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Binding of ^{239}Pu and ^{90}Sr to Organic Colloids in Soil Solutions: Evidence from a Field Experiment

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Colloidal transport has been shown to enhance the migration of plutonium in groundwater downstream from contaminated sites, but little is known about the adsorption of ^{90}Sr and plutonium onto colloids in the soil solution of natural soils. We sampled soil solutions using suction cups, and separated colloids using ultrafiltration to determine the distribution of ^{239}Pu and ^{90}Sr between the truly dissolved fraction and the colloidal fraction of the solutions of three Alpine soils contaminated only by global fallout from the nuclear weapon tests. Plutonium was essentially found in the colloidal fraction (>80%) and probably associated with organic matter. A significant amount of colloidal ^{90}Sr was detected in organic-rich soil solutions. Our results suggest that binding to organic colloids in the soil solutions plays a key role with respect to the mobility of plutonium in natural alpine soils and, to a lesser extent, to the mobility of ^{90}Sr .

Introduction

^{239}Pu and ^{90}Sr were deposited worldwide in the soil as a result of the atmospheric nuclear weapon tests (NWT), occurring mainly between 1950 and 1963. Pu strongly binds to soil constituents such as organic matter or hydrous oxides and consequently has a low mobility (1). However, migration of Pu farther than expected has been reported in groundwater and runoff water (2–6) close to contaminated sites or in field experiments. The most important form of Pu in the environment, especially in the presence of humic substances, is Pu(IV) (ref 6 and refs therein, and ref 7). Pu(IV) is barely soluble but the above cited studies show that migration is possible due to plutonium associated with the colloidal fraction in the mobile water phase. Kersting et al. (2) showed that association of plutonium with colloids resulted in an enhanced migration of this radioelement in the groundwater of the Nevada Test Site, whereas Novikov et al. (4) found an association of plutonium with colloidal iron (hydr)oxides in groundwater near the Mayak nuclear site. Santschi et al.

hypothesized that elevated $^{239+240}\text{Pu}$ and ^{241}Am concentrations in Rocky Flats runoff water were related to their association with colloids rich in organic matter (5). In a subsequent study, these authors showed that the enhanced mobility of plutonium was related to its affinity for cutin-like organic colloids (6).

In contrast to plutonium, ^{90}Sr is much more soluble, and migration into the soil's deeper layers is often observed (8). Moreover, as a chemical analogue to calcium, ^{90}Sr can be easily taken up by plants and transferred into the food chain, possibly leading to human contamination (9). Despite this biological uptake, few studies exist with respect to determining amounts of ^{90}Sr in the soil solution.

For both elements, most of the studies about colloidal transport concern either groundwater or runoff water, often in highly contaminated areas (2–6). In contrast, little is known about their association with the soil solution components in an environment contaminated by NWT fallout only. Besides the difficulty of measuring these radionuclides at the very low activity levels found in the environment, it is difficult to sample soil solutions without altering in situ conditions (10). Nevertheless, the soil is the primary receptor of atmospheric deposition, and understanding the processes of radionuclide migration in soils is a keystone for predicting radionuclide mobility and potential hazards for the biosphere and humans.

In this study we aimed to determine the fraction of ^{239}Pu and ^{90}Sr associated with colloids in the soil solutions of a natural Alpine environment, which were contaminated exclusively by global NWT fallout. Furthermore, we aimed to characterize the colloids involved in the adsorption of ^{239}Pu and ^{90}Sr on the colloidal fraction.

Materials and Methods

Experimental Design and Sampling. We collected soil solutions from three different soils in Val Piora (Ticino, Switzerland), an alpine valley in the Central Alps. The studied soils were located at an altitude ranging between 1920 and 2020 m above sea level. The soil profiles and the inventory of the radionuclides are described in detail elsewhere (11). Briefly, the first soil (Luvisol 1) was a relatively dry Luvisol with $^{239+240}\text{Pu}$ and ^{90}Sr deposition inventories of 242 Bq/m² and 2326 Bq/m², respectively. The second soil (Histosol 2) was a Histosol under a basic wetland subjected to a surface runoff with $^{239+240}\text{Pu}$ and ^{90}Sr deposition inventories of 190 Bq/m² and 615 Bq/m², respectively. The third soil (Histosol 8) was a temporarily water saturated Histosol, with $^{239+240}\text{Pu}$ and ^{90}Sr deposition inventories of 76 Bq/m² and 752 Bq/m², respectively.

At all three sites, we collected soil solutions using plastic (nylon and polyethylene) suction lysimeters (EcoTech, Germany) with a cut off at 0.45 μm . In June 2007, suction cups were installed in the three soils at 5, 10, and 15 cm depth using an adapted auger. Four suction cups per depth were installed in each soil at a distance of 60 cm \times 60 cm. The soil solution was collected daily under a vacuum of 60 hPa during the summer of 2007. Depending on the site, we were able to collect daily between 100 mL and 3 L per depth (four suction lysimeters). The pH, conductivity, and redox state of the solutions were measured in the field. Particle size distribution (PSD) was determined in the soil solutions in the range of 50–2000 nm using a single particle counter (12). The determination of ^{239}Pu and ^{90}Sr required large volume of soil solution (between 2–4 L of bulk solution). Therefore, the solution collected each day at one sampling point was pooled in order to have one sample per depth and soil for the analysis of ^{239}Pu and ^{90}Sr in the bulk soil solutions

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at the end of the sampling period. Additional samples were collected for ultrafiltration. Each day these soil solutions were ultrafiltered at 10 kDa (13) using a regenerated cellulose membrane (Pellicon XL 50, Millipore). Each fraction of the ultrafiltered soil solution was then again pooled to give one sample of retentate and one sample of permeate per depth and soil at the end of the sampling period for the determination of ^{239}Pu and ^{90}Sr activities. The ultrafiltration was carried out directly after sampling in the nearby laboratories of the Alpine Biology Center of Val Piora.

Hereafter, the initial solution as collected in the field is called "bulk", the solution that did not pass the membrane and was therefore enriched in colloids is called "retentate", and the solution passing through the ultrafiltration membrane, corresponding to the truly dissolved fraction, is named "permeate". During the ultrafiltration, we aimed to reach a concentration of the retentate, or concentration factor (cf), around 10. The true concentration factor (cf) was calculated after each ultrafiltration as the ratio between the volume of the bulk solution and the volume of the retentate (13). The volumetric activity of the radionuclide (Bq/L) and the concentration of the stable element (mg/L) in the colloidal fraction (A_c) were calculated as follows:

$$A_c = \frac{A_r - A_p}{cf} \quad (1)$$

where A_r is the volumetric activity of the radionuclide (Bq/L) or the concentration of stable elements (mg/L) in the retentate and A_p is the volumetric activity (Bq/L) or the concentration of stable elements in the permeate.

The recovery R (%) of the elements after the ultrafiltration was calculated as follows:

$$R = \frac{A_p + A_c}{A_b} \times 100 \quad (2)$$

where A_b is the volumetric activity of radionuclide (Bq/L) or the concentration of stable element (mg/L) in the bulk.

All solutions intended for analysis of ^{239}Pu and ^{90}Sr were immediately treated with 2 mL/L of 65% HNO_3 . For the analyses of UV-vis fluorescence of the organic matter, dissolved organic carbon (DOC), microscopy, and ζ -potential determination, the solutions were treated with 9 $\mu\text{L/mL}$ of 1 M NaN_3 and stored at 4 °C prior to measurement.

In Luvisol 1, we simulated rain events (approximately 16 mm/day) with demineralized water (conductivity around 3 $\mu\text{S/cm}$) in order to enhance the volume of the soil solution collected because it was initially too low for determining radionuclide activities. Even so, the collected volume of solution was sufficient for the determination of ^{239}Pu and ^{90}Sr in the bulk solutions only.

To confirm results, the same experimental design was set up during the summer of 2008. As an additional precaution, we flushed the collecting bottles with N_2 and the ultrafiltration procedure was carried out in a N_2 atmosphere in a portable hood. This precaution was intended to avoid changes in the oxidation state of the soil solutions. Moreover, to prevent precipitation of elements on the membrane of ultrafiltration (13), we used a larger ultrafiltration membrane (PrepScale, Millipore) and we reduced the concentration factor (cf) to approximately 5. After simulated rain events, waters from the three depths of the Luvisol 1 were mixed together for the ultrafiltration experiment. Further sampling was carried out in the summer of 2009 for the determination of the size distribution of the colloids.

Laboratory Analyses. We performed ^{239}Pu analyses on the permeate, the bulk, and the retentate solutions using sf-ICP-MS (Institute of Geosciences, University of Heidelberg, Germany) after chemical separation using TEVA resin (14).

As the determination of plutonium requires an initial iron hydroxides precipitation during which ^{90}Sr stays in solution, we used the supernatant for the analysis of ^{90}Sr . ^{90}Sr was coprecipitated on calcium phosphates at pH 8. After redissolution and equilibration between ^{90}Sr and its daughter product ^{90}Y , yttrium was extracted on a AG1x8 resin as a dipicolinate anionic complex and measured in a proportional counter (15). The absolute detection limit (DL) for the determination of ^{90}Sr is 5 mBq. Typically 3–10 L of bulk and permeate and 0.3–1 L of retentate were needed for the determination of plutonium and ^{90}Sr above the DL.

DOC, Fe, Si, Ca, and ζ -potential were measured using standard procedures described in Supporting Information. The excitation–emission matrix (EEM) of UV-vis fluorescence of the organic matter was measured with a Perkin-Elmer LS-50, equipped with FL-WINLAB software, at the Institute of Chemical Science and Engineering (EPFL, Lausanne, Switzerland). The emission spectra were measured at wavelengths from 280 to 580 nm, for excitation wavelengths between 220 and 470 nm with increments of 5 nm and a scan speed of 1200 nm/min. Colloids of the soil solutions were characterized by transmission electronic microscopy (TEM, CM-100, Philips) coupled to an EDX analyzer, after the deposition of the colloids on carbon-coated 200 mesh grids (S162, Plano GmbH, Wetzlar, Germany) using a 4-h centrifugation ($\text{rcf} = 2344 \text{ g}$; size of particles deposited >50 –100 nm).

Results

The pH, conductivity, and redox state of the soil solutions are presented in Supporting Information (Table SI-2).

^{239}Pu and ^{90}Sr in the Soil Solutions. ^{239}Pu activities measured in the bulk solutions ranged between 0.007 mBq/L and 0.076 mBq/L (Table 1). ^{239}Pu activities were in the same range in the soil solutions from 2007 and 2008. Calculation using data presented in Table 1 shows that between 68% and 92% of the ^{239}Pu was in the colloidal fraction, to the exception of the solution from Histosol 2, 15 cm in 2007, where the colloidal ^{239}Pu fraction was 48% (Figure 1a). Compared to the activity in the soils (11), the ^{239}Pu adsorbed on colloids amounted for 0.0005–0.03% of the total activity of plutonium in the soils (see calculation in the Supporting Information). The recoveries of plutonium (Table SI-5, Supporting Information) show that no loss on the filtration membrane occurred for the two periods of sampling. However, these results contain additional uncertainty coming from the use of a different sample for the bulk analysis and the ultrafiltration procedure.

The activities of ^{90}Sr in the soil solutions were close to or below the detection limit (5 mBq/sample; Table 2). The activities of ^{90}Sr measured in the bulk solutions ranged from 1.5 mBq/L to 16 mBq/L and were usually higher in 2007 than in 2008. ^{90}Sr was measurable in the retentate of Luvisol 1 and Histosol 8 but not in the retentate of Histosol 2. In contrast, it was usually measurable in the permeate of Histosol 2 and not in the permeate of Luvisol 1 and Histosol 8. Therefore, for the calculation of the colloidal fraction (eq 1), we used the detection limit (DL) as the activity of the sample, when the ^{90}Sr activity in a sample was below the DL. As a consequence, in samples with permeate activity below the DL, the calculated colloidal activity gives a minimum value for the real activity associated with the colloidal particles. In samples where the retentate activity was below the DL, the calculated colloidal fraction is a maximum value for the real activity associated with the colloidal particles. The calculated colloidal percentages (Figure 1b) showed that ^{90}Sr is distributed rather equally between the colloidal fraction and the truly dissolved fraction in Histosol 8 (min. 40%–70% or more of colloidal ^{90}Sr , $n = 4$). In Luvisol 1, ^{90}Sr was also partly found in the colloidal fraction (min. 20% of colloidal ^{90}Sr , n

TABLE 1. ^{239}Pu Activities Measured in the Truly Dissolved Fraction, Bulk, and Colloidal Fraction of the Soil Solutions in 2007 and 2008

sample	^{239}Pu in 2007 (mBq/L)			^{239}Pu in 2008 (mBq/L)		
	truly dissolved fraction	bulk	colloidal fraction	truly dissolved fraction	bulk	colloidal fraction
Luvisol 1, 5 cm	n.m.	0.076 ± 0.006	n.m.	n.m.	n.m.	n.m.
Luvisol 1, 10 cm	n.m.	0.056 ± 0.012	n.m.	n.m.	n.m.	n.m.
Luvisol 1, 15 cm	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Luvisol 1 ^b	n.m.	n.m.	n.m.	0.006 ± 0.001	0.054 ± 0.002^a	0.049 ± 0.002
Histosol 2, 5 cm	0.002 ± 0.001	0.01 ± 0.001	0.010 ± 0.001	0.0022 ± 0.0002	0.007 ± 0.001^a	0.005 ± 0.001
Histosol 2, 10 cm	0.002 ± 0.001	0.028 ± 0.001	0.012 ± 0.001	0.0023 ± 0.0003	0.011 ± 0.001^a	0.009 ± 0.001
Histosol 2, 15 cm	0.014 ± 0.001	0.037 ± 0.003	0.013 ± 0.001	0.0008 ± 0.0002	0.008 ± 0.001^a	0.008 ± 0.001
Histosol 8, 5 cm	n.m.	0.075 ± 0.003	n.m.	0.006 ± 0.001	0.057 ± 0.002^a	0.051 ± 0.002
Histosol 8, 10 cm	0.003 ± 0.001	0.059 ± 0.004	0.065 ± 0.002	0.006 ± 0.001	0.058 ± 0.001	0.077 ± 0.003
Histosol 8, 15 cm	n.m.	0.045 ± 0.002	n.m.	0.006 ± 0.001	0.037 ± 0.001	0.039 ± 0.001

^a Calculated as the sum of the colloidal and the truly dissolved fraction. ^b Mixed sample of all three depths of the soil solutions of Luvisol 1. n.m.= not measured. The factor 2 between the activities of the retentate measured in 2007 and in 2008 is partly due to the difference in the cf of the ultrafiltration that was set at 10 in 2007 and at 5 in 2008.

= 1). In Histosol 2, ^{90}Sr was mainly present in the truly dissolved fraction (40%–20% or less colloidal ^{90}Sr , $n = 5$).

The 2007 data set for ^{90}Sr determination was in good agreement with quantitative recoveries of ^{90}Sr after the ultrafiltration; in 2008 ^{90}Sr recoveries above 100% were obtained. This is mainly due to large uncertainties resulting from activities close to the detection limit.

DOC, Ca, Fe, and Si in the Soil Solutions. With respect to major elements, all fractions of the soil solutions of Histosol 2 differed from the other two soils by having lower DOC concentrations and higher concentrations of inorganic elements, especially Ca and Fe (Figure 1c, and Tables SI-3 and SI-4 of the Supporting Information).

^{239}Pu activity in the colloidal fraction was correlated with the content of colloidal organic carbon (COC) ($n = 11$, $\rho = 0.7$, p -value < 0.05 , see Figure 2). In the bulk solutions, ^{90}Sr activity was correlated with DOC ($n = 18$, $\rho = 0.66$, p -value < 0.05) and anticorrelated with Si ($n = 18$, $\rho = -0.78$, p -value < 0.05).

Data from Tables SI-3 and SI-4 show that Ca, similarly to ^{90}Sr , was partly found in the colloidal fraction of the soil solutions of Luvisol 1 (colloidal fraction = 32%, $n = 2$) and Histosol 8 (colloidal fraction = $45 \pm 6\%$, $n = 4$) and was mainly in the truly dissolved fraction of soil solutions of Histosol 2 (truly dissolved fraction = $97 \pm 1\%$, $n = 6$) (Figure 1c). The percentage of COC of the soil solutions of Histosol 8 (colloidal fraction = $57 \pm 6\%$, $n = 4$) was slightly higher than in Histosol 2 (colloidal fraction = $40 \pm 11\%$, $n = 6$) and Luvisol 1 (colloidal fraction = $33 \pm 1\%$, $n = 2$). Fe was mostly found in the colloidal fraction (colloidal fraction = $76 \pm 11\%$, $n = 12$) of the solutions of all three soils while Si was mostly found in the truly dissolved fraction (truly dissolved fraction = $97 \pm 3\%$, $n = 12$).

Recoveries after ultrafiltration (Table SI-5) were higher than 85% for DOC, calcium, and silicon. In contrast, iron showed some losses during the 2007 ultrafiltration process, possibly due to the precipitation of iron hydroxides on the membrane. Better recoveries of iron were obtained in 2008, probably because we used a larger surface for the ultrafiltration membrane and we diminished the concentration factor to 5. Moreover, we flushed the overall system with N_2 . It is important to note that the loss of iron during the ultrafiltration in 2007 did not influence the recoveries of ^{239}Pu and ^{90}Sr , indicating that these radionuclides were not adsorbed on iron hydroxide precipitates.

Characterization of the Colloids. The size distribution of the colloids in the bulk solutions is presented in Supporting Information, Table SI-6 and Figure SI-1. Results cannot be directly compared to chemical results, as they have been

obtained from different water samples. The total number of colloids in the 100–2000 nm range varied between 2.4×10^6 and $4.2 \times 10^7 \text{ mL}^{-1}$. No significant differences were recorded between the three sampling sites.

To help understand the interaction of ^{239}Pu and ^{90}Sr with the colloids, the latter were qualitatively analyzed by TEM/EDX, 3D-fluorescence of the organic matter, and the ξ -potential of the colloids. Observations of colloids using TEM were performed on eight grids from the solution of the three soils. All grids contained bacteria of around 500 nm of diameter associated with organic and mineral matter (Figure SI-2a). EDX analyses ($n = 13$) were performed on four grids to determine the composition of mineral colloids frequently observed on all samples. The main mineral colloids observed on the grid were iron-rich colloids (Figure SI-2b), probably iron hydroxides (for EDX, $n = 6$). Ca-rich colloids (for EDX, $n = 2$), possibly calcite, were observed mainly on grids from the solutions of Histosol 8 and Luvisol 1 (Figure SI-2a) and to a lesser extent on grids from the solutions of Histosol 2.

The ζ -potential of zero-charge for bulk, permeate, and retentate solutions measured at pH between 1.5 and 2.0 (Figure SI-3) indicate that the ζ -potential of the colloids was mainly influenced by the presence of carboxylic groups such as those present in humic and fulvic acids (16). The ζ -potentials at an environmental pH of about 6.5–7 for these solutions were situated between -10 to -30 mV , depending on the soil type and depth. Colloid stability is expected for ζ -potentials below -30 mV (17). Consequently, some solutions may show potential instability during the ultrafiltration process resulting in aggregation.

UV-vis Fluorescence of the Organic Matter. 3D-EEM maps ($n = 21$) (Figure SI-4) of the soil solutions were mainly composed of two intensity regions (region 1: $\lambda_{\text{ex}} = 260 \text{ nm}$ and $\lambda_{\text{em}} = 450 \text{ nm}$, and region 2: $\lambda_{\text{ex}} = 335 \text{ nm}$ and $\lambda_{\text{em}} = 440 \text{ nm}$). On the basis of literature data, these two regions, designated as peak A and peak C, indicate the presence of humic-like substances (18). The peak associated with bacteria ($\lambda_{\text{ex}} = 225 \text{ nm}$ and $\lambda_{\text{em}} = 350 \text{ nm}$) was not present (19). 3D-EEM maps of the retentate diluted to $<15 \text{ mg/L}$ of DOC showed an enhanced intensity of peak C while the permeate showed an enhanced intensity for peak A, compared to the bulk samples.

Discussion

The results of our study demonstrate the association of ^{239}Pu and, to a lesser extent ^{90}Sr , with the colloidal fraction of the solutions of three alpine soils. Results show reproducibility between the two sampling periods even if some parameters

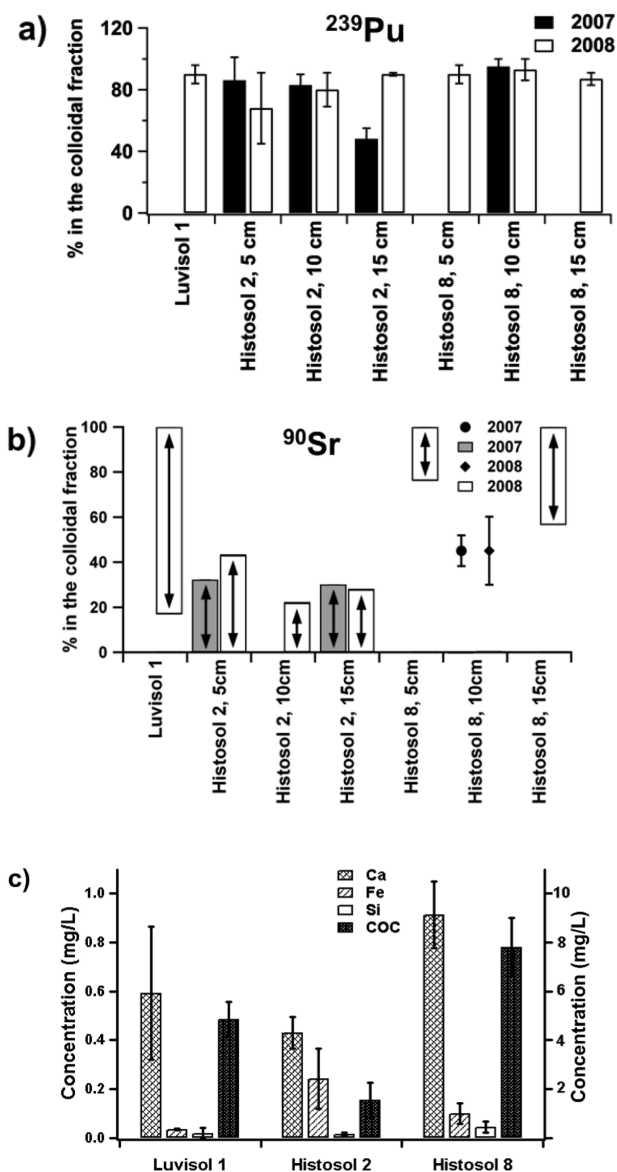


FIGURE 1. (a) Percentage of colloidal ^{239}Pu in the soil solutions. (b) Percentage of colloidal ^{90}Sr in the soil solutions. The actual value is between the two arrows. The percentages of colloidal ^{90}Sr and ^{239}Pu have been calculated as the ratio between the colloidal activity and the sum of the colloidal and truly dissolved activity. (c) Concentration of colloidal organic carbon (COC), colloidal calcium, colloidal iron, and colloidal silicon in the soil solutions over the two years of the experiment (2007–2008). Error bars for a coverage factor $k = 1$. COC is on right axis.

such as the concentration factor and ultrafiltration membrane surface were changed. The ultrafiltration process yielded almost quantitative recovery. Therefore, the methodology used in our study seems reliable for collecting the soil solution and for isolating the colloidal fraction. However, some artifact may have appeared during the ultrafiltration procedure (cf. explanation below), especially for ^{90}Sr . Potential artifacts of the ultrafiltration procedure include precipitation on the membranes and retention of free ionic species.

The fact that the loss of iron during ultrafiltration (2007 field season) had no impact on the recovery of ^{239}Pu indicates that ^{239}Pu is not significantly adsorbed with Fe-precipitates, presumably iron hydroxides; thus, iron hydroxide colloids in the soil solution seem a less likely candidate as ^{239}Pu -carriers. Iron was found in the colloidal phase, and thus the association of ^{239}Pu with iron-containing colloids cannot be ruled out.

However, the clear correlation between the colloidal ^{239}Pu activity and the COC content suggests that ^{239}Pu in the soil solutions was associated with COC. The composition of bulk DOM, as revealed through fluorescence analysis, shows a predominance of highly altered substances. It is commonly accepted that peak A and peak C are indicators for humic substances, but the attribution of one peak to humic acid and the other to fulvic acid is currently still under debate (18). For example, Mounier et al. (20) attributed the fluorescence of peak A to fulvic acid-like (FAL) fluorophores and the fluorescence of peak C to humic acid-like (HAL) fluorophores. Therefore, the enhanced fluorescence of peak C in the retentate would indicate a higher contribution of HAL substances to the colloidal fraction. The ζ -potential values suggest that the charge of the colloids was due to the presence of carboxylic groups. These groups, together with phenols, are the most common functional groups of humic substances and are responsible for their net negative charge under environmental conditions (21). In the soil environment, plutonium is generally found in the oxidation state of IV and would have a high affinity for negatively charged HS, most likely through interaction with deprotonated carboxylic functional groups (7). Moreover, Pu(V) can be reduced to Pu(IV) and then become complexed especially in the presence of humic acids (22). The association of Pu with humic substances in soils is reported by Santschi et al. (5) who demonstrated association of plutonium with organic colloids of storm runoff and in soil resuspensions in the laboratory. These authors found that the colloidal Pu amounted to 0.1 to 1% of total Pu in the Rocky Flats grassland soil, which is considerably more than the 0.003–0.02% of colloidal ^{239}Pu found in the Val Piora soils. The difference is probably explicable by the nature of the Pu contamination: local contamination with high Pu activities at Rocky Flats versus global fallout with low Pu activities in Val Piora; and by the applied methodologies: laboratory extraction with a solid to liquid ratio of 1:380 for Rocky Flats versus in situ study with solid to liquid ratio of approximately 1 for Val Piora. Our results indicate that the remobilization potential of colloid-bound Pu from global fallout in natural alpine soils is orders of magnitudes lower than what would be expected from laboratory experiments with comparably high Pu activities involved.

We found 30% or more of ^{90}Sr to be associated with the colloidal fraction in the soil solutions of Histosol 8, while it was much less in Histosol 2 (Figure 1b). The fractions of ^{90}Sr in the retentates of the ultrafiltration experiments were similar to the corresponding fractions of Ca. A part of this retention might be related to an ultrafiltration artifact. Guo et al. (23) reported retention of 14% of Ca during ultrafiltration of low salinity natural water. These authors conclude that most of the retained Ca was present in free ionic form and was retained due to repulsion by the negatively charged membrane. In contrast, Dahlqvist et al. (24) found both ionic and colloidal Ca in the retentate of ultrafiltered river Kalix water. In their samples, on average 16% of the total Ca was colloidal Ca. Since we find a high percentage of Ca and ^{90}Sr in the retentates of samples with high DOC and low percentage of Ca and ^{90}Sr in the retentates of samples with low DOC, we argue that a significant portion of Ca and ^{90}Sr in the retentates indeed represents colloidal forms. Our interpretation is in line with results of Pédrot et al. (25) who determined the majority of stable Ca and Sr in the colloidal fraction of soil solution in batch experiments (soil suspensions) at a pH near 7. These authors attribute this association to weak interactions (ion exchange) between Sr (or Ca) and humic substances. Another ultrafiltration artifact which is the precipitation of ^{90}Sr (and Ca) on a carbonate phase due to CO_2 degassing during the ultrafiltration (26) seems less likely since the soil solutions containing the higher content of Ca are those with

TABLE 2. ^{90}Sr Activities Measured in the Truly Dissolved Fraction, Bulk, and Colloidal Fraction of the Soil Solutions in 2007 and 2008

sample	^{90}Sr in 2007 (mBq/L)			^{90}Sr in 2008 (mBq/L)		
	truly dissolved fraction	bulk	colloidal fraction	truly dissolved fraction	bulk	colloidal fraction
Luvisol 1, 5 cm	n.m.	13 \pm 4	n.m.	n.m.	n.m.	n.m.
Luvisol 1, 10 cm	n.m.	<9.5	n.m.	n.m.	n.m.	n.m.
Luvisol 1, 15 cm	n.m.	<8.5	n.m.	n.m.	n.m.	n.m.
Luvisol 1 ^a	n.m.	n.m.	n.m.	<1.7	<1.6	<0.76–1.07
Histosol 2, 5 cm	2.8 \pm 0.9	4.7 \pm 0.7	<1.4	1.5 \pm 0.7	2.2 \pm 0.4	<1.1
Histosol 2, 10 cm	<2.6	7.3 \pm 0.7	<1.1	2.6 \pm 0.6	1.5 \pm 0.4	<0.7
Histosol 2, 15 cm	4.5 \pm 1.7	9.1 \pm 0.3	<1.94	2.4 \pm 0.6	<0.7	<0.9
Histosol 8, 5 cm	n.m.	15.6 \pm 1.2	n.m.	<2.7	11 \pm 1	<8.3–8.7
Histosol 8, 10 cm	8 \pm 2	11 \pm 2	75 \pm 7	4.2 \pm 1.9	12 \pm 1.5	3.4 \pm 1.5
Histosol 8, 15 cm	n.m.	16 \pm 1.5	n.m.	<4.3	7.4 \pm 0.8	<5.6–6.3

^a Mixing of the three depths of the soil solutions of Luvisol 1. n.m.= not measured. The factor 2 between the activities of the retentate measured in 2007 and in 2008 is partly due to the difference in the cf of the ultrafiltration that was set at 10 in 2007 and at 5 in 2008.

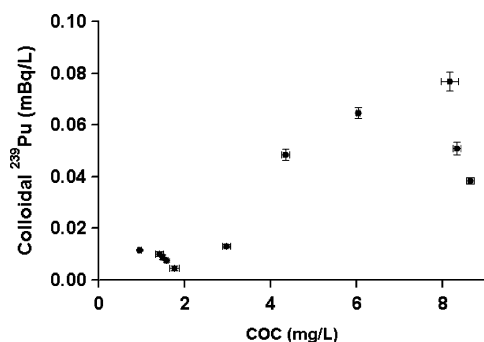


FIGURE 2. Correlation between the activity of ^{239}Pu and the concentration of organic carbon in the colloidal fraction of the soil solutions.

the lower colloidal Ca content (Histosol 2). Although the calcium and ^{90}Sr in the retentate partly may be free ions, we think, based on the above reasoning, that our results show the association of ^{90}Sr and calcium with organic colloids and that this association was stronger in Histosol 8 than in Histosol 2 (Figure 1b). We explain this difference by the approximately 5 times higher concentrations of COC in the soil solutions of Histosol 8 (Figure 1c). Furthermore, outcompeting by Ca ions may explain the lower concentration of colloidal ^{90}Sr in Histosol 2, as dissolved Ca concentrations are much higher in Histosol 2 and the ratio of colloidal Ca to COC in Histosol 2 is more than double that of Histosol 8. Associations of calcium with organic matter are reported using TEM observation (27) in peatland-derived colloids with calcium and iron coatings on organic matter, probably humic acids. Alternatively, differences in the nature of the colloids found in the peat-type Histosols 8 and the “wetland-type” Histosol 2, respectively, could be of importance.

The association of plutonium and ^{90}Sr with the colloidal fraction may lead to an enhanced migration of these radionuclides in soils, as in the case for plutonium in groundwater (2). However, in contrast to the situation in an aquifer, colloidal transport of contaminants in soils may be limited by structural properties of the soils, as colloids can get entrapped in micropores of the soils, plugging the porous media and therefore reducing the flow rate (28). The extent of the actual migration of plutonium and ^{90}Sr due to the colloidal fraction will then depend on the porosity and the connectivity of the pores in the soil.

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Supporting Information Available

Coordinates of the sampling sites. Method for the physico-chemical characterization of the soil solutions; pH, redox state, and conductivity of the soil solutions; recovery of the elements after ultrafiltration; calculation of the percentage of colloidal ^{239}Pu in the soil; concentration of DOC, Ca, Fe, and Si in all fractions of the solutions for the two years of experiment; correlation between colloidal organic matter concentration and colloidal ^{239}Pu activity; particle size distribution of the colloids; TEM images of the colloids; ζ -potential determination of the colloids; 3D EEM-map of the fluorescence of the organic matter in soil solutions. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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