 0.029$ . For all three sub-samples of LP\_B2 (15–40 cm below the surface)  $^{239}\text{Pu}$  was far below the blank value and therefore no atomic ratio could be determined. The mean  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of bulk sample LP\_A was  $0.287 \pm 0.025$  which is slightly higher than the expected value for global fallout.

Table 4 shows the  $^{236}\text{U}/^{239}\text{Pu}$  results for all layers and bulk samples, respectively. According to the isotopic ratios of  $^{240}\text{Pu}/^{239}\text{Pu}$  found in the La Palma soil samples (Table 3), the source of contamination seems to be global fallout. Ketterer et al. (2007) reported  $^{236}\text{U}/^{239}\text{Pu}$  atomic ratios between 0.05 and 0.5 for samples containing Pu of purely stratospheric fallout. The wide range was attributed to the evidently higher mobility of fallout  $^{236}\text{U}$  compared to Pu (Ketterer et al., 2007). However, this migration behaviour of U and Pu was not observed by Sakaguchi et al. (2009), who investigated at three sites 20 m apart from each other soil samples (0–30 cm) from Ishikawa Prefecture (Japan); here the  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratios were in the much smaller range of 0.212–0.253. In our work (compare Table 1 and 2) the overwhelming part of  $^{236}\text{U}$  in the core samples was found in the surface layers, while the (unfortunately sparse) Pu data indicates a more even distribution. Consequently, the three topmost samples reveal an enhanced  $^{236}\text{U}/^{239}\text{Pu}$  ratio higher than 3. All other values are in the range supposed by Ketterer et al. (2007) and for the bulk sub-samples LP\_B1 (0–5 cm) a  $^{236}\text{U}/^{239}\text{Pu}$  value of 0.2 similar to the bulk

samples of Sakaguchi et al. (2009) was found. We obtained for the bulk sample LP\_A (0–5 cm) a higher average ratio ( $^{236}\text{U}/^{239}\text{Pu} = 0.5$ ) but with a larger scatter between sub-samples.

#### 4. Conclusion

Soil samples from a remote clean air site, the La Palma Island, were investigated with the emphasis on the  $^{236}\text{U}/^{238}\text{U}$  ratio. A conventional and a new tandem column procedure were applied for the sequential and simultaneous separation of U and Pu, respectively. Samples were measured both by alpha spectrometry and AMS. The isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  was between  $10^{-7}$  for the surface samples and  $10^{-9}$  for deeper layers. The  $^{236}\text{U}$  [atoms/g] results at each surface layer were surprisingly high and the decrease to deeper layers were around two orders of magnitude; this phenomenon was not observed for Pu. The isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  is a well established indicator for the identification of the contamination source. In our samples the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios of 0.149–0.267 for site IA, IB and IID indicate that global fallout is the probable source for the Pu isotopes similarly to site LP\_B1 where the mean isotopic ratio is  $0.221 \pm 0.029$ . In accordance with the  $^{240}\text{Pu}/^{239}\text{Pu}$  results, most of our measured  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratios were in the order of 0.04 and 0.78 and agree with the sparse set of already published values for the global fallout signature.

**Table 3**  
Results of  $^{240}\text{Pu}/^{239}\text{Pu}$  by AMS in soil samples from La Palma. The measurement uncertainties are given in  $\pm 1\sigma$ .

Sample	Core, depth [cm]	$^{240}\text{Pu}/^{239}\text{Pu}$
Depth profile – IA		
LP01a	IA, 2–6	$0.267 \pm 0.056$
LP02a	IA, 6–8	–
LP03	IA, 8–10	–
Depth profile – IB		
LP04	IB, 0–2	$0.149 \pm 0.006$
LP05a	IB, 2–4	$0.178 \pm 0.015$
LP06	IB, 4–6	$0.198 \pm 0.050$
LP07	IB, 6–8	$0.149 \pm 0.051$
LP08a	IB, 8–10	–
LP09	IB, 10–12	–
Depth profile – IID		
LP10	IID, 0–2	$0.150 \pm 0.018$
LP11	IID, 2–4	$0.195 \pm 0.089$
LP12a	IID, 4–6	$0.189 \pm 0.035$
LP13	IID, 6–8	–
LP14	IID, 8–10	–
IIC bulk sample		
LP15a	IIC, 0–8	$0.131 \pm 0.029$
Sample	Depth [cm]	$^{240}\text{Pu}/^{239}\text{Pu}$
LP_B1 bulk sample, again from IIC/IID		
LP_B1_1	0–5	$0.251 \pm 0.060$
LP_B1_2	0–5	$0.198 \pm 0.027$
LP_B1_3	0–5	$0.215 \pm 0.055$
LP_B2 bulk sample, again from IIC/IID		
LP_B2_1	15–40	–
LP_B2_2	15–40	–
LP_B2_3	15–40	–
LP_A bulk sample		
LP_A_1	0–5	$0.323 \pm 0.041$
LP_A_2	0–5	$0.222 \pm 0.028$
LP_A_3	0–5	$0.315 \pm 0.057$

**Table 4**  
Results of  $^{236}\text{U}/^{239}\text{Pu}$  in La Palma soil samples. The measurement uncertainties are given in  $\pm 1\sigma$ .

Sample	Core, depth [cm]	$^{236}\text{U}/^{239}\text{Pu}$
Depth profile – IA		
LP01a	IA, 2–6	$14 \pm 3$
LP02a	IA, 6–8	–
LP03	IA, 8–10	–
Depth profile – IB		
LP04	IB, 0–2	$3.3 \pm 0.5$
LP05a	IB, 2–4	–
LP06	IB, 4–6	$0.38 \pm 0.07$
LP07	IB, 6–8	$0.27 \pm 0.08$
LP08a	IB, 8–10	–
LP09	IB, 10–12	–
Depth profile – IID		
LP10	IID, 0–2	$4.6 \pm 1.5$
LP11	IID, 2–4	$0.04 \pm 0.01$
LP12a	IID, 4–6	–
LP13	IID, 6–8	$0.08 \pm 0.02$
LP14	IID, 8–10	–
IIC bulk sample		
LP15a	IIC, 0–8	$0.14 \pm 0.03$
Sample	Depth [cm]	$^{236}\text{U}/^{239}\text{Pu}$
LP_B1 bulk sample, again from IIC/IID		
LP_B1_1	0–5	$0.23 \pm 0.03$
LP_B1_2	0–5	$0.17 \pm 0.02$
LP_B1_3	0–5	$0.21 \pm 0.03$
LP_B2 bulk sample, again from IIC/IID		
LP_B2_1	15–40	–
LP_B2_2	15–40	–
LP_B2_3	15–40	–
LP_A bulk sample		
LP_A_1	0–5	$0.78 \pm 0.14$
LP_A_2	0–5	$0.43 \pm 0.08$
LP_A_3	0–5	$0.23 \pm 0.11$

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