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Measurements of ^{236}U in Ancient and Modern Peat Samples and Implications for Postdepositional Migration of Fallout Radionuclides

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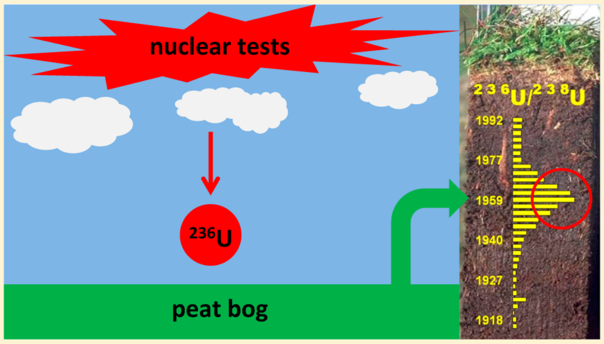
Supporting Information

ABSTRACT: ^{236}U was analyzed in an ombrotrophic peat core representing the last 80 years of atmospheric deposition and a minerotrophic peat sample from the last interglacial period. The determination of ^{236}U at levels of 10^7 atoms/g was possible by using ultraclean laboratory procedures and accelerator mass spectrometry. The vertical profile of the ^{236}U/^{238}U isotopic ratio along the ombrotrophic peat core represents the first observation of the ^{236}U bomb peak in a terrestrial environment. A constant level of anthropogenic ^{236}U with an average ^{236}U/^{238}U isotopic ratio of $(1.24 \pm 0.08) \times 10^{-6}$ in the top layers of the core was observed. Comparing the abundances of the global fallout derived ^{236}U and ^{239}Pu along the peat core, the post depositional migration of plutonium clearly exceeds that of uranium. However, the cumulative ^{236}U/^{239}Pu ratio of 0.62 ± 0.31 is in agreement with previous studies on the global fallout uranium and plutonium. In the interglacial peat samples a ^{236}U/^{238}U isotopic ratio of $(3.3 \pm 0.7) \times 10^{-12}$ was detected; although this measurement is an upper limit, it constitutes a significant step forward in the experimental determination of the natural ^{236}U abundance and represents a true background sample for the ombrotrophic peat core.



■ INTRODUCTION

Naturally occurring uranium (U) is mainly composed of the two primordial isotopes ^{238}U (~99.3%) and ^{235}U (~0.72%) and of the radiogenic isotope ^{234}U (~0.005%).[1] The rare isotope ^{236}U is produced in nature primarily by thermal neutron capture on ^{235}U. Since the production of ^{236}U depends on both the concentration of U and the thermal neutron flux, its abundance in nature is highly variable depending on the environmental matrix. ^{236}U/^{238}U isotopic ratios on the order of $\sim 3 \times 10^{-14}$ in typical rocks in the uppermost 1 km of the Earth's surface and between 10^{-14} and 10^{-13} in river water and the oceans have been estimated.[2] In uranium ores with U contents ranging from 1% to 75%, representing the highest natural U concentrations, ^{236}U/^{238}U isotopic ratios between 1×10^{-12} and 2.8×10^{-10} have been measured.[3]

Since World War II, the environmental abundance of ^{236}U has increased significantly due to anthropogenic inputs from the stratospheric nuclear weapons test fallout superimposing themselves on the natural levels of ^{236}U. Between 1945 and 1980, 543 atmospheric nuclear denotations were carried out. The most intensive testing took place between 1957 and 1963, producing a peak of the annual radionuclide deposition during 1963 in the Northern Hemisphere.[4] In thermonuclear explosions ^{236}U is produced mainly by the (n, 3n) nuclear reaction of fast neutrons on ^{238}U present in the so-called "tamper" of the nuclear device. Global fallout derived ^{236}U/^{238}U isotopic ratios range from 10^{-7} to 10^{-9} in several studies of various environmental matrixes, such as soils, river sediments, and corals as well as river and oceanic water.[5−13] Some of these studies have demonstrated the great potential of ^{236}U as tracer of oceanic circulations.[10−13] From the study of ^{236}U in the environment, several estimates of the global inventory of ^{236}U from stratospheric nuclear testing have been suggested, ranging from 900 to 2100 kg.[5,11,12] The abundance of ^{236}U in soil, river, and oceanic water contaminated solely by global fallout has been compared to that of the corresponding plutonium (Pu) and expressed as ^{236}U/^{239}Pu ratios.[5,7,10,14] The values of such ^{236}U/^{239}Pu ratios and previous estimates of the global inventory of ^{236}U from stratospheric nuclear tests are listed in Table 1.

Another source of anthropogenic ^{236}U in the environment is the contamination from irradiated nuclear fuel, which can occur through routine discharges of nuclear power plants,[8] nuclear

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fuel reprocessing plants,[15] and accidents such as that of Chernobyl (1986).[16] The predominant source of ^{236}U contamination in a natural sample can be identified by studying the corresponding Pu isotopic composition and activity.

Table 1. Comparison of the Estimates of the Worldwide Inventory of Global Fallout ^{236}U and ^{236}U/^{239}Pu Isotopic Ratios from Literature Data and the Present Work

sample	^{236}U/^{239}Pu	worldwide inventory of global fallout ^{236}U (kg)	ref
soil, peat, and lake sediment	0.05−0.5	[a]	14
soil	0.19 ± 0.04	[a]	38
soil	0.212−0.252	~900	5
deep soil	0.04−0.78	[a]	7
top soil	3−14		
ocean water	[a]	~2100	11
coral	[a]	1060 ± 212	12
sea and river water	1−12	[a]	10
ombrotrophic peat	0.62 ± 0.31	1698 ± 850	this work

[a] Data not reported.

Ombrotrophic peat is an excellent terrestrial matrix for the analysis of the atmospheric deposition of heavy elements, such as Hg, Pb, and As.[17] Furthermore, given the well-established immobility of Pb in ombrotrophic peat bogs, the ^{210}Pb method can be used for the accurate dating of the past 150 y of peat accumulation with the constant-rate-of-supply model.[18]

The present study was undertaken using an undisturbed peat core from the Wildseemoor, an ombrotrophic bog in the Black Forest (Germany). The peat core was dated using the ^{210}Pb method as part of a previous project carried out at the University of Heidelberg.[19,20] Recently, the Pu isotopic composition (^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, and ^{242}Pu/^{239}Pu) in this peat core was investigated, and global fallout was recognized as the unique detectable source of Pu contamination.[20] In the present study, the U isotopic composition (^{236}U/^{238}U and ^{234}U/^{238}U) was analyzed in order to investigate the behavior of ^{236}U and to estimate its inventory from the stratospheric fallout deposition recorded in the peat core. The behavior of ^{236}U and ^{239}Pu was then compared by studying the profile of the ^{236}U/^{239}Pu ratio along the peat core.

The ^{236}U/^{238}U isotopic ratio measured in every natural sample which has been exposed to the stratospheric nuclear tests fallout (starting from 1945) represents the contribution of the global fallout derived ^{236}U to the naturally occurring U in the sample. In order to assess the natural abundance of ^{236}U in peat samples, an ancient minerotrophic peat collected in Trentino Alto-Adige/Südtirol, northern Italy, was chosen; this peat deposit is assumed to have been isolated from the Earth's surface due to burial by glacial sediments for more than 21 000 years. As such, it is expected to contain the preanthropogenic background of ^{236}U for comparison with the ombrotrophic peat bog at the Wildseemoor.

An efficient chemical separation procedure for the extraction of uranium from peat samples was developed and accelerator mass spectrometry (AMS) chosen for determination of the U isotopic compositions. Since the pioneer studies which developed the potential of AMS for the sensitive measurement of ^{236}U in uranium ores,[21] uranium minerals, and standards[22] as well as for the suppression of U background in the detection of Pu isotopes in natural samples,[23] AMS has become the technique which presently offers the highest sensitivity for the measurement of ^{236}U/^{238}U isotopic ratios ($\sim 10^{-13}$).[24] To keep the blank levels as low as possible, handling and chemical processing of the peat samples were carried out in ultraclean laboratories following well established clean-room procedures.

EXPERIMENTAL SECTION

Samples. The ombrotrophic peat core was collected in 2006 at the Wildseemoor in the Black Forest (Germany) (GPS-point N 48° 43′ 03″ E 08° 27′ 34″). We have analyzed a section of 47 cm in depth of the peat core; this section was sliced into 32 individual peat layers. From the same samples (1 g dry mass) already investigated with AMS for Pu,[20] the ^{234}U/^{238}U and ^{236}U/^{238}U isotopic ratios were analyzed employing a chemical separation procedure for the sequential extraction of Pu and U. The peat core had been characterized previously for its ^{238}U concentration with ICP-MS (Table S1)[19] and dated using the ^{210}Pb method; details of which were reported earlier.[19,20]

The minerotrophic peat collected in Trentino Alto-Adige/Südtirol was formed during the last interglacial period, from 100 000 to 150 000 y ago, and subsequently buried beneath several meters of sediment during the last glacial maximum which occurred from 21 000 to 25 000 y ago. This peat, dating from the last interglacial period, was supposed to have been isolated from the input of meteoric water since at least 21 000 y and therefore not to have been affected by the stratospheric weapons tests fallout. We have investigated 3 aliquots (250 mg, 500 mg, and 750 mg dry mass) of this buried peat collected at a depth of 3 m from the interface with the glacial sediments.

Chemical Separation of Uranium and AMS Measurements. The weighing and manipulation of the minerotrophic and ombrotrophic peat samples were undertaken in Class 100 clean benches. The following dissolution and chemical treatment were carried out in a metal-free, ultraclean environment (laboratory Class 100 and work benches Class 10) at the Institute for Geosciences, University of Heidelberg, Germany. Before use, all materials in contact with the samples were cleaned thoroughly in accordance with procedures developed for the analysis of ultratrace element concentrations in Arctic ice and snow.[25] New Teflon vessels were employed for the investigated set of samples. The nitric acid used during the entire chemical procedure and for cleaning of the vessels was sub-boiled twice (DuoPUR, MLS, Leutkirch, Germany) in a clean room. High purity water (18.2 MΩ cm) from a Milli-Q Element (Millipore) water supply system was used for dilution of the reagents as well as rinsing of the employed vessels. All of the reagents were of ultrapure quality.

The peat samples were each digested with 12 mL of concentrated HNO_3, following procedures employing a microwave-assisted high-pressure autoclave (ultraCLAVE II, MLS, Leutkirch, Germany).[26,27] Subsequently, the dissolved samples were diluted to 7.2 M HNO_3, and U was separated from the digestion solutions by extraction chromatography using an UTEVA resin column (0.8 mL resin bed). To avoid potential cross-contamination, a freshly prepared chromatographic column was employed for each sample and precleaned from U by rinsing the resin bed 3 times with a solution of 10 mL of 0.1 M HNO_3. After this cleaning step, the resin column was conditioned with 7.2 M HNO_3.

For the ombrotrophic peat samples, the U fraction was eluted with 20 mL of 0.1 M HNO_3 after the separation of the corresponding Pu fraction with 0.2 M hydroxylammonium hydrochloride and 0.02 M ascorbic acid in 2 M HNO_3. Details of the separation of Pu have been reported earlier.[20] For the minerotrophic peat samples, no Pu fraction was separated, and U was eluted with 0.1 M HNO_3 directly after rinsing the column with 12 mL of 3 M HNO_3.

The purified U fractions were coprecipitated with $Fe(OH)_3$ and transported to the Vienna Environmental Research Accelerator (VERA) laboratory in Vienna. There, after conversion to iron oxide in a muffle furnace at 900 °C, the samples (∼1.5 mg iron oxide) were pressed into the sputtering cathodes suited for the 3 MV tandem accelerator facility at VERA. The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios were measured following the experimental procedures developed at VERA for heavy isotopes.[24] Specifically in this study, in order to achieve the highest possible efficiency, the use of the Time of Flight (ToF) detector was avoided, since this would have reduced the detection efficiency by a factor of at least 5. For this reason an ionization chamber with essentially 100% intrinsic efficiency was used as detector. This setup does not allow for suppression of certain kinds of instrumental background caused by $^{235}UH^-$ breakup products,[24] but due to its higher sensitivity was considered the best option to approach expected low levels of ^{236}U in the peat samples.

The measurements of the $^{236}U/^{238}U$ isotopic ratios of the minerotrophic peat samples were performed in reference to the in-house reference material Vienna-KkU, whose $^{236}U/^{238}U$ ratio has been determined to $(6.98 \pm 0.32) \times 10^{-11}$.[24] This normalization is needed mainly to correct for the different detection efficiency of the $^{238}U^{5+}$ current measurement in a Faraday cup and the single-ion counting of $^{236}U^{5+}$ in the gas ionization chamber. The $^{238}U^{5+}$ current for the ombrotrophic peat samples was very small (see Table S2), thus, the count rates of $^{234}U^{5+}$ and $^{235}U^{5+}$ were additionally measured in the rare isotope detector. The same detection efficiency can be assumed for $^{234}U^{5+}$, $^{235}U^{5+}$, and $^{236}U^{5+}$, making a normalization unnecessary.

Six procedural blanks without any U were prepared and measured together with the peat samples, following the same chemical procedure and with the same configuration of the AMS instrument. Most of the instrumental background of the AMS for ^{236}U is proportional to the uranium content of the sample and thus cannot be traced by uranium-free process blanks. However, no ^{236}U-free uranium material is readily available. U-specimens are usually prepared from uranium ores, which inevitably leads to increased neutron flux and production of ^{236}U. The uranium from the minerotrophic peat was extracted mainly for this purpose, since it is expected to derive from low-concentration ambient uranium, and the age suggests that there should be no anthropogenic contamination. The relatively high uranium content simplifies extraction of sufficient uranium amounts. Besides this role as a blank material for the ombrotrophic peat, the minerotrophic peat samples certainly are interesting by themselves.

■ RESULTS AND DISCUSSION

AMS Measurements of $^{234}U/^{238}U$ and $^{236}U/^{238}U$ Isotopic Ratios in the Ombrotrophic and Minerotrophic Peat Samples. The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios in each ombrotrophic peat layer are presented in Figure 1. The average of the measured $^{234}U/^{238}U$ isotopic ratios in all the peat layers is $(5.8 \pm 0.5) \times 10^{-5}$, a value consistent with the natural abundance of ^{234}U in terrestrial environments, which is equal to $\sim 5.5 \times 10^{-5}$.[1]

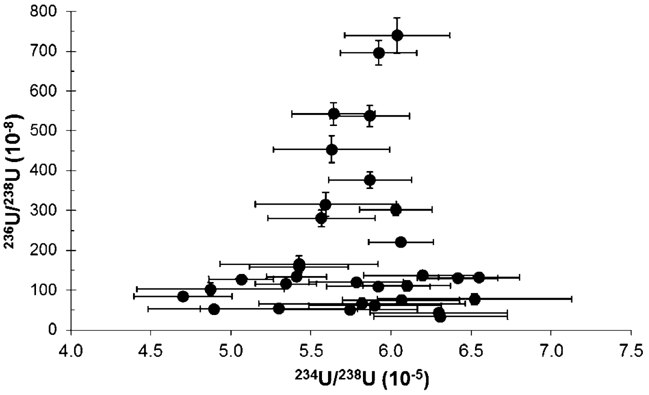

Figure 1. $^{236}U/^{238}U$ isotopic ratios versus $^{234}U/^{238}U$ isotopic ratios. ^{236}U is shown to be uncorrelated to ^{234}U in the 32 peat samples from the ombrotrophic peat core (Black Forest, Germany). While the $^{236}U/^{238}U$ isotopic ratios, well above prenuclear levels, vary over 2 orders of magnitude, the $^{234}U/^{238}U$ isotopic ratios scatter consistently to the natural abundance of ^{234}U.

The $^{236}U/^{238}U$ isotopic ratios in the ombrotrophic peat samples are considerably higher than the corresponding values expected in natural uranium ($^{236}U/^{238}U \sim 10^{-14}$).[2] As highlighted in Figure 1, the measured $^{236}U/^{238}U$ isotopic ratios span over 2 orders of magnitude, from the lowest value of $(3.4 \pm 0.5) \times 10^{-7}$ to the maximum of $(7.4 \pm 0.4) \times 10^{-6}$. These values are consistent with the global fallout levels of ^{236}U in the natural environment.[5−13] The global fallout origin of the anthropogenic ^{236}U is confirmed by the corresponding Pu isotopic ratios ($^{240}Pu/^{239}Pu = 0.19 \pm 0.02$, $^{241}Pu/^{239}Pu = 0.0012 \pm 0.0005$ and $^{242}Pu/^{239}Pu = 0.004 \pm 0.001$) found in the same peat core.[20]

It is important to note that there is no correlation between the measured $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios in each peat layer (Figure 1). The $^{236}U/^{238}U$ isotopic ratios denounce the anthropogenic input of U from global fallout, whereas the corresponding $^{234}U/^{238}U$ isotopic ratios do not indicate any contamination to the natural U. The $^{236}U/^{238}U$ isotopic ratio provides a far more sensitive tool for the detection of nuclear contamination with respect to the other minor U isotopes.

Three out of the five procedural blanks for the ombrotrophic peat gave no counts of ^{236}U during AMS measurement times of about 900 and 2600 s; in the remaining two blanks, 1 count and 5 counts of ^{236}U were detected during measurement times of 900 and 1800 s, respectively. For these two blanks the ^{236}U count rates were equal, respectively, to the 2% and 6% of the lowest count rate measured within the set of the ombrotrophic peat samples; this is a negligible contribution to the relative overall uncertainty (16%) of the $^{236}U/^{238}U$ isotopic ratio of this peat sample. The ^{238}U current in all five blanks was consistent with the instrumental noise of the AMS. The count rate of ^{234}U of the blanks was typically 4 counts per second, corresponding to about 20 ng of U in secular equilibrium. Since negligible ^{236}U counts and ^{238}U current were found in our blanks, there was no need to subtract a blank from the measured samples.

The three aliquots of the minerotropic (interglacial) peat sample yielded up to 20 nA $^{238}U^{5+}$. A total of 260 counts in the ^{236}U region-of-interest were detected within the measurement time of ∼5200 s. The corresponding process blanks for the minerotropic peat (prepared without any uranium, but using the same procedures and reagents) showed no detectable ^{238}U current (which corresponds to an upper limit 50 ng U in the sputtering cathode) and no ^{236}U counts within the measurement time of 1700 s. Each of the three aliquots of the minerotrophic peat sample was measured for two measurement runs, obtaining a total of 6 independent measurements of the ^{236}U/^{238}U ratio, whose mean value and standard deviation are $(3.3 \pm 0.7) \times 10^{-12}$; the reported uncertainty includes the reproducibility of the measurements, taking into account the deviation between the two runs and the deviation among the three aliquots. With the exception of the ^{236}U/^{238}U isotopic ratios measured in certain uranium ore samples,[3] our interglacial peat sample presents, so far, the lowest ^{236}U abundance ever detected in uranium extracted from a natural terrestrial sample. This value is, however, still 2 orders of magnitude higher than expected.[2] Although the procedural blanks related to the chemical separation of U revealed no detectable contamination from anthropogenic U, we cannot exclude a previous anthropogenic influence due to the contact of the peat deposit with meteoric water or due to contamination during sample collection. In fact the present study cannot demonstrate the expected geological isolation of the peat deposit and procedural blank related to the collection of the peat sample are not available. Another source of background can be identified as an instrumental AMS background. In fact, as explained above, in the AMS setup chosen with the aim to maximize the transmission of the ^{236}U signal the background caused by breakup of ^{235}UH^{-} in the terminal of the accelerator cannot be suppressed.[24]

In virtue of the listed possible interference sources, the detected ^{236}U/^{238}U isotopic ratio in the minerotrophic peat sample must be considered an upper limit for the typical natural ^{236}U abundance. However this measurement represents a significant step forward in the experimental determination of natural ^{236}U abundances in environmental samples paving the way to future developments.

Bomb Peak of ^{236}U in the Ombrotrophic Peat Core. The uranium extracted from minerotrophic peat sample constitutes the best blank for the ^{236}U/^{238}U isotopic ratios detected in the ombrotrophic peat core. In fact the ^{236}U/^{238}U measured in the ombrotrophic peat samples are from 5 to 6 orders of magnitude greater than the signal found for the interglacial peat samples. As such, we can conclude that also the uranium related background for ^{236}U in the ombrotrophic peat samples is negligible. These results clearly reflect the anthropogenic signature of the levels of ^{236}U in the ombrotrophic samples.

In Figure 2 the ^{236}U/^{238}U isotopic ratios are presented as function of the depth and the radiometric age of the peat layers assessed with the ^{210}Pb method. The ^{236}U/^{238}U isotopic ratio is rather constant in the range of $\sim 1 \times 10^{-6}$ from 6 and 14 cm depth (AD 1992 and AD 1977, respectively) and subsequently increases gradually to the maximum of $(7.4 \pm 0.4) \times 10^{-6}$ at 22 cm depth (AD 1959). After this peak, the ^{236}U/^{238}U isotopic ratios decrease gradually down to $\sim 7 \times 10^{-7}$ at 47 cm depth (AD 1917).

The maximum of global fallout derived ^{236}U is very close to the age/depth layer of maximum atmospheric bomb testing (AD 1963),[4] as determined by ^{210}Pb dating in the investigated peat core. This finding demonstrates that the ^{236}U bomb peak can be successfully used as an independent chronological marker complementing the ^{210}Pb dating of peat cores.

The ^{236}U/^{238}U isotopic ratios greater than the expected prenuclear age values observed in the deeper layers of the core preceding AD 1945 could be an indication of either remobilization of the deposited weapons tests fallout U or an additional input of recent U from atmospheric precipitation through the water column. Regardless, the detection of anthropogenic ^{236}U at depths preceding the occurrence of the global fallout demonstrates the mobility of ^{236}U downward the peat core.

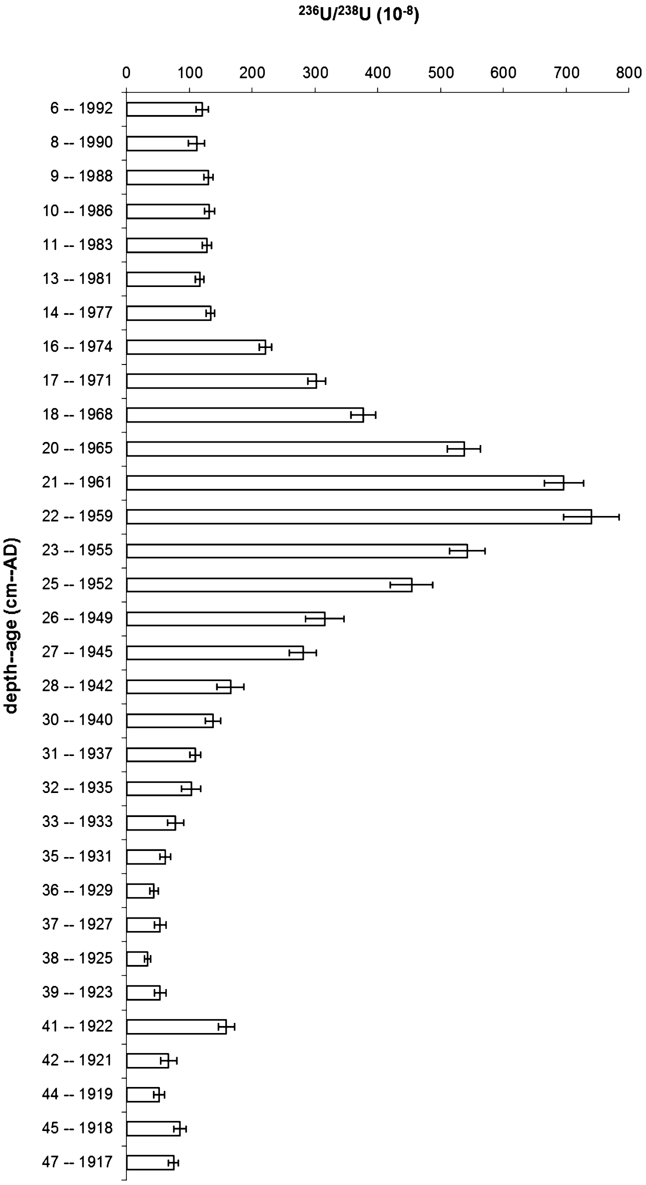

Figure 2. ^{236}U/^{238}U isotopic ratios as function of the depth and age. The maximum of global fallout derived ^{236}U is found in correspondence to layers whose age is close to the maximum atmospheric bomb testing (AD 1963) as determined by ^{210}Pb dating in the ombrotrophic peat core. Postdepositional migration of ^{236}U is observed in the layers deposited before AD 1945, while the deposition of resuspended global fallout ^{236}U is observed in correspondence to the layers deposited after AD 1983. The depths refer to the lower border of the peat layers.

The rather constant ^{236}U/^{238}U isotopic ratios in the peat layers from the top down to 11 cm depth (AD 1983) have an average of $(1.24 \pm 0.08) \times 10^{-6}$. Considering that at AD 1983 no more significant direct global fallout occurred, then the ^{236}U detected above the depth of 11 cm (AD 1983) might originate from redeposition of global fallout derived U which was deposited elsewhere and subsequently resuspended. Addition-

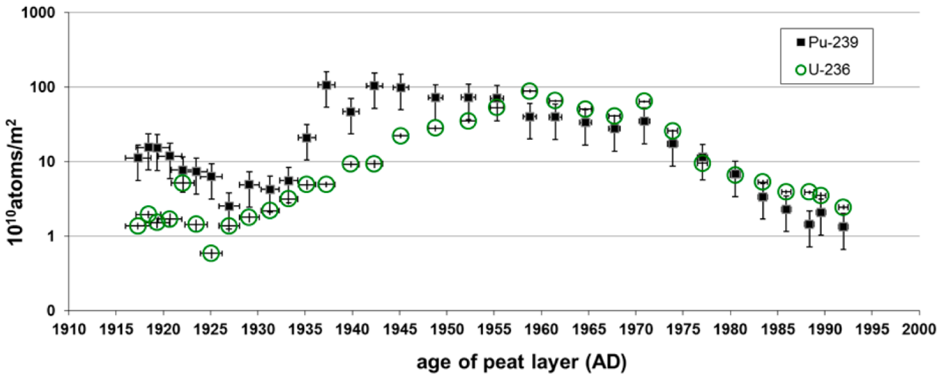

Figure 3. ^{236}U and ^{239}Pu areal inventories as function of the age. The areal inventories of ^{236}U and ^{239}Pu are represented on a logarithmic scale as function of the age of the ombrotrophic peat layers. The different behavior of ^{236}U (empty circles) and ^{239}Pu (solid squares) along the peat core is highlighted. Pu shows a much higher postdepositional migration with respect to U.

Table 2. Cumulative Areal Inventories of ^{236}U and ^{239}Pu in the Ombrotrophic Peat Core[a]

	upper interval	interval of direct global fallout	lower interval	total
	(6–11) cm (1992–1983) AD	(13–26) cm (1981–1949) AD	(27–47) cm (1945–1917) AD	(6–47) cm (1992–1917) AD
^{236}U (atoms/m^2)	(1.90 ± 0.14) × 10^{11}	(4.65 ± 0.26) × 10^{12}	(7.24 ± 0.79) × 10^{11}	(5.57 ± 0.35) × 10^{12}
^{239}Pu (atoms/m^2)	(1.05 ± 0.52) × 10^{11}	(4.25 ± 2.12) × 10^{12}	(4.68 ± 2.34) × 10^{12}	(9.04 ± 4.52) × 10^{12}
^{236}U relative to total (%)	3.4 ± 0.5	84 ± 5	13 ± 1	100
^{239}Pu relative to total (%)	1.2 ± 0.6	47 ± 23	52 ± 26	100
^{236}U/^{239}Pu	1.8 ± 0.9	1.1 ± 0.5	0.15 ± 0.08	0.62 ± 0.31

[a] Inventories are expressed in atoms/m^2, and the corresponding ^{236}U/^{239}Pu ratios are given as well. The fractions of ^{236}U and ^{239}Pu detected in each interval of peat layers considered (see text) are reported as percentage of the corresponding total inventories.

ally, considering the mobility detected for downward migration, it is not possible to exclude that an upward migration of ^{236}U had contributed to the observed level of ^{236}U in the upper layers of the core since there exists no proof that the dominant direction of water movement and transport of elements in the investigated peat bog was vertically downward. A third minor contribution to the ^{236}U abundance in correspondence of the peat layers dated across AD 1986 (9–10 cm depth) might originate from the deposition of the Chernobyl fallout; an estimate of this possible contribution is presented in the following paragraph discussing the areal inventories of ^{236}U in the investigated peat core.

Areal Inventories and Mobility of ^{236}U and ^{239}Pu in the Ombrotrophic Peat Core. The areal inventories of ^{236}U and ^{239}Pu (Table S3) were obtained from the dry mass and surface area of the peat layers (Table S1).[19] The ^{236}U inventories were calculated from the ^{238}U concentration of the peat layers measured using ICP-MS (Table S1)[19] and the ^{236}U/^{238}U isotopic ratios measured with AMS in this study, while for ^{239}Pu, the inventories were calculated from the ^{239}Pu concentrations measured using AMS.[20]

Figure 3 highlights the areal inventories of ^{236}U and ^{239}Pu on a logarithmic scale as a function of the age of the peat layer. The vertical profile of the areal inventory of ^{236}U resembles that of the corresponding ^{236}U/^{238}U isotopic ratios (Figure 2), with the bomb peak of (8.8 ± 0.5) × 10^{11} ^{236}U atoms/m^2 at the depth of 22 cm (AD 1959). The minimum values of the areal inventory of ^{236}U were detected at the deepest layers on the order of 10^{10} ^{236}U atoms/m^2. The corresponding concentrations of ^{236}U per dry mass in the peat samples ranged from 10^7 to 10^9 atoms/g.

As for ^{236}U, the ^{239}Pu areal inventory reveals a vertical profile similar to that of the corresponding ^{239}Pu concentration.[20] The maximum of the ^{239}Pu areal inventory reaches (1.1 ± 0.5) × 10^{12} ^{239}Pu atoms/m^2 at 31 cm depth (AD 1937), followed by an abrupt decline to values spanning from (2.1 ± 0.10) × 10^{11} ^{239}Pu atoms/m^2 to (2 ± 1) × 10^{10} ^{239}Pu atoms/m^2 between 33 and 47 cm depth (from AD 1935 to AD 1917). The maximum of the Pu areal inventory is moved downward by ~9 cm with respect to the peak of ^{236}U; this shift corresponds to a time interval of ~22 years. Furthermore, an increased ^{239}Pu abundance of 10^{11} atoms/m^2 (1 order of magnitude lower than the ^{239}Pu occurrence at the maximum) is observed in the deepest analyzed layers, while the corresponding ^{236}U abundance declines to values lower than those found at the top of the peat core. The shift between the maxima of the ^{236}U and ^{239}Pu inventories, their different vertical profiles, and the consequent variability in the corresponding ^{236}U/^{239}Pu ratios (whose details are given in Table S3) indicate that the behavior of ^{236}U differs from that of ^{239}Pu. It is possible to quantify the postdepositional migration of ^{236}U and ^{239}Pu relative to the interval of the peat core layers in which direct global fallout occurred. This interval of peat layers spans from 13 to 26 cm depth, corresponding to the time interval AD (1981–1949). From 27 cm (AD 1945) down to 47 cm (AD 1917) depth in the investigated peat core, the fractions of ^{236}U and ^{239}Pu mobilized from the upper layers are found, together with a possible input of these isotopes with meteoric water percolating through the peat profile. In the upper layers of the investigated peat core from 6 cm (AD 1992) to 11 cm (AD 1983) depth, the detected ^{236}U and ^{239}Pu can be ascribed to the redeposition of global fallout derived U and Pu and to the upward postdepositional migration of these isotopes from the lower layers. The cumulative areal inventories of ^{236}U and ^{239}Pu relative to these aforementioned intervals as well as to the entire investigated peat core are presented in Table 2. In correspondence to the interval of layers where direct global fallout occurred, ~84% of ^{236}U is found; the remaining ~13% and ~3% are detected in correspondence to the lower and upper intervals, respectively (Table 2). ^{239}Pu demonstrates a higher mobility in the investigated peat core with respect to ^{236}U, since only ~47% of ^{239}Pu is found in the interval of direct global fallout, while ~52% is found in the lower interval; the remaining ~1.2% belongs to the upper interval (Table 2).

Despite the Pu isotopic distribution gave no indication of a contamination source other than global fallout,[20] in the upper layers of the investigated peat core from 6 cm (AD 1992) to 11 cm (AD 1983) depth, a contribution of the deposition of ^{236}U released from the Chernobyl (AD 1986) accident might be recorded. To our knowledge, there are no measurements of deposition of actinides from Chernobyl accident in the area of the Black Forest under study, but exhaustive data on $^{239+240}$Pu deposition from Chernobyl fallout in the vicinity of Munich (Germany) were published two years after the accident.[28] The area of Munich was reported to be more intensively affected by the Chernobyl fallout with respect the South West of Germany;[29] therefore, it is reasonable to consider the cited $^{239+240}$Pu deposition from Chernobyl in Munich,[28] equal to ~0.051 Bq/m^2, as an upper limit for the corresponding deposition in the area of the Black Forest under study. An estimate of the ^{236}U deposition from Chernobyl fallout can be obtained considering the isotopic composition of Chernobyl fuel particles and in particular the activity ratio ^{238}U/$^{239+240}$Pu ~ 0.00095[30] and the isotopic ratio ^{236}U/^{238}U ~ 0.001.[31] According to this estimate, an upper limit for the total deposition of ^{236}U from Chernobyl fallout in the area under study of ~1 × 10^{10} atoms/m^2 is obtained, representing the 10% of the global fallout derived ^{236}U in the upper interval (Table 2). Because of the dominating global fallout contamination in the area under study, it was not possible to discriminate the possible Chernobyl contribution.

As discussed above, the mobility of global fallout ^{236}U is lower compared to that of ^{239}Pu (Table 2), and the position of the ^{236}U bomb pulse is preserved in the chronology of the peat formation (Figures 2 and 3) in contrast to the ^{239}Pu profile in the same peat core (Figure 3). These different behaviors of U and Pu seem to reflect the chemical properties and the formation of mobile species of these elements in the acidic organic-rich environment of the ombrotrophic peat bog. Under the strongly reducing conditions characterizing the peat environment below the bogwater table, U(IV) can be considered the predominant species over the oxidized U(VI).[32] In organic-rich environments the speciation of U is dominated by its association with the organic fraction, as demonstrated in a study concerning the accumulation of natural U in an organic rich soil, [33] where the main mechanism responsible for U immobilization was identified in the binding of U(VI) to soil organic matter. Also in a laboratory column study, [34] the migration of U(IV) and U(VI) in a quartz sand was observed to be accelerated by association with humic acids, and the U(IV) breakthrough was found to be similar to that of U(VI). The postdepositional migration of Pu in the actual peat core might be explained with the complexing of Pu(III) as well as Pu(IV) with humic and fulvic acids and their transport as colloids.[35−37,20] Given the observed reduced mobility of U relative to Pu, the behavior of U in the investigated peat bog seems to be driven by different mechanisms. The different distributions of ^{236}U and ^{239}Pu are highlighted by the different ^{236}U/^{239}Pu atom ratios (Table 2) relative to the aforementioned sections of the peat core. The depletion of ^{239}Pu with respect to ^{236}U from the interval of direct global fallout is expressed by the higher ^{236}U/^{239}Pu ratio in this interval (1.1 ± 0.5) compared to that of the total investigated core (0.62 ± 0.31) and from the lower ratio (0.15 ± 0.08) corresponding to the lower interval. The higher ^{236}U/^{239}Pu ratio (1.8 ± 0.9) of the upper interval might be explained with the oxidizing conditions of the peat above the bogwater table playing a role in the preferential mobilization of U with respect to Pu toward the upper layers or might as well support the assumption that the U and Pu detected in the top layers are mainly originated from the redeposition of global fallout derived U and Pu; in this case, the increased ^{236}U/^{239}Pu atom ratio in the top layers of the core would indicate that a higher fraction of global fallout U relative to Pu is suspended from other locations. While the present study cannot provide an unambiguous interpretation of the observed phenomena, speciation experiments in the investigated environment could help to identify the mechanisms responsible for the different mobility of U and Pu. However, the actual study reveals novel information on the behavior of global fallout U and Pu at femtograms to attograms levels directly in situ in an environmental scale experiment. It demonstrates how the identification of the sources of U and Pu contamination can be successfully used in order to investigate their behaviors in real natural systems. The documented mobility of U and Pu can have significant implications in the assessment of the risks related to other kinds of radioactive contamination, such as nuclear accidents and releases from nuclear installations and nuclear waste disposal repositories.

Cumulative Areal Inventories of ^{236}U and ^{239}Pu in the Ombrotrophic Peat Core and Estimate of the Global Fallout Deposition of ^{236}U. Due to the difference in the migration behavior, the ^{236}U/^{239}Pu atom ratios vary over 2 orders of magnitude from a maximum of ~2.7 to a minimum of ~0.05 along the peat profile (Table S3 and Table 2). However, the cumulative areal inventories along the section of the peat profile (47 cm depth) studied here are equal to (5.6 ± 0.3) × 10^{12} atoms/m^2 and (9.0 ± 4.5) × 10^{12} atoms/m^2 of ^{236}U and ^{239}Pu, respectively. The ^{236}U/^{239}Pu ratio of the cumulative deposition in the actual peat core is equal to 0.62 ± 0.31, which is compatible to previous estimates of this ratio for global fallout (Tables 1 and 2) ranging from 0.05−0.5.[14] ^{236}U/^{239}Pu ratios in the narrow range of 0.212−0.253 have been reported for soil cores from a forest area in Japan,[5] for the deeper layers of soil cores from La Palma Island with a ^{236}U/^{239}Pu ratio of ~0.20,[7] and for soil cores from the Washington State whose average ^{236}U/^{239}Pu ratio is equal to 0.19 ± 0.04.[38] The measurement of the cumulative ^{236}U/^{239}Pu ratio allows estimating the global stratospheric deposition of ^{236}U in reference to the global fallout inventory of $^{239+240}$Pu.[5] Using the cumulative ^{236}U/^{239}Pu ratio measured in the present study, the ^{236}U global stratospheric deposition is estimated from the global fallout inventory of $^{239+240}$Pu given by UNSCEAR.[4] Using this approach, a value of (1698 ± 850) kg ^{236}U is obtained, which lies in between the estimates found in earlier studies (see Table 1).

The cumulative areal inventory of ^{236}U obtained from the peat core is 4 to 5 times lower than the levels estimated in a vertical profile of seawater from the Japan Sea[13] and in a soil core from Ishikawa (Japan).[6] Considering the ^{240}Pu/^{239}Pu isotopic ratio equal to ~0.19,[20] the cumulative areal inventory of ^{239}Pu in our peat core corresponds to (14 ± 7) Bq/m^2 $^{239+240}$Pu. This value is significantly lower than that of (141

± 3) Bq/m^2 $^{239+240}$Pu obtained from the soil core from Ishikawa.[6] However, in grassland and forest soils of southern Bavaria, an area which is geographically close to the Wildseemoor and has similar latitude, a cumulative deposition of $^{239+240}$Pu of 49 Bq/m^2 and 64 Bq/m^2, respectively, was established.[39] These cited values[25] are in agreement with the total integrated deposition density $^{239+240}$Pu of 58 Bq/m^2 at the North Temperate Zone latitude band (40°−50°) provided by UNSCEAR.[4] The spatial distribution of ^{137}Cs from global fallout[40] shows that the UNSCEAR value for the 45 degree latitude band is caused by high deposition near Japan and in the northern Atlantic and Pacific. Continental Europe was less affected, and it is well-known that the global fallout deposition is patchy even on a smaller scale, controlled mainly by precipitation.[41] Thus it is reasonable that the value of (14 ± 7) Bq/m^2 $^{239+240}$Pu for the peat core from Wildseemoor is influenced by local variation of the fallout deposition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, ^{236}U/^{238}U isotopic ratios of the samples. Shown are 32 ombrotrophic peat samples, three aliquots of the preanthropogenic minerotrophic peat sample, and the in-house reference material Vienna KkU. Table S1, depth, surface, dry mass, and ^{238}U content of the ombrotrophic peat samples. Table S2, raw data of the AMS measurement of the ombrotrophic peat samples. Table S3, depth profile of ^{236}U and ^{239}Pu of the ombrothrophic peat core. ^{210}Pb-Age, ^{236}U/^{238}U isotopic ratios, ^{236}U and ^{239}Pu areal inventories in atoms/m^2, and ^{236}U/^{239}Pu isotopic ratios are given for each layer of the peat core. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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