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Suitability of $^{239+240}$Pu and ^{137}Cs as tracers for soil erosion assessment in mountain grasslands

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HIGHLIGHTS

- Plutonium deposition in the Swiss Alps is mainly from nuclear bomb fallout.
- The distribution of $^{239+240}$Pu in soils was more homogenous as for ^{137}Cs.
- Pu isotopes are suitable tracers for soil erosion assessment in Alpine grasslands.
- Erosive processes have a high dynamic and spatial heterogeneity.

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ABSTRACT

Anthropogenic radionuclides have been distributed globally due to nuclear weapons testing, nuclear accidents, nuclear weapons fabrication, and nuclear fuel reprocessing. While the negative consequences of this radioactive contamination are self-evident, the ubiquitous fallout radionuclides (FRNs) distribution form the basis for the use as tracers in ecological studies, namely for soil erosion assessment. Soil erosion is a major threat to mountain ecosystems worldwide. We compare the suitability of the anthropogenic FRNs, ^{137}Cs and $^{239+240}$Pu as soil erosion tracers in two alpine valleys of Switzerland (Urseren Valley, Canton Uri, Central Swiss Alps and Val Piora, Ticino, Southern Alps). We sampled reference and potentially erosive sites in transects along both valleys. ^{137}Cs measurements of soil samples were performed with a Li-drifted Germanium detector and $^{239+240}$Pu with ICP-MS. Our data indicates a heterogeneous deposition of the ^{137}Cs, since most of the fallout origins from the Chernobyl April/May 1986 accident, when large parts of the European Alps were still snow-covered. In contrast, $^{239+240}$Pu fallout originated mainly from 1950s to 1960s atmospheric nuclear weapons tests, resulting in a more homogenous distribution and thus seems to be a more suitable tracer in mountainous grasslands.

Soil erosion assessment using $^{239+240}$Pu as a tracer pointed to a huge dynamic and high heterogeneity of erosive processes (between sedimentation of 1.9 and 7 t ha^{-1} yr^{-1} and erosion of 0.2–16.4 t ha^{-1} yr^{-1} in the Urseren Valley and sedimentation of 0.4–20.3 t ha^{-1} yr^{-1} and erosion of 0.1–16.4 t ha^{-1} yr^{-1} at Val Piora). Our study represents a novel and successful application of $^{239+240}$Pu as a tracer of soil erosion in a mountain environment.

1. Introduction

To date, relatively little attention has been paid to the quantification of soil erosion affecting mountain grasslands (Felix and Johannes, 1995; Descroix and Mathys, 2003; Isselin-Nondedeu and Bedecarrats, 2007; Alewell et al., 2008, 2009). This lack of soil erosion studies in mountain environments may be partly due to the small scale diversity of process rates caused by the complex interaction of extreme climate, sensitive vegetation, steep topography and partly intensive land use (Alewell et al., 2008). As such, methods to describe and predict ecosystem stability in Alpine systems are urgently needed, which has been postulated over the last 20 years (Lange, 1994; Alewell et al., 2009). The use of classical techniques (e.g. sediment plots) to estimate soil erosion in mountainous grassland areas is limited due to landscape topographic complexity and harsh climatic conditions (especially

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snow processes), which do not allow proper monitoring during winter periods with traditional investigation tools (Alewell et al., 2009; Konz et al., 2012).

One of the most widely used and validated approaches to evaluate soil erosion rates is the analysis of the fallout radionuclide (FRN) ^{137}Cs [half-life = 30.2 years], which originated from thermonuclear weapon tests in the 1950s–1960s and from nuclear power plant accidents such as Chernobyl (see Mabit et al., 2013). Documenting the subsequent redistribution of FRN, which moves across the landscape in association with soil and sediment particles primarily through physical processes, provides an effective means of tracing rates and patterns of erosion and deposition within landscapes. However, preliminary studies of the authors using ^{137}Cs in alpine grasslands resulted in an unusually high heterogeneity of the fallout at the reference sites (Juretzko, 2011; Polek, 2011), which is most likely due to its fallout origin from the Chernobyl accident (Schaub et al., 2010).

Recently, anthropogenic radioisotopes of plutonium (Pu) have been suggested to the research community as new soil and sediment tracers to determine soil erosion rates (Schimmack et al., 2002). The two major Pu isotopes (i.e. ^{239}Pu [half-life = 24 110 - years] and ^{240}Pu [half-life = 6561 years]) are alpha-emitting actinides that originate from nuclear weapon tests, nuclear weapons manufacturing, nuclear fuel re-processing and nuclear power plant accidents (Ketterer and Szechenyi, 2008). On a global basis, above-ground nuclear weapons testing fallout is the dominant contributor, and the distribution of this 1950s–1960s fallout is very similar to that of ^{137}Cs. However, Pu, in contrast to ^{137}Cs, is contained in the non-volatile fraction of nuclear fuel debris released from reactor accidents such as the 1986 Chernobyl accident. Accordingly, the geographic distribution of Chernobyl Pu fallout is more confined regionally to specific, proximal portions of Russia, Ukraine, Belarus, Poland, the Baltic countries, and Scandinavia (Mietelski and Was, 1995). It is therefore very unlikely that Chernobyl Pu would represent a significant contributor to the total Pu activity deposited in distal locations such as the Alps. Furthermore, Pu deposited from the Chernobyl accident can be distinguished based upon its isotopic composition. The ^{240}Pu/^{239}Pu atom ratio of Northern Hemisphere mid-latitude weapons testing fallout is 0.180 ± 0.014 (Kelley et al., 1999); in contrast, several studies of Pu atom ratios of Chernobyl fallout indicate values of 0.37–0.41 (Muramatsu et al., 2000; Boulyga and Becker, 2002; Ketterer et al., 2004).

Like ^{137}Cs, Pu isotopes are strongly absorbed to fine soil particles and transported mainly by physical processes such as erosion (Everett et al., 2008; Ketterer et al., 2004, 2011). To date, only a few applied studies using Pu as a tracer for soil erosion have been performed, and mainly in the Southern Hemisphere (Australia; Everett et al., 2008; Tims et al., 2010; Hoo et al., 2011; Lal et al., 2013) with the exception of Schimmack et al. (2002) who investigated sites in Southern Germany.

If $^{239+240}$Pu is (i) mostly linked to the past nuclear bomb tests, which took place from 1954 to the mid-1960s and (ii) deposited throughout the year not connected to a few specific deposition events on snow covered ground, we can expect a more homogenous fallout distribution than ^{137}Cs. We hypothesize that (i) $^{239+240}$Pu at our sites in the Central Swiss Alps is bomb derived with no major impact from the Chernobyl nuclear accident and (ii) $^{239+240}$Pu as a tracer for soil erosion is more homogenously distributed than ^{137}Cs at references sites and is thus, better suited to assess soil erosion rates in Alpine grasslands. To test these hypotheses, we determined soil depth profiles and heterogeneity of $^{239+240}$Pu and ^{137}Cs at reference sites and sampled several potentially erosive transects in two Alpine valleys in the Swiss Central Alps.

2. Materials and methods

2.1. Sites description

The Urseren Valley (30 km^2) in Central Switzerland (Canton Uri, Fig. 1) has an elevation ranging from 1440 to 3200 m a.s.l. At the valley bottom (1442 m a.s.l.), average annual air temperature for the years 1980–2012 is around 4.1 ± 0.7 °C and the mean annual precipitation is 1457 ± 290 mm, with 30% falling as snow (MeteoSwiss, 2013). The U-formed valley is snow-covered from November to April. On the slopes, pasture is the dominant land use, whereas hayfields are prevalent near the valley bottom. The valley has already been nearly completely deforested in the 11th century by the Romans and ever since has been prone to dominant changes in land use. In the last decades anthropogenic activity has been intensified on the lower slopes and extensified or even abandoned on the higher, more remote areas (Meusburger and Alewell, 2008). The vegetation type and cover is strongly influenced by anthropogenic activities such as pasturing. Grasslands with dwarf shrubs dominate (64%), while the proportion of forests (which protect from avalanches) represents only 1% of the surface. Because of the intensive deforestation of the valley, the frequency of avalanches is relatively high (Meusburger and Alewell, 2008). The valley bottom consists of sediment deposits and is situated between the Aare-Massif in the north and the Gotthard-Massif in the south with dominating substratum of mica schists and gneiss. The predominant soils are Cambic Podzols (anthric) and Podzols (anthric) based on the IUSS Working Group (2006) classification. Most of the soils are characterized by a migration horizon (M) which has a typical thickness of 5–45 cm and the soil textures vary from sandy loam to loamy sands.

The Val Piora (22.6 km^2) is located at the southern part of the Alps (Canton Ticino, South Central Alps, Switzerland, Fig. 1) and elevation ranges from 1850 to 2773 m a.s.l. The average annual precipitation is between 1500 and 1750 mm with approximately 35% falling as snow (MeteoSwiss, 2013). The "Piora-Mulde", which became famous in the context of the Gotthard-Tunnel, constitutes the valley floor. The bedrock is dominated by mica schist and gneiss with small sediment layers and areas of granites (Gotthard-Massif in the north, Lukmanier-Massif in the south). Soils of the catchment are mainly Podzols and dystric Cambisols or cumulic Anthrosols with a soil texture of mainly sandy loam to loam. Streets and paths mostly located at the bottom of the south-exposed slopes are often prone to avalanches (Knoll-Heitz, 1991). Pasture is the dominant land use in the valley. The valley was deforested by the Romans and land use change plays a minor role in the valley since management is very constant over centuries due to guidelines established in the year 1227 regulating the alp zoning and stocking (Knoll-Heitz, 1991).

2.2. Soil sampling

Flat reference sites with a permanent vegetation cover were selected, which lacked visual disturbance, and had no connection to upslope sites with potential sediment input. We sampled 6 reference sites distributed over the length of the Urseren Valley and 7 reference sites at the Val Piora (Fig. 1). Samples of the reference sites at the Val Piora were all collected within a 2 ha area because no other suitable sites in the valley were available. Each reference sample was a composite bulk sample from 3 cores sampled within 1 m^2. All reference cores were sectioned into 3 cm increments down to a total depth of 30 cm to obtain detailed information on ^{137}Cs and $^{239+240}$Pu profile shape.

The measurement of $^{239+240}$Pu to determine soil erosion was a follow-up of a preliminary study in this area, where a high

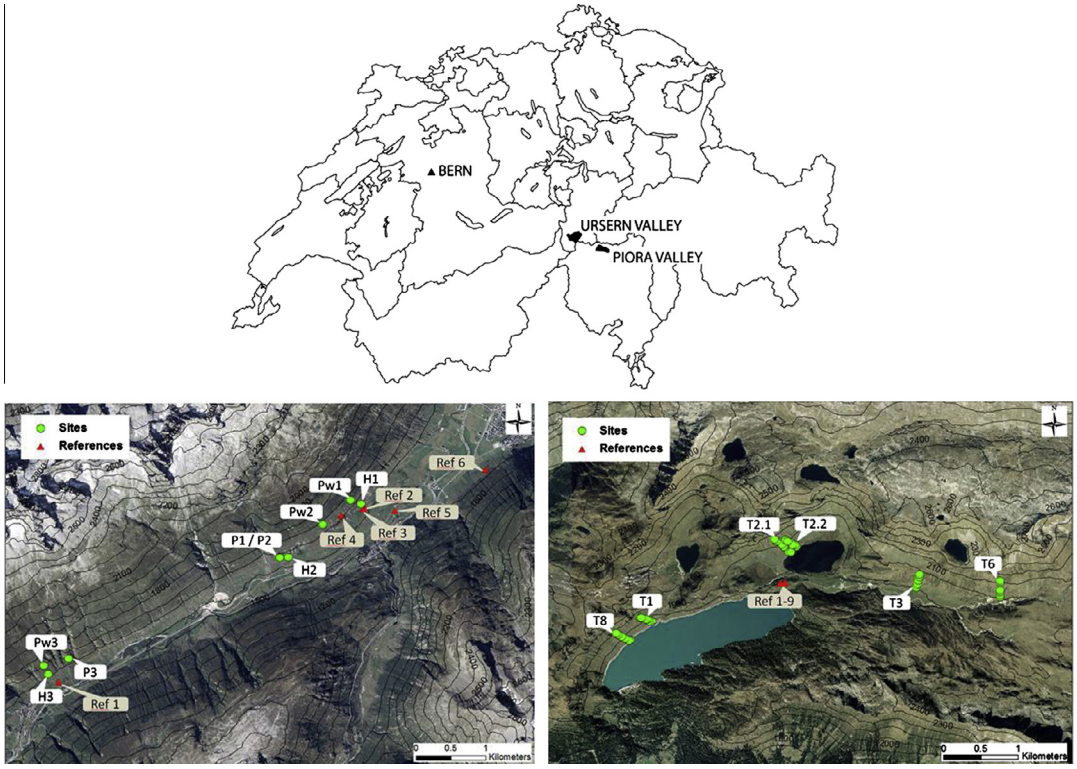

Fig. 1. Location of the investigated sites within Switzerland. Lower panels: Urseren Valley (left) and Val Piora (right). Ref = reference sites (red). P = pastures. Pw = pastures with dwarf shrubs. H = hayfields. T = sampling transects.

heterogeneity of ^{137}Cs soil contents in reference sites was noted especially at the Val Piora experimental site (Juretzko, 2011). Because we intended to compare our results of potentially erosive sites with ^{137}Cs measurements from the previous studies (see Konz et al., 2009; Schaub et al., 2010; Juretzko, 2011), the same sampling sites and strategies as performed in the previous studies were implemented. In the Urseren Valley, 5–10 bulk cores with soil material of the uppermost 10 cm were sampled on 12 sites. In the Val Piora, we sampled 36 sites and bulked 3 cores of 15 cm depth within 1 m^2 at each site (Table 1).

2.3. Analysis of ^{137}Cs and $^{239+240}$Pu soil contents and origin of $^{239+240}$Pu in the samples

The activities of ^{137}Cs in soil samples were determined by gamma spectrometry using a Li-drifted Ge detector (20% relative efficiency) at the Department for Physics and Astronomy, University of Basel. The counting time for each sample (i.e. approximately 30–40 g of dry soil) was set at 30 000 s to reach an acceptable level of detection limit and of measurement error. Calibration of equipment, analysis and quality control of the measurements were performed following IAEA standard procedure (Shakhashiro and Mabit, 2009). The resulting measurement uncertainty for ^{137}Cs was lower than 8% (error of measurement at 1-sigma).

The measurement of Plutonium isotopes ($^{239+240}$Pu) was performed using a Thermo X Series II quadrupole ICP-MS instrument located at Northern Arizona University. The ICP-MS instrument was equipped with a high-efficiency desolvating sample introduction system (APEX HF, ESI Scientific, Omaha, NE, USA). A detection limit of 0.1 Bq kg^{-1} for $^{239+240}$Pu was obtained for samples of nominal 1 g of dry-ashed material; for $^{239+240}$Pu activities > 1 Bq kg^{-1}, the measurement error was 1–3%. Prior to mass spectrometry analysis, the samples were dry-ashed and spiked with ~ 0.005 Bq of a ^{242}Pu yield tracer (obtained as a licensed solution from NIST). Pu was leached with 16 M nitric acid overnight at 80 °C, and was subsequently separated from the leach solution using a Pu-selective

Table 1
Soil sampling design, mean values (Bq m^{-2}) and heterogeneity of $^{239+240}$Pu and ^{137}Cs inventories as coefficient of variation (CV) in% at reference sites in the Urseren Valley (n = 6) and the Piora Valley (n = 7). ^{137}Cs reference data from Polek (2011) and Juretzko (2011), ^{137}Cs sampling site data from Konz et al. (2009) and Schaub et al. (2010).

		Reference sites		Sampling sites	
		Urseren	Piora	Urseren	Piora
Number of sites		6	7	9	36
Total sampling depth (cm)		30	30	10	15
Thickness of increments (cm)		3	3	10	15
Replicates within 1 m^2		3	3	3	3
^{137}Cs	Mean	6892	10 355	8148	10 190
	Stdev	2199	10 107	2805	4265
	CV (%)	32	98	34	42
^{240}Pu/^{239}P	Mean	83	77	71	90
	Stdev	11	13	25	23
	CV (%)	13	17	36	27

TEVA resin (Ketterer et al., 2011). The masses of ^{239}Pu and ^{240}Pu present in the sample, determined by isotope dilution calculations, were converted into the summed $^{239+240}$Pu activity as has long been used in alpha spectrometric determinations of Pu activity. The ^{240}Pu/^{239}Pu atom ratios were determined in the same analytical run. Data quality was evaluated through the analysis of preparation blanks (soils or rocks devoid of Pu), duplicates, and control samples having known $^{239+240}$Pu activities.

2.4. Inventory changes and conversion of $^{239+240}$Pu activities into soil redistribution rates

The mass activities of ^{137}Cs and $^{239+240}$Pu (Bq kg^{-1}) were converted into inventories (Bq m^{-2}) with measured mass depth of fine soil material (kg m^{-2} sampling depth^{-1}). Inventory change (Inv_{change}) was calculated as

$$Inv_{change} = \frac{Inv - Inv_{ref}}{Inv_{ref}} \times 100 \quad (1)$$

with Inv_{ref} = the local reference inventory as mean of all reference sites (Bq m^{-2}) and Inv = measured total inventory at the sampling point (Bq m^{-2}).

The Inventory Method (IM) published by Lal et al. (2013) was used to convert $^{239+240}$Pu inventory reductions into soil erosion rates with the assumption of the particle size factor to be equal to 1:

$$L = -\frac{1}{\alpha} \ln\left(1 - \frac{Pu_{change}}{Pu_{ref}}\right) \quad (2)$$

With L = loss of soil (cm), $Pu_{change} = Pu_{ref} - Pu$ and with Pu_{ref} = the local reference inventory as mean of all reference sites (Bq m^{-2}) and Pu = measured total inventory at the sampling point (Bq m^{-2}).

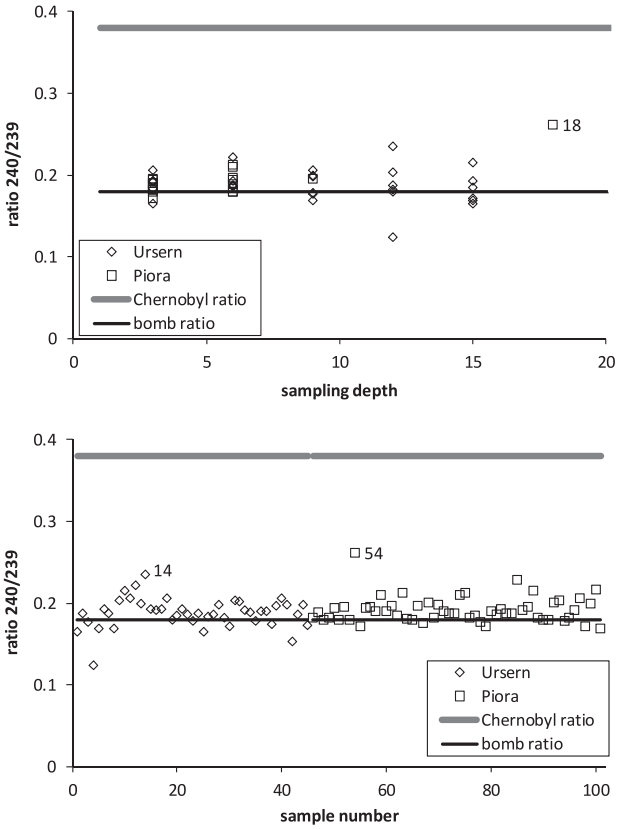

Fig. 2. Ratio of ^{240}Pu/^{239}Pu of reference samples against sampling depth (top) and of all samples in the Urseren Valley and Val Piora (bottom). Note that samples with relatively high ratios (sample 14; 18 and 54) have a high standard deviation of measurement with 0.043, 0.03 and 0.118, respectively.

The coefficient α was obtained from a least squared exponential fit of the Pu depth profile (Fig. 3).

The simple Proportional Model developed by Walling et al. (2011) for ^{137}Cs was used to convert Pu increases in inventories (positive inventory reductions) into sedimentation rates:

$$Pu_{sed} = 10\frac{B \times Pu_{change}}{100\ T} \quad (3)$$

With Pu_{sed} = $^{239+240}$Pu sedimentation rate (t ha^{-1} yr^{-1}), B = mass depth of fine soil material (kg m^{-2} sampling depth^{-1}) and T = time elapsed since the accumulation of $^{239+240}$Pu (which was set as 2012–1963). We used the proportional model even though sites were never tilled, but we assumed that constant sedimentation would have a similar effect, e.g. through mixing, than ploughing. Another option to calculate sedimentation rates is be the profile distribution model (see Walling et al., 2002). The Macro tool in this model obviously also assumes mixing. Since we could not follow the exact formula in this macro and thus did not know what exactly is calculated we compared the values to the proportional model.

3. Results and discussion

3.1. Establishment of the origin of $^{239+240}$Pu in the Alpine valleys

Soils from our Alpine valleys have ^{240}Pu/^{239}Pu ratios very close to global fallout values of 0.18, which is associated with bomb fallout (Fig. 2). Soil samples of both valleys, which were connected to relatively high ^{240}Pu/^{239}Pu ratios showed also relatively high measurement uncertainty (expressed as standard deviation of the ^{240}Pu/^{239}Pu which was calculated from three sequential measurements of the same Pu extract solution from a single preparation

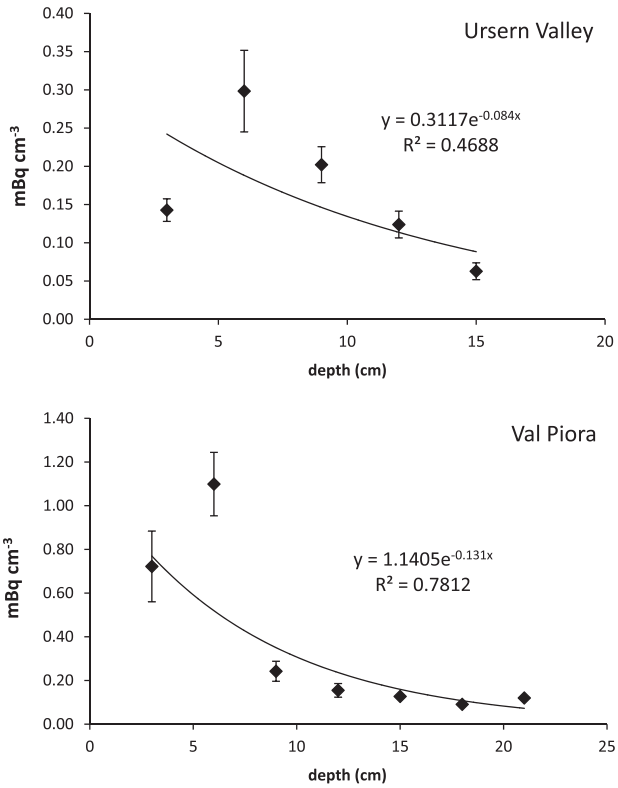

Fig. 3. Depth distribution of the $^{239+240}$Pu (measurement of bulked reference cores, error bars give standard deviation) and exponential fitting to the mean of all reference sites to derive the coefficient α (according to Lal et al., 2013).

of the sample). For example, sample 14 which is an increment from 9 to 12 cm soil depth of reference site 3 at the Urseren valley has a $^{240}Pu/^{239}Pu$ ratio of 0.23 (Fig. 2). The standard deviation connected to this ratio is 0.04, which is unusually high (average standard deviation of $^{240}Pu/^{239}Pu$ ratios for all samples from Urseren Valley is 0.018). Similarly, sample 54, the 15–18 cm depth increment from reference site 3 at Val Piora has a $^{240}Pu/^{239}Pu$ ratio of 0.26 with a standard deviation of 0.118 (average standard deviation for Val Piora samples is 0.017). Furthermore, these higher ratios have been determined for sub soils with no indication of increased ratios in the respective top soils (please note that there is no significant relationship between $^{240}Pu/^{239}Pu$ ratio and sampling depth, see Fig. 2). As such, the higher $^{240}Pu/^{239}Pu$ ratios of samples are not pointing to Chernobyl contribution but are rather analytical artefacts. Eikenberg et al. (2001) also concluded for Switzerland, that Pu fallout from Chernobyl was negligible.

In contrast, the $^{137}Cs/^{239+240}Pu$ clearly point to Chernobyl origin for the ^{137}Cs. The $^{137}Cs/^{239+240}Pu$ ratios in soils and sediments from the northern hemisphere, due to fallout from atmospheric atomic weapons testing, have generalized values of 36 ± 4 (Turner et al., 2003). The reference top soils (0–3 cm) in our Alpine valleys have average $^{137}Cs/^{239+240}Pu$ ratios of 136 (range 99–249) and 413 (range 90–898) for the Urseren and the Piora Valley, respectively.

3.2. Heterogeneity and depth distribution of $^{239+240}Pu$ and comparison to ^{137}Cs

Levels of $^{239+240}Pu$ in top soil layers at reference sites (0–3 cm) varied between 0.71 and 1.77 Bq kg^{-1} with an average of 1.14 Bq kg^{-1} at the Urseren Valley and between 2.53 and 4.69 Bq kg^{-1} with an average of 3.42 Bq kg^{-1} at Val Piora. Bulk samples of potentially erosive sites resulted in 0.46–1.27 Bq kg^{-1} (average of 0.92 Bq kg^{-1}) and 0.08–1.92 Bq kg^{-1} (average of 0.54 Bq kg^{-1}) at Urseren Valley and Val Piora, respectively (note that sampling depth was 0–10 cm for Urseren Valley and 0–15 cm for Val Piora). The latter compares well with the published range for Switzerland with 0.1–3.2 Bq kg^{-1} for top soil layers (Geering et al., 2000 quoted from Eikenberg et al., 2001). The top soil layers of Val Piora in the Ticino at the southern slopes of the Alps have clearly higher Pu concentrations than the Swiss average.

The depth distribution of $^{239+240}Pu$ at reference sites follows a polynomial function at both valleys (Fig. 3). The latter has been shown in others studies in Sweden, Poland (Matisoff et al., 2011), Australia (Lal et al., 2013) as well as in the USA (Van Pelt and Ketterer, 2013) and can be explained by the downward migration of $^{239+240}Pu$ during the last 50–60 years since the major bomb fallout events (Everett et al., 2008). As the investigation of FRN contaminated soil by the recent tragic nuclear accident of the Fukushima Daiichi Nuclear Power Plant (FDNPP) has shown, the fresh deposition of FRN into soils results in a clear exponential depth function (Kato et al., 2012).

The mean total inventory of reference sites with standard deviation at the Urseren Valley is 83 ± 11 Bq m^{-2} and 77 ± 13 Bq m^{-2} at the Val Piora (Table 1). As such, the higher Pu concentrations in the top soils at the Val Piora transfer to even slightly lower Pu inventories as in the Urseren valley, due to the very low bulk densities of the soils at Val Piora (average of all measured samples 1.3 g cm^{-3} for Urseren Valley and 0.9 g cm^{-3} for Val Piora). The inventories of ^{137}Cs are about 83 (Urseren Valley) to 135 times (Val Piora) higher than those of $^{239+240}Pu$ (Table 1). Simultaneously, the ^{137}Cs reference inventories have a higher heterogeneity than the $^{239+240}Pu$ inventories (Fig. 4, Table 1). According to Sutherland (1991) a reference site could be suitable for soil erosion assessment if the condition of a FRN coefficient of variance < 30% is met. Regarding the ^{137}Cs distribution in the Val Piora, there are 2 outlier points (references 2 and 3, Fig. 4) with very high inventories resulting in a coefficient of variation of 98%. Please note, that the seven points were sampled on a relatively small area of about 2 ha (Fig. 1). In spite of an intensive local survey, we were not able to identify other potentially suitable reference sites in the Val Piora. Thus, regarding ^{137}Cs, reference sites at the Val Piora are not suitable for soil erosion assessment (at least not according to criteria of Sutherland, 1991). The pattern for Pu is different with a much more homogenous distribution and a coefficient of variance of 10% and 18% for the Urseren and the Piora, respectively (Table 1).

The number of samples required to provide a reliable estimate of a FRN reference inventory within a specified level of confidence can be calculated using a simple statistical function as suggested by Mabit et al. (2010) and Sutherland (1991). The validity and accuracy of an initial FRN value can be verified using a control test that provides the minimum number of samples required to estimate the population mean of a FRN baseline inventory with an allowable error (AE) of 10% at 90% or 95% confidence level (see Mabit et al., 2010). Based on the 6 reference soil samples of the Urseren Valley and the 7 of the Val Piora, the $^{239+240}Pu$ baseline inventory can be estimated with an allowable error of 10% and 15%, respectively (at 95% confidence level).

Spearman rank correlations indicate no significant correlation for $^{239+240}Pu$ and ^{137}Cs inventories. Generally, a correlation of ^{137}Cs and $^{239+240}Pu$ cannot be expected at our sites, since ^{137}Cs is mostly from Chernobyl origin while $^{239+240}Pu$ represents global fallout. Schimmack et al. (2001) investigated sites in southern Bavaria and subtracted the Chernobyl ^{137}Cs fraction from the total ^{137}Cs by using the ^{134}Cs content of samples. However, the resulting global fallout ^{137}Cs fraction for their Bavarian soils where still not correlated with $^{239+240}Pu$ contents which the authors explained with the different binding behavior of the two isotopes in soils ($^{239+240}Pu$ binds relatively strong to organic material).

In general, we can state that our second hypothesis has been upheld: $^{239+240}Pu$ is more homogeneously distributed compared to ^{137}Cs. The main origin of the ^{137}Cs fallout in the Swiss alpine valleys originates from a few single rain events occurring in late April and beginning of May 1986 shortly after the Chernobyl accident. In addition to the heterogeneous distribution, which can be expected of a few single rain events, partial snow cover in the Alps at the end of April 1986 might have caused additional heterogeneity. Wherever ^{137}Cs was deposited on snow covered spots, melting and infiltration processes will have caused heterogeneous ^{137}Cs distribution during later snowmelt. In contrast, $^{239+240}Pu$ is mainly of nuclear bomb fallout origin which spanned more than a decade, and short-term rainfall heterogeneities can be assumed to cancel over this extended timeframe. Furthermore, fallout occurred during the entire year, and two thirds of the $^{239+240}Pu$ was deposited during snow free periods (note that snow contributes approximately 30–35% of the total precipitation amount in both valleys).

3.3. Inventory change of $^{239+240}Pu$ and conversion to erosion rates

A comparison of ^{137}Cs and $^{239+240}Pu$ inventory changes as a measure of erosion resulted in no correlation neither for the whole data set nor for an evaluation of the two valleys separately. The latter might be due to (i) the above discussed problems with ^{137}Cs under alpine conditions and (ii) the different time frames covered by $^{239+240}Pu$ and ^{137}Cs inventory changes (50 versus 25 years, respectively). Because of the discussed limitations and uncertainties regarding the ^{137}Cs use as a soil erosion tracer in Alpine grasslands, we did not use the ^{137}Cs data to calculate soil erosion rates.

At the Urseren Valley, $^{239+240}Pu$ inventory reduction ranged from −34% to +54% with three of the sites showing positive inventory changes pointing to sedimentation (2.7–8.3 t ha^{-1} yr^{-1} (Profile Distribution Model, Walling et al., 2002 and 1.9–7 t ha^{-1}

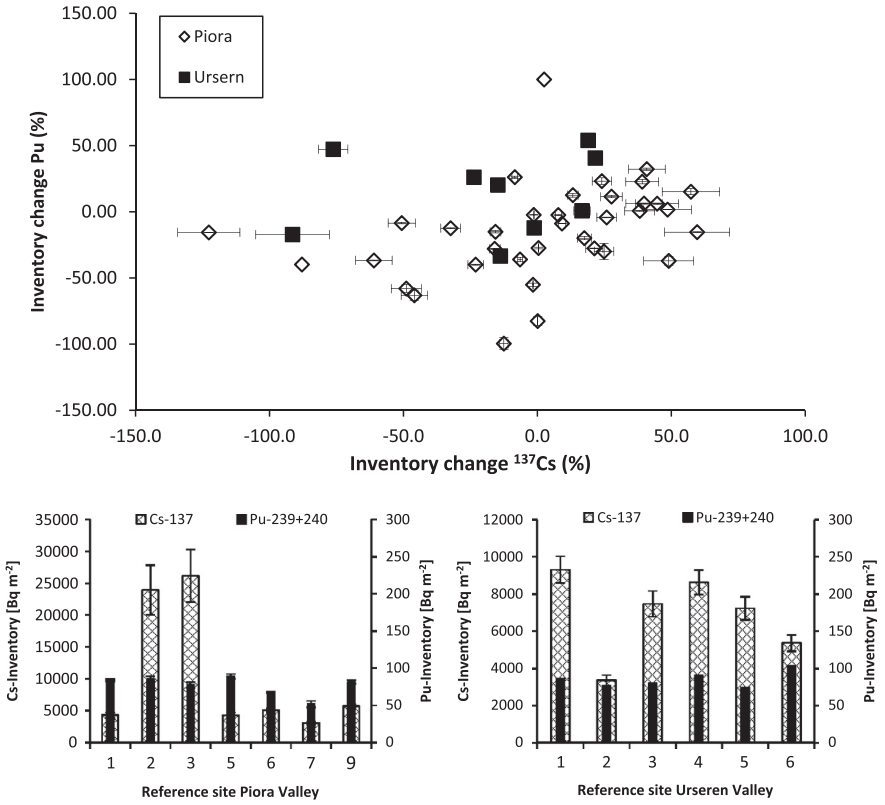

Fig. 4. Comparison of ^{137}Cs and $^{239+240}$Pu inventory change (top) and reference inventories for the Val Piora (bottom left) and Urseren Valley (bottom right).

yr^{-1} (Proportional Model, Walling et al., 2011)). The other 6 sites indicated erosion with an average inventory reduction of −32% which corresponds to an average erosion rate of 8.3 t ha^{-1} yr^{-1} (with a range of 0.2–16.4 t ha^{-1} yr^{-1}) according to the Inventory Method (Lal et al., 2013) or 5.4 t ha^{-1} yr^{-1} (range 0.2–8.9 t ha^{-1} - yr^{-1}) according to the Profile Distribution Model of Walling et al. (2002)). Konz et al. (2012) yielded erosion rates from ^{137}Cs inventories for the same sites which ranged from 7 to 30 t ha^{-1} yr^{-1} with an average of 18 t ha^{-1} yr^{-1}. In their study, all 9 sites showed a reduction in ^{137}Cs inventories indicating erosion. It is noteworthy, that $^{239+240}$Pu data indicated sedimentation for three out of the nine sites at the Urseren Valley, while ^{137}Cs data pointed to soil erosion for all nine sites. Apart from the problems connected to the Chernobyl fallout and the different time spans covered by the two FRNs (see above), Konz et al. (2012) investigated in their preliminary study only two reference sites, which might lead to a misinterpretation of resulting soil redistribution rates.

At Val Piora, 24 of the 35 sampling sites had an increase in $^{239+240}$Pu inventories compared to reference sites (negative inventory reduction), thus pointing to sedimentation rather than erosion. Increases in inventories ranged between 2.4% and 97%. The proportional model by Walling et al. (2011) indicated sedimentation rates between 0.4 and 20.3 t ha^{-1} yr^{-1}, the profile distribution model by Walling et al. (2002) resulted in 0.6–138 t ha^{-1} yr^{-1}. Thus, both models pointed to a huge dynamic and heterogeneity of erosive processes at these slopes and resulted in very similar values except for the higher range of erosion rates, where the profile distribution model delivered extremely high values. Erosive sites ranged from −0.7% to −32% in inventory reduction which corresponds to estimated erosion rates of 0.2–7 t ha^{-1} yr^{-1} using the Profile Distribution Model (Walling et al., 2002) or 0.1–4.5 t ha^{-1} yr^{-1} according to the Inventory Method (Lal et al., 2013). An evaluation of soil erosion rates calculated from ^{137}Cs inventories of the Val Piora was not carried out since no suitable reference sites for ^{137}Cs were available.

4. Conclusions

$^{239+240}$Pu contamination in our two Alpine Valleys originates mostly from nuclear bomb fallout. Thus, Plutonium is more homogeneously distributed than ^{137}Cs fallout from the Chernobyl accident. Coefficient of variance (CV) for reference sites was 32% for ^{137}Cs distribution in the Urseren Valley (n = 6) and 98% in the Val Piora (n = 7). In contrast, reference $^{239+240}$Pu values had a CV of 13 and 17% for the reference sites at Urseren Valley (n = 6) and Val Piora (n = 7), respectively. We conclude that Plutonium is a suitable tracer for soil erosion assessment in Alpine grasslands, while the use of ^{137}Cs data is connected to high uncertainties, as a CV higher than 30% is considered problematic in using FRN for soil erosion assessment. In addition, mass spectrometric measurements of $^{239+240}$Pu are advantageous with respect to sample size, analytical throughput, and the ability to distinguish different sources based upon ^{240}Pu/^{239}Pu measurements. Furthermore, the long half-life of Plutonium ensures long term environmental availability of the tracer.

Soil erosion assessment using plutonium as a tracer pointed to a huge dynamic and high heterogeneity of erosive processes. Conversion of $^{239+240}$Pu inventories into soil redistribution rates in the Urseren Valley indicated for three sites sedimentation between 1.9 and 7 t ha^{-1} yr^{-1} (Proportional Model, Walling et al., 2011) and for six sites soil erosion (between 0.2 and 16.4 t ha^{-1} yr^{-1} according to the Inventory Method (Lal et al., 2013) and between 0.2 and 8.9 t ha^{-1} yr^{-1} according to the Profile Distribution Model of Walling et al. (2002)). At Val Piora, data resulted in sedimentation for 24 sites (0.4–20.2 t ha^{-1} yr^{-1}; Proportional Model, Walling et al., 2011) and in erosion for 11 sites (between 0.1 and 4.5 t ha^{-1}

yr^{-1} according to the Inventory Method (Lal et al., 2013) and between 0.2 and 7 t ha^{-1} yr^{-1} according to the Profile Distribution Model (Walling et al., 2002)).

To date, Pu has mainly been used as a tracer for soil erosion in the southern hemisphere (i.e. Australia) with the exception of the studies performed in Southern Germany (Schimmack et al., 2001, 2002). Our approach to use $^{239+240}$Pu activities measured by quadrupole ICP-MS, has the potential to be expanded for use in many settings and laboratories. The ICP-MS technique is the one of the preferred analytical tools for routine elemental analysis at thousands of laboratories worldwide. As demonstrated herein, the same instrumental facility can be utilized for determinations of anthropogenic Pu fallout in soils. Both capital and operating costs are affordable and sample throughput can exceed 100 samples per day at a reduced cost of less than 50 € per sample.

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