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Resolving Chernobyl vs. global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry

Michael E. Ketterer [a,*], Kevin M. Hafer [a], Jerzy W. Mietelski [b]

[a] *Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698, USA*
[b] *Environmental Radioactivity Laboratory, The Henryk Niewodniczański Institute of Nuclear Physics, PL 31-324 Kraków, Radzikowskiego 152, Poland*

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Abstract

Plutonium in Polish forest soils and the Bór za Lasem peat bog is resolved between Chernobyl and global fallout contributions via inductively coupled plasma mass spectrometric measurements of $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ atom ratios in previously prepared NdF_3 α spectrometric sources. Compared to global fallout, Chernobyl Pu exhibits higher abundances of ^{240}Pu and ^{241}Pu. The ratios $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ co-vary and range from 0.186 to 0.348 and 0.0029 to 0.0412, respectively, in forest soils ($^{241}Pu/^{239}Pu = 0.2407\times[^{240}Pu/^{239}Pu] - 0.0413$; $r^2 = 0.9924$). Two-component mixing models are developed to apportion $^{239+240}Pu$ and ^{241}Pu activities; various estimates of the percentage of Chernobyl-derived $^{239+240}Pu$ activity in forest soils range from <10% to >90% for the sample set. The $^{240}Pu/^{239}Pu$–$^{241}Pu/^{239}Pu$ atom ratio mixing line extrapolates to estimate $^{241}Pu/^{239}Pu$ and the $^{241}Pu/^{239+240}Pu$ activity ratio for the Chernobyl source term (0.123 ± 0.007; 83 ± 5; 1 May 1986). Sample ^{241}Pu activities, calculated using existing alpha spectrometric $^{239+240}Pu$ activities, and the $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ atom ratios, agree relatively well with previous liquid scintillation spectrometry measurements. Chernobyl Pu is most evident in locations from northeastern Poland. The ^{241}Pu activities and/or the $^{241}Pu/^{239}Pu$ atom ratios are more sensitive than $^{240}Pu/^{239}Pu$ or $^{238}Pu/^{239+240}Pu$ activity ratios at detecting small Chernobyl $^{239+240}Pu$ inputs, found in southern Poland. The mass spectrometric data show that the

* Corresponding author. Tel.: +1-928-523-7055; fax: +1-928-523-8111.
E-mail address: michael.ketterer@nau.edu (M.E. Ketterer).

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^{241}Pu activity is 40–62% Chernobyl-derived in southern Poland, and 58–96% Chernobyl in northeastern Poland. The Bór za Lasem peat bog (49.42° N, 19.75° E), located in the Orawsko-Nowotarska valley of southern Poland, consists of global fallout Pu.

Keywords: Chernobyl; Contamination; Plutonium; Poland; Soils; Isotopic ratios; Inductively coupled plasma mass spectrometry

1. Introduction

Plutonium in the environment is almost exclusively of antropogenic origin. This element typically consists of mixtures of five isotopes: ^{238}Pu ($t_{1/2} = 87.74$ years), ^{239}Pu ($t_{1/2} = 24\,110$ years), ^{240}Pu ($t_{1/2} = 6563$ years), ^{241}Pu ($t_{1/2} = 14.4$ years), and ^{242}Pu ($t_{1/2} = 376\,000$ years). The 1986 Chernobyl accident released about 10^{14} Bq of $^{239+240}$Pu (Krüger et al., 1996). Several studies have reported the levels of Pu in the immediate vicinity of the site after the accident. Substantial evidence indicates that Chernobyl-derived Pu has been deposited regionally; examples include its identification in the Black Sea (Gulin et al., 2002), the Pripyat River (Sanada et al., 2002); Finland (Reponen et al., 1993), and in Poland (Mietelski and Was, 1995, 1997; Mietelski et al., 1999; Komosa, 1996, 1999). Pu from Chernobyl was deposited mainly in the form of large diameter aerosols (Zheltonozhsky et al., 2001).

Information on the Pu isotopic composition is useful in "fingerprinting" studies, which attempt to distinguish between Chernobyl Pu and other sources such as global fallout. Mietelski and Was (1995) used alpha spectrometric ^{238}Pu/$^{239+240}$Pu ratios to evaluate the percentage of Chernobyl-derived $^{239+240}$Pu activity (%F_{ch}). The basis of the %F_{ch} model is that the ^{238}Pu/$^{239+240}$Pu activity ratios of global fallout and Chernobyl Pu are about 0.04 and 0.55, respectively. A similar study of Pu in peats of southern and central Finland was conducted by Reponen et al. (1993). Komosa (1996, 1999) examined soils in the Lublin region of Poland and determined %F_{ch} in the same manner. Chernobyl Pu contains ^{241}Pu activities that are greatly elevated vs. global fallout (Mietelski et al., 1999). ^{241}Pu is a pure β emitter that decays to the α, γ emitter ^{241}Am ($t_{1/2} = 432$ years). The radiochemical determination of ^{241}Pu is not performed concurrently with alpha spectrometric ^{238}Pu and $^{239+240}$Pu measurements; it requires a separate analysis by either alpha measurements of ^{241}Am ingrowth, or liquid scintillation spectrometry (LSC). Enhanced levels of ^{241}Pu, ranging up to 284 ± 31 Bq kg^{-1}, were observed in northeastern Poland. The in situ decay of ^{241}Pu will result in substantial ingrowth of ^{241}Am, whose activity will peak in the mid-21st century.

There is substantial interest in tracing the deposition of Chernobyl Pu in northern and eastern Europe. In addition to resolving Chernobyl Pu from global fallout Pu by analysis of the isotopic composition, the analysis of large numbers of samples will be required to better understand the distribution and behavior of the first-release Chernobyl actinides plume in the environment. It is therefore attractive to use mass spectrometry in these studies. Pu can be determined using several forms

of mass spectrometry (thermal ionization MS, accelerator MS, resonance ionization MS, and inductively coupled plasma MS). All these techniques can determine ^{239}Pu and ^{240}Pu activities at fallout or elevated levels and can readily measure the atom ratio ^{240}Pu/^{239}Pu, which is not ordinarily possible by alpha spectrometry. Potentially, mass spectrometry can also be used to determine ^{241}Pu and ^{242}Pu if sufficient number of atoms are present. However, mass spectrometric measurements of ^{238}Pu at fallout levels are difficult due to the very small numbers of atoms. Further, it is very difficult in practice to remove U completely from the sample solution, the sample introduction system, and all reagents; hence, the isobaric $^{238}U^{+}$ interference obviates determination of ^{238}Pu in most situations. Therefore, mass spectrometric and decay-counting approaches provide complimentary information regarding Pu levels and source fingerprints. Of the MS techniques, ICPMS is arguably the best-suited for large-scale analytical applications, and there has been substantial recent interest in applications of ICMPS to monitoring Pu in the environment (e.g. Chiappini et al., 1999; Muramatsu et al., 2000, 2001; Lee et al., 2001; Ketterer et al., 2002; Kenna and Sayles, 2002; Warneke et al., 2002).

Despite the significant impact of the Chernobyl accident, the mass isotopic composition of Chernobyl Pu has been studied to a limited extent, as shown in Table 1. Muramatsu et al. (2000) measured ^{240}Pu/^{239}Pu atom ratios and $^{239+240}$Pu activities for forest soils from three sites within the 30 km exclusion zone; the ^{240}Pu/^{239}Pu for eight samples was 0.403 ± 0.003 ($n = 5$, 1σ) as an amended average which excluded the lower-activity soils from Ah and B horizons. This ^{240}Pu/^{239}Pu ratio is significantly higher than the 0.180 ± 0.014 ($n = 23$, 2σ)for ^{240}Pu/^{239}Pu in the Northern Hemisphere global fallout (Kelley et al., 1999). The enhanced production of ^{240}Pu, ^{241}Pu, and ^{242}Pu by neutron capture processes is expected in reactor fuels subjected to long irradiation times (i.e. "burn-up"). Therefore, the atoms ratios ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu should also be elevated in Chernobyl deposition vs. global fallout. However, limited MS data exist for Pu atom ratios other than ^{240}Pu/^{239}Pu in environmental samples.

In the present work, we have used high-sensitivity sector ICPMS to re-analyze previously prepared NdF_3 α spectrometric sources obtained from Polish forest soils and peat bog cores. ICPMS allows the rapid and direct determination of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu. We show that these ratios allow direct apportionment between global fallout and Chernobyl source terms. This MS-based apportionment complements previous ^{238}Pu/$^{239+240}$Pu studies.

2. Methods

2.1. Samples

Forest soils were collected in 1991 as part of earlier work (Mietelski and Was, 1995, 1997; Mietelski et al., 1999). Soils were obtained from undisturbed locations in coniferous forests, and the soil horizons were divided into A_0 and A_1 horizons.

Table 1
Published Pu atom ratios of Chernobyl vs. global fallout

Sample type	Technique	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
Reactor core[a]	Estimate	0.563	0.140	0.0429
Reactor core[b]	Estimate	0.39	0.12	0.045
Hot particle, Masany[c]	RIMS (1σ)	0.329 ± 0.032	0.067 ± 0.011[d]	0.021 ± 0.006
Soil sample, Masany[c]	RIMS	0.378	0.088[d]	0.0239
Soil sample, Shpilevskaja[e]	RIMS	0.394	0.083[d]	0.0272
Hot particle, 30 km zone[f]	RIMS	0.378 ± 0.037	NA	0.088 ± 0.009
Five soils, 30 km zone[g]	ICPMS (1σ)	0.408 ± 0.003	NA	NA
Eight soils, 30 km zone[h]	ICPMS (1σ)	0.396 ± 0.014	NA	NA
Soil, 10 km northeast[i]	TIMS	0.350	0.09	0.025
Soil, 30 km (Kryuki)[i]	TIMS	0.303	0.07	0.04
Soil, 30 km (Radin)[i]	TIMS	0.300	0.08	0.04
24 Northern hemisphere soils[j]	TIMS (2σ)	0.180 ± 0.014	0.00175 ± 0.00025[k]	0.0039 ± 0.0007

NA = not analyzed.
[a] Estimated composition of the reactor core, reference date 1 May 1986, given by Kirchner and Noack (1988).
[b] Begichev et al. (1990) estimate of reactor core, 1 May 1986.
[c] Boulyga et al. (1997).
[d] Reference date for $^{241}Pu/^{239}Pu$ not given.
[e] Nunnemann et al. (1998).
[f] Wendt et al. (1999).
[g] Muramatsu et al. (2000).
[h] Boulyga and Becker (2002).
[i] Belyaev et al. (1997); reference date 1 May 1986.
[j] Kelley et al. (1999).
[k] Corrected to 1 March 2002.

The A_0 and A_1 horizons were collected from 30×30 cm and 20×20 cm areas, respectively. The approximate locations of the samples analyzed in the present work are shown in Fig. 1. Also analyzed were two 100 cm cores (W1 and W2) obtained from the Bór za Lasem peat bog, which is situated in the Orawsko-Nowotarska Valley of southern Poland at 49.42° N, 19.75° E. The Bór za Lasem peat bog and its radionuclide characteristics have been discussed in Boroń et al. (2001).

Samples were dried at 105 °C and homogenized by grinding. 20–40 g subsamples of soil (i.e. 10–20% of the total sample mass) and 7–230 g peat were prepared for Pu determinations. Procedures for dry-ashing, decomposition, alpha spectrometry, and determination of ^{241}Pu by LSC are given elsewhere (Mietelski and Was, 1995; Mietelski et al., 1999; Boroń et al., 2001). Previously prepared NdF_3 α spectrometric sources have been re-analyzed in the present work. Since the original studies utilized ^{236}Pu ($t_{1/2} = 2.85$ years) as a yield tracer, the NdF_3 sources contain only the indigenous distribution of the heavier Pu isotopes.

2.2. Solution preparation for ICPMS analyses

The NdF_3 sources consisted of material collected on a 25 mm diameter membrane affixed to a Cu disk (Mietelski and Was, 1995). The membranes were

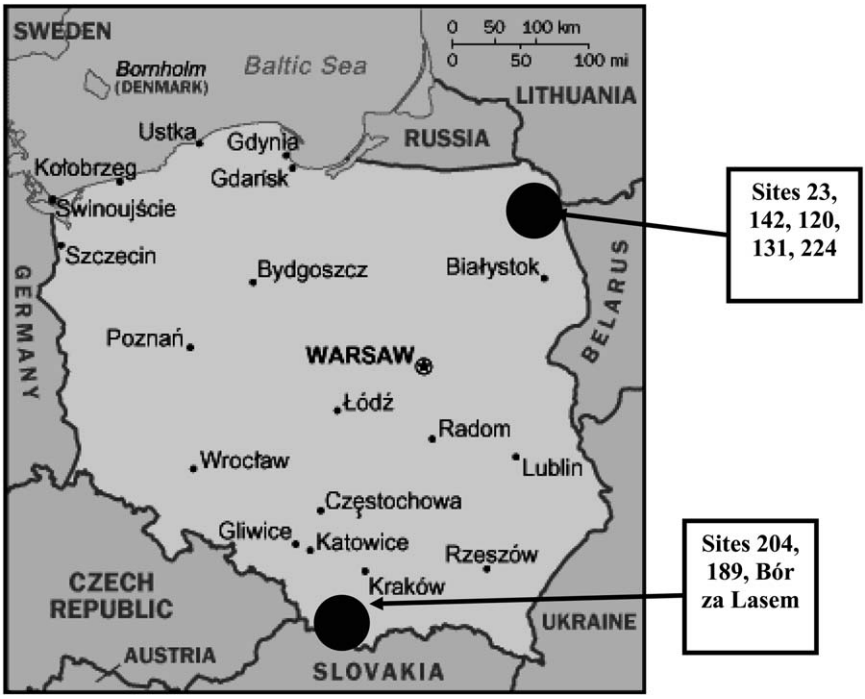

Fig. 1. Location of sampling sites. Further details are given by Mietelski and Was (1995) and Boroń et al. (2001).

removed from the Cu disk and were placed in a 50 ml polypropylene centrifuge tube along with 2 ml of 16 M HNO_3 and 0.2 ml of saturated aqueous boric acid solution. The mixtures were heated at 50 °C for 14–16 h, and then diluted to 10 ml with water. 0.2 g $NaNO_2$ was added to adjust the Pu oxidation state to Pu(IV), and 0.015 g TEVA resin (ElChrom, Darien IL, USA; TE-B25-A, 100–150 μm) was added to the solutions, which were stirred occasionally for ≥2 h. Subsequently, the resin was quantitatively collected in 1 ml pipette tips fitted with a glass wool plug. The columns were rinsed with 5–10 ml of 2 ml of 0.05 M aqueous ammonium oxalate, and the fractions were diluted to 20 ml with water prior to analysis. This batch preconcentration scheme is based upon the resin characteristics described by Horwitz et al. (1995). The Pu fractions obtained from this procedure are devoid of ^{241}Am. A ^{241}Am interference does not occur in determination of ^{241}Pu since the TEVA resin preparation scheme isolates Pu fractions devoid of Am, which is not retained from HNO_3 solutions (Horwitz et al., 1995).

2.3. Sector ICPMS measurements

A VG Axiom MC instrument, operated in the single collector (electron multiplier) mode, was used for all studies. Sample solutions were introduced at 1.0 ml/min using an ultrasonic nebulizer (CETAC Model U5000AT, Omaha, NE). Measurements were conducted in the low resolution mode ($m/\Delta m = 410$, full width at 5% maximum height). This experimental setup yields a measurement efficiency of one atom collected per approximately 2000 atoms introduced as an aqueous solution into the nebulizer. The abundance sensitivity was ~5 ppm and corrections were unnecessary. The $^{238}U^1H^+/^{238}U^+$ ratio was $\cong 3 \times 10^{-5}$, and subtractive corrections, corresponding to a maximum of about 1% of the $^{239}Pu^+$ signal, were performed. Mass discrimination was 0.7–0.8% per m/z and corrections were performed using a factor determined based upon the $^{238}U/^{235}U$ measured for a natural U solution ($^{238}U/^{235}U = 137.88$).

For isotopic measurements, signals were collected at m/z 238, 239, 240, 241, and 242 using magnetic field peak-jumping and a dwell time of 20 ms. Data were collected in three 3.3 min acquisitions for each sample solution. Mass spectra were also obtained for each solution by collecting magnet scans over the mass range 236–245. The mass spectral scans failed to detect ^{244}Pu in any of the samples. However, several of the measured $^{242}Pu/^{239}Pu$ ratios for the Polish forest soils were much higher than expected and were discordant from trends in $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ (refer to Fig. 2). While an explanation for this cannot be determined with certainty, we believe that the "extra" ^{242}Pu represents contamination in the ICPMS sample introduction system, since ^{242}Pu is routinely used at NAU as a spike in other studies. Alternatively, there may be an unknown polyatomic ion that produces an unresolved signal interfering upon ^{242}Pu. Regardless of the reason, the $^{242}Pu/^{239}Pu$ data for the forest soils are considered unreliable and hence are not tabulated herein. $^{242}Pu/^{239}Pu$ results from Bór za Lasem peat bog did not exhibit this difficulty.

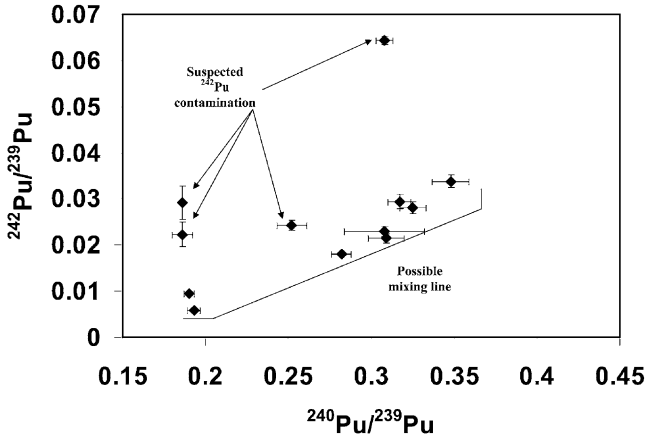

Fig. 2. Plot of $^{242}Pu/^{239}Pu$ vs. $^{240}Pu/^{239}Pu$ for Polish forest soils; points exhibiting suspected ^{242}Pu contamination (see text) as indicated. Error bars are ±1 standard deviation.

3. Results and discussion

3.1. ICP mass spectral results

Fig. 3 depicts ICP mass spectral scans for (A) Pu extracted from Plaska soil sample A1 120, and (B) "global fallout" Pu in Bór za Lasem peat sample W1 15–20 cm. Mass spectra such as more shown in Fig. 3 require <5 min of collection time, and represent a rapid and powerful means of screening samples for Pu content and/or isotopic composition.

Some of the differences in isotopic composition between "global fallout" Pu and Pu in A1 120 are apparent in Fig. 3. The logarithmic *y*-scale obscures the significant differences in $^{240}Pu/^{239}Pu$ between Bór za Lasem peat sample W1 15–20 cm (0.193 ± 0.004) and A1 120 (0.282 ± 0.006). However, the less abundant isotopes ^{241}Pu and ^{242}Pu are also detected, and substantial differences in the abundances of these minor isotopes are also evident. The peaks at m/z 238 are $^{238}U^+$, which is present at ≤ 0.05 μg l^{-1} in all solutions. Our experience with the column chemistry indicates that ^{238}U concentrations in the resulting solutions vary between ~0.001 and 0.05 μg l^{-1}, corresponding to signal levels of ~10^4 to 5×10^5 ions s^{-1}. Variations in U concentrations probably reflect differences in efficacy of the 2 M aqueous HNO_3 column wash step and/or differences in U impurities in column reagents. In no case did the levels of $^{238}U^+$ produce detrimental levels of $^{238}U^1H^+$ interference upon $^{239}Pu^+$.

^{238}Pu does not significantly contribute to signals measured at m/z 238. The small peak at m/z 237 corresponds to $^{237}Np^+$, which is present in sample solutions prepared for Pu analysis. The isotope ^{237}Np ($t_{1/2} = 2.14 \times 10^6$ years) is associated with stratospheric fallout (Kelley et al., 1999). The separation behaviors of Np and Pu are very similar (Horwitz et al., 1995); ^{237}Np is tolerable in Pu measurements by

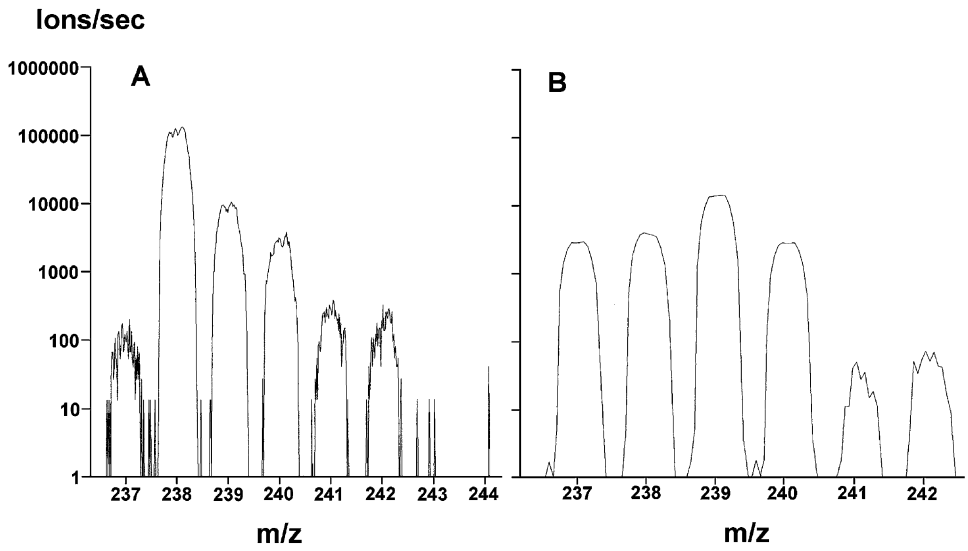

Fig. 3. ICP mass spectral scans of Pu from (A) forest soil A1 120, mixture of Chernobyl+ global fallout Pu; and (B) peat core sample W1 15–20 cm, global fallout Pu. Spectrum (A) consists of one sequential 284 s scan in the m/z range 236.0–245.0; Spectrum (B) consists of an average of 50 sequential 1.2 s sweeps of the m/z range 236.2–242.8. Apparent differences in peak shape and signal/noise result from differences in the scanning parameters and the improved S/N obtained through averaging rapid mass sweeps.

both alpha spectrometry and mass spectrometry since its α energy and nuclide mass, respectively, are well-resolved from Pu isotopes of concern.

3.2. *Pu atom ratios in forest soils*

Table 2 presents results for $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ atom ratios in Polish forest soils, along with previous radiochemical results for activities of ^{238}Pu, $^{239+240}Pu$, and ^{241}Pu. It is apparent that eight of the samples exhibit $^{240}Pu/^{239}Pu$ atom ratios which differ significantly ($p < 0.001$) from Kelley et al.'s (1999) global fallout range of 0.180 ± 0.014 (2σ). The remaining four samples (A1 189, A0 204, A1 204, and A1 224) are indistinguishable based upon $^{240}Pu/^{239}Pu$.

Although Table 2 presents data from a very limited sample set, several other important trends are evident. First, there are apparent geographic differences in the Pu atom ratios; all the elevated $^{240}Pu/^{239}Pu$ ratios are found in northeast Poland, while $^{240}Pu/^{239}Pu$ is fully consistent with global fallout Pu in samples from southern Poland. This trend resembles what was previously determined (Mietelski and Was, 1995, 1997; Mietelski et al., 1999) based upon $^{238}Pu/^{239+240}Pu$ apportionment, namely, this region demonstrated the highest contribution of Chernobyl deposition. Evidently, this deposition in northeast Poland consisted of very small hot

Table 2
Pu activities and atom ratios in Polish forest soils

Sample/location	^{238}Pu (Bq kg^{-1})[a]	$^{239+240}$Pu (Bq kg^{-1})[a]	^{241}Pu (Bq kg^{-1})[b]	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu[c]
A0 23, Szczerba (NE)	1.18 ± 0.16[d]	3.24 ± 0.27	197 ± 22	0.309 ± 0.011[e]	0.0338 ± 0.0018
A1 23, Szczerba (NE)	0.97 ± 0.16	2.70 ± 0.25	160 ± 19	0.308 ± 0.005	0.0339 ± 0.0029
A0 120, Plaska (NE)	1.83 ± 0.20	3.98 ± 0.33	256 ± 28	0.348 ± 0.011	0.0412 ± 0.0017
A1 120, Plaska (NE)	2.17 ± 0.22	6.88 ± 0.53	262 ± 26	0.282 ± 0.006	0.0266 ± 0.0008
A0 131, Lipsk (NE)	0.52 ± 0.19	1.95 ± 0.21	135 ± 16	0.325 ± 0.008	0.0379 ± 0.0015
A1 131, Lipsk (NE)	2.20 ± 0.31	5.61 ± 0.48	284 ± 31	0.317 ± 0.007	0.0323 ± 0.0018
A1 142, Gleboki Brod (NE)	0.71 ± 0.23	4.78 ± 0.41	144 ± 17	0.252 ± 0.009	0.0201 ± 0.0006
A1 189, Widly (S)	0.07 ± 0.05	1.93 ± 0.15	30 ± 5	0.190 ± 0.003	0.0029 ± 0.0002
A0 204, Wisla (S)	0.07 ± 0.03	0.73 ± 0.07	7 ± 2	0.186 ± 0.006	0.0046 ± 0.0004
A1 204, Wisla (S)	0.18 ± 0.09	1.66 ± 0.17	41 ± 7	0.186 ± 0.001	0.0038 ± 0.0004
A0 224, Trzcianka (NE)	1.74 ± 0.16	3.40 ± 0.25	228 ± 23	0.308 ± 0.024	0.0344 ± 0.0020
A1 224, Trzcianka (NE)	1.53 ± 0.27	5.27 ± 0.50	74 ± 20	0.193 ± 0.004	0.0044 ± 0.0004

NE = northeastern Poland; S = southern Poland (refer to Fig. 1).

[a] Activities of ^{238}Pu and $^{239+240}$Pu are from Mietelski and Was (1995).

[b] Activities of ^{241}Pu are from Mietelski et al. (1999); referenced to the time of the accident (1 May 1986).

[c] Reference date for ^{241}Pu/^{239}Pu atom ratios: 1 March 2002.

[d] Uncertainties for ^{238}Pu and $^{239+240}$Pu activities refer to counting statistics only (1 standard deviation); uncertainties for ^{241}Pu determined as described by Mietelski et al. (1999).

[e] Atom ratio uncertainties are ± 1 standard deviation of 3–8 measurements.

particles from the initial plume, which was transported toward Scandinavia on 26–27 April 1986.

The data of Table 2 are too limited to permit a sound comparison of the isotopic compositions in collective groups of A0 vs. A1 layers. Nevertheless, in two locations from northeast Poland (Plaska and Trzcianka), $^{240}Pu/^{239}Pu$ is significantly higher ($p < 0.01$) in the A0 horizon. This difference is consistent with the recent deposition of Chernobyl actinides in the A0 horizon, with the underlying A1 horizon containing a relatively larger proportion of global fallout Pu. On the other hand, no difference exist between the A0 and A1 horizons at Szczerba and Lipsk; at these locations, both horizons contain a similar mixture of global fallout and Chernobyl Pu. Vertical trends in Pu activities and isotopic compositions are most likely sensitive to soil characteristics as well as potential disturbances by humans and/or biota. At the one location from southern Poland (Wisla) where both the A0 and A1 horizons were analyzed, both horizons exhibit $^{240}Pu/^{239}Pu$ ratios that are indistinguishable from global fallout.

An examination of the $^{241}Pu/^{239}Pu$ ratios reinforces the non-global fallout character of Pu in northeast Poland as determined by $^{240}Pu/^{239}Pu$. However, the $^{241}Pu/^{239}Pu$ ratios *for all 12 samples* differ significantly ($p < 0.01$) from the global fallout ratio range of 0.00175 ± 0.00025 (2σ). These findings are not at all disparate; they point to $^{241}Pu/^{239}Pu$ ratios as being a more sensitive indicator of small Chernobyl contributions in samples such as A1 189, A0 204, A1 204, and A1 224 (vide infra). The precision is ~10% (1σ) for samples having $^{241}Pu/^{239}Pu$ ratios less than 0.01; the precision of this measurement would ultimately limit the detection of very small elevations in $^{241}Pu/^{239}Pu$ ratio vs. the global fallout range. The finding of "excess ^{241}Pu" based upon mass spectrometric determination of $^{241}Pu/^{239}Pu$ is supported by the independent measurements of ^{241}Pu activity. Kelley et al.'s (1999) survey of global fallout $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios corresponds to a $^{241}Pu/^{239+240}Pu$ activity ratio of 1.78 ± 0.25 (1 March 2002) or 3.8 ± 0.5 at the time of the disaster (1 May 1986). The ^{241}Pu and $^{239+240}Pu$ activity data of Table 2 all produce $^{241}Pu/^{239+240}Pu$ activity ratios significantly larger than 3.8 ± 0.5. Thus, the "excess ^{241}Pu" found in Polish samples for which $^{240}Pu/^{239}Pu$ is within fallout range is a real effect that is supported by two independent types of analytical testing.

3.3. Pu atom ratios in the Bór za Lasem peat bog

In Table 3, the results are presented for $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$ atom ratios in cores W1 and W2 from the Bór za Lasem peat bog. Also given in Table 2 are previously determined activities of ^{238}Pu and $^{239+240}Pu$. With the exception of sample W1 0–5 cm, all $^{240}Pu/^{239}Pu$ ratios are indistinguishable from the global fallout range. The $^{240}Pu/^{239}Pu$ ratio of sample W1 0–5 cm is obviously quite anomalous, and would apparently indicate mixing between global fallout and weapons-grade Pu (as would the $^{241}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$ ratios). Although a re-analysis of the remaining solution prepared from the dissolved

Table 3
Pu activities and atom ratios in the Bór za Lasem peat bog

Sample	^{238}Pu (Bq kg^{-1})[a]	$^{238+240}$Pu (Bq kg^{-1})[a]	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu[b]	^{242}Pu/^{239}Pu
W1 0–5 cm	0.112 ± 0.025[c]	1.72 ± 0.14	0.081 ± 0.004[d]	0.0012 ± 0.0004	0.0014 ± 0.0010
W1 5–10 cm	0.025 ± 0.011	0.81 ± 0.07	0.179 ± 0.005	0.0024 ± 0.0003	0.0061 ± 0.0004
W1 10–15 cm	0.080 ± 0.009	2.75 ± 0.17	0.194 ± 0.008	0.0022 ± 0.0004	0.0043 ± 0.0004
W1 15–20 cm	0.159 ± 0.012	5.07 ± 0.32	0.193 ± 0.004	0.0022 ± 0.0001	0.0042 ± 0.0002
W1 20–50 cm	0.024 ± 0.007	0.75 ± 0.04	0.176 ± 0.008	0.0017 ± 0.0005	0.0041 ± 0.0003
W1 50–75 cm	0.017 ± 0.013	0.17 ± 0.01	0.179 ± 0.008	Not determined[e]	Not determined
W1 75–100 cm	0.008 ± 0.006	0.17 ± 0.01	0.181 ± 0.009	Not determined	Not determined
W2 0–5 cm	0.038 ± 0.003	1.34 ± 0.08	0.189 ± 0.004	0.0021 ± 0.0002	0.0039 ± 0.0003
W2 5–10 cm	0.03 ± 0.02	0.87 ± 0.06	0.168 ± 0.003	0.0018 ± 0.0002	0.0034 ± 0.0003
W2 10–15 cm	0.017 ± 0.002	0.53 ± 0.03	0.190 ± 0.002	0.0021 ± 0.0006	0.0042 ± 0.0006
W2 15–20 cm	0.018 ± 0.003	0.47 ± 0.03	0.189 ± 0.009	0.0024 ± 0.0005	0.0046 ± 0.0004
W2 20–50 cm	<0.032	0.038 ± 0.004	0.196 ± 0.020	Not determined	Not determined
W2 50–75 cm	<0.003	0.04 ± 0.01	0.186 ± 0.012	Not determined	Not determined
W2 75–100 cm	<0.002	0.05 ± 0.01	0.164 ± 0.015	Not determined	Not determined

[a] ^{238}Pu and $^{239+240}$Pu activities are from Boroń et al. (2001).

[b] Reference date for ^{241}Pu/^{239}Pu atom ratios: 1 March 2002.

[c] Uncertainties for ^{238}Pu and $^{239+240}$Pu activities refer to counting statistics only (1 standard deviation).

[d] Atom ratio uncertainties are ±1 standard deviation of 3–8 measurements.

[e] The ratios ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu were not determined in these low-activity samples due to insufficient signal levels.

NdF_3 source confirmed these anomalous values, we cannot ascertain whether this is a real result or reflects some type of an analytical artifact (contamination, etc.).

The $^{241}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$ atom ratios of the Bór za Lasem peat samples (other than W1 0–5 cm and in the case of $^{242}Pu/^{239}Pu$, W1 5–10 cm) all indicate that the Pu is consistent with global fallout origin. If any, the Chernobyl contribution to the total Pu activity is minimal, e.g. the $^{241}Pu/^{239}Pu$ for W1 5–10 cm and W1 15–20 cm may be slightly elevated vs. the global fallout range of 0.00175 ± 0.00025 (2σ). Evidently, Chernobyl deposition of non-volatile particulates at the Bór za Lasem was minimal; this same conclusion was reached by Boroń et al. (2001) using $^{238}Pu/^{239+240}Pu$ apportionment. Boroń et al. (2001) estimated the global fallout and Chernobyl $^{239+240}Pu$ inventories at 114 and 0.5 Bq m^{-2}, although a substantial Chernobyl ^{137}Cs inventory was present. The Pu atom ratio results independently support the estimate of Boroń et al. (2001) that less than ~5% of the $^{239+240}Pu$ inventory in W1 and W2 is of Chernobyl origin.

3.4. $^{241}Pu/^{239}Pu$–$^{240}Pu/^{239}Pu$ mixing plot and estimation of $^{241}Pu/^{239}Pu$ in Chernobyl releases

In Fig. 4, a plot of $^{241}Pu/^{239}Pu$ vs. $^{240}Pu/^{239}Pu$ is given for the data of Table 2. This plot is described by linear function ($r^2 = 0.9924$): $^{241}Pu/^{239}Pu = 0.2407 \times (^{240}Pu/^{239}Pu) - 0.0413$. Since the plot is linear, it supports the analytical self-consistency of the data; no problems with measurements of $^{241}Pu/^{239}Pu$ or $^{240}Pu/^{239}Pu$ are apparent (as discussed previously for $^{242}Pu/^{239}Pu$ in the forest soils). Presuming analytical self-consistency, a linear common-denominator isotope ratio scatter plot gives a strong indication of a two-component mixing process; of course, these plots cannot rule out the presence of contributions from a third

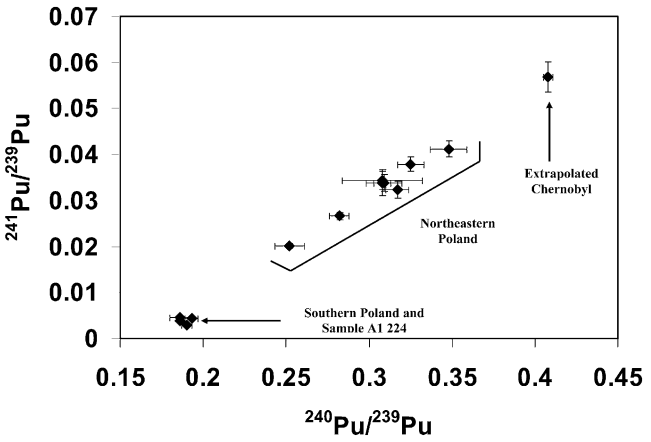

Fig. 4. Mixing plot of $^{241}Pu/^{239}Pu$ vs. $^{240}Pu/^{239}Pu$ for Polish forest soils; extrapolated composition of the Chernobyl source term as shown (refer to Section 3.4). Error bars are ±1 standard deviation.

collinear component. We interpret Fig. 4 as demonstrating mixing between the global fallout and Chernobyl Pu source terms.

It is possible to utilize the Fig. 4 trendline in the estimation of $^{241}Pu/^{239}Pu$ in Chernobyl releases. The $^{241}Pu/^{239}Pu$ source term has not been well-characterized by previous mass spectrometric studies; however, the works of Muramatsu et al. (2000) and Boulyga and Becker (2002) represent the best estimates of the Chernobyl $^{240}Pu/^{239}Pu$ source term. Using Muramatsu et al.'s $^{240}Pu/^{239}Pu$ (0.408 ± 0.003), the mixing line yields a Chernobyl $^{241}Pu/^{239}Pu$ value of 0.0569 ± 0.0033 (1 March 2002). Back-correcting this result to the date of the Chernobyl disaster (1 May 1986) produces $^{241}Pu/^{239}Pu = 0.123 \pm 0.007$. By combining $^{241}Pu/^{239}Pu = 0.123 \pm 0.007$ and $^{240}Pu/^{239}Pu$ (0.408 ± 0.003), one obtains a Chernobyl plume $^{241}Pu/^{239+240}Pu$ activity ratio of 83 ± 5. This estimate of the 1 May 1986 $^{241}Pu/^{239+240}Pu$ activity ratio agrees very well with independent estimates of the Chernobyl $^{241}Pu/^{239+240}Pu$; Mietelski et al. (1999) calculated values of (86 ± 47) and (87 ± 31) using a model given in their paper. Similarly, Paatero et al. (1994) found a Chernobyl $^{241}Pu/^{239+240}Pu$ of 94.8 in Finland, and an estimate of the Chernobyl core inventory yields $^{241}Pu/^{239+240}Pu = 83$ (IAEA, 1986).

3.5. Apportionment of % Chernobyl $^{239+240}Pu$ and ^{241}Pu in Polish soils

Several approaches exist for determining the percentage of Chernobyl-derived $^{239+240}Pu$ activity ($\%F_{239+240,ch}$) in the samples of Table 2. Mietelski and Was (1995) used a linear interpolation of the $^{238}Pu/^{239+240}Pu$ activity ratios:

$$\%F_{239+240,ch} = 100\frac{\left[\left(^{238}Pu/^{239+240}Pu\right)_{sample} - 0.04\right]}{[0.55 - 0.04]} \tag{1}$$

where 0.04 and 0.55 are the $^{238}Pu/^{239+240}Pu$ activity ratios of global fallout and Chernobyl Pu, respectively. An apportionment is also possible based upon the $^{240}Pu/^{239}Pu$ atom ratio:

$$^{239+240}Pu_{ch}/^{239+240}Pu_{gf} = \frac{\left[(R_{gf} - R_{samp})/(R_{samp} - R_{ch})\right]}{\left[(1 + 3.674R_{ch})/(1 + 3.674R_{gf})\right]} \tag{2}$$

$$\%F_{239+240,ch} = \frac{\left[^{239+240}Pu_{ch}/^{239+240}Pu_{gf}\right]}{\left[1 + \left(^{239+240}Pu_{ch}/^{239+240}Pu_{gf}\right)\right]} \tag{3}$$

The formulation of Eq. (2) is based upon the work of Krey (1976). The term $^{239+240}Pu_{ch}/^{239+240}Pu_{gf}$ is the ratio of $^{239+240}Pu$ activities associated with Chernobyl and global fallout, respectively; R_{gr}, R_{samp}, and R_{ch} are the $^{240}Pu/^{239}Pu$ atom ratios from global fallout, the unknown sample, and Chernobyl, respectively. The constant 3.674 is the $^{240}Pu/^{239}Pu$ specific activity ratio obtained from IAEA-recom-

mended half-lives of $24\,110 \pm 30$ and 6563 ± 7 years for ^{239}Pu and ^{240}Pu, respectively. A calculation of the same type as shown in Eqs. (2) and (3) can also be performed using $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratios, with $R_{gf} = 0.00175 \pm 0.00013$ (1σ) and $R_{ch} = 0.0569 \pm 0.0033$ (1σ).

It is also possible to determine $\%F_{241,ch}$ for a sample's ^{241}Pu activity, using a common reference date. This can be done using the $^{239+240}$Pu and ^{241}Pu activity results from Table 2, and the $\%F_{239+240,ch}$ reported previously (Mietelski and Was, 1995):

$$\%F_{241,ch} = A_{241,ch}/A_{241,total} \tag{4}$$

$$A_{241,ch} = A_{241,total} - \left[4.2\left(A_{239+240,total}\right)\left(1 - \left[\frac{\%F_{239+240,ch}}{100}\right]\right)\right] \tag{5}$$

Eqs. (4) and (5) use the total $^{239+240}$Pu activity and the $\%F_{239+240,ch}$ to calculate and subtract the fallout-derived contribution to $A_{241,total}$; the balance of $A_{241,total}$ is assumed to originate from Chernobyl. The value of 4.2 is the global fallout $^{241}\mathrm{Pu}/^{239+240}\mathrm{Pu}$ activity ratio, decay corrected to 1 May 1986, based upon the 40°–50° N latitude belt fallout characteristics reported by UNSCEAR (1982). This global fallout $^{241}\mathrm{Pu}/^{239+240}\mathrm{Pu}$ activity ratio from UNSCEAR (1982) is similar to a ratio of 3.8 ± 0.5 (2σ, 1 May 1986) calculated from the data of Kelley et al. (1999).

The $\%F_{241,ch}$ can also be determined using the mass spectrometric $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratios. This method assumes that any "excess ^{241}Pu" from Chernobyl produces an elevation in $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratios above $R_{gf} = 0.00175 \pm 0.00013$:

$$A_{241,ch}/A_{241,gf} = \frac{\left[R_{sample} - R_{gf}\right]}{R_{gf}} \tag{6}$$

$$\%F_{241,ch} = \frac{\left[A_{241,ch}/A_{241,gf}\right]}{\left[1 + \left(A_{241,ch}/A_{241,gf}\right)\right]} \tag{7}$$

In Eq. (6), we use a reference date of 1 March 2002, $R_{gf} = 0.00175 \pm 0.00013$ (1σ); R_{sample} is the sample's $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratio.

Table 4 presents results for various determinations of $\%F_{239+240,ch}$ and $\%F_{241,ch}$. There is agreement between $\%F_{239+240,ch}$ estimates based upon $^{238}\mathrm{Pu}/^{239+240}\mathrm{Pu}$ activity ratios and $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratios for eight of the 12 samples. For the other four points (A0 131, A1 142, A0 224, and A1 224), one of the two methods determines a higher $\%F_{239+240,ch}$. No explanation is apparent for the $\%F_{239+240,ch}$ differences observed for A0 131, A1 142, A0 224, and A1 224, although both methods detect a significant, non-zero Chernobyl component. The $^{238}\mathrm{Pu}/^{239+240}\mathrm{Pu}$ method determines a range of $\%F_{239+240,ch}$ ranges from 0 to $(93 \pm 10)\%$, and the $\%F_{239+240,ch}$ ranges from $(4 \pm 6)\%$ to $(81 \pm 12)\%$ using $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$. The $\%F_{239+240,ch}$ values determined using $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ are indistinguishable from the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ estimates, which is not unexpected since a strong correlation exists between $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ ($r^2 = 0.9924$). Values of $\%F_{239+240,ch}$ determined using

Table 4
Apportionment of $^{239+240}$Pu and ^{241}Pu activity between global fallout and Chernobyl contributions

Sample/location	$\%F_{239+240}$ (α)[a]	$\%F_{239+240}$ (MS 1)[b]	$\%F_{239+240}$ (MS 2)[c]	$\%F_{241}$ (α + β)[d]	$\%F_{241}$ (MS)[e]
A0 23, Szczerba (NE)	64 ± 10	66 ± 10	63 ± 11	97 ± 16	95 ± 12
A1 23, Szczerba (NE)	63 ± 12	66 ± 6	63 ± 13	98 ± 17	95 ± 15
A0 120, Plaska (NE)	82 ± 10	81 ± 12	75 ± 18	99 ± 15	96 ± 11
A1 120, Plaska (NE)	54 ± 6	55 ± 6	50 ± 6	95 ± 14	93 ± 10
A0 131, Lipsk (NE)	44 ± 17	72 ± 9	70 ± 14	97 ± 17	95 ± 11
A1 131, Lipsk (NE)	69 ± 10	69 ± 8	60 ± 10	97 ± 15	95 ± 12
A1 142, Gleboki Brod (NE)	21 ± 7	41 ± 7	37 ± 4	89 ± 16	91 ± 10
A1 189, Widly (S)	0	7 ± 5	3.2 ± 0.5	73 ± 21	40 ± 10
A0 204, Wisla (S)	12 ± 5	4 ± 6	6 ± 1	61 ± 34	62 ± 12
A1 204, Wisla (S)	14 ± 7	4 ± 5	4.4 ± 0.9	85 ± 22	54 ± 13
A0 224, Trzcianka (NE)	93 ± 10	66 ± 20	64 ± 12	100 ± 14	95 ± 9
A1 224, Trzcianka (NE)	49 ± 9	9 ± 6	6 ± 1	85 ± 36	58 ± 12

NE = northeastern Poland; S = southern Poland (refer to Fig. 1).

[a] Apportionment based upon Eq. (1); $(^{238}\mathrm{Pu}/^{239+240}\mathrm{Pu})_{gf} = 0.04$ and $(^{238}\mathrm{Pu}/^{239+240}\mathrm{Pu})_{ch} = 0.55$; results discussed in Mietelski and Was (1995).

[b] Apportionment using $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ based upon Eqs. (2) and (3); $R_{gf} = 0.180 \pm 0.007$ and $R_{ch} = 0.408 \pm 0.003$.

[c] Apportionment using $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ based upon Eqs. (2) and (3); $R_{gf} = 0.00175 \pm 0.00013$ and $R_{ch} = 0.0569 \pm 0.0033$.

[d] Apportionment based upon Eqs. (4) and (5); $AR_{gf} = 4.2$ and $AR_{ch} = 83$ (refer to Section 3.5).

[e] Apportionment based upon Eqs. (6) and (7); $R_{gf} = 0.00175 \pm 0.00013$ and $R_{ch} = 0.0569 \pm 0.0033$.

$^{241}Pu/^{239}Pu$ ratios appear to be more reliable when $\%F_{239+240,ch} < 10\%$; this is a consequence of the ~33-fold variance in $^{241}Pu/^{239}Pu$ compared to a ~2.3-fold variance in $^{240}Pu/^{239}Pu$ arising from Chernobyl–global fallout mixing. Therefore, large relative increases in $^{241}Pu/^{239}Pu$ are more useful in detecting small inputs of Chernobyl Pu in the environment than are relatively small increases in $^{240}Pu/^{239}Pu$. Naturally, the usefulness of the $^{241}Pu/^{239}Pu$ signature will diminish in the next several decades, as decay of ^{241}Pu generates ^{241}Am; however, a similar analysis is possible based upon $^{241}Am/^{239+240}Pu$ activity ratios. The activity ratio $^{241}Am/^{239+240}Pu$ already exceeds global fallout values in soils containing Chernobyl-derived actinides (Mietelski and Was, 1997); $^{241}Am/^{239+240}Pu$ will continue to increase in the future.

In the broadest sense, the collective set of $\%F_{239+240,ch}$ results imply that various mixtures of global fallout and Chernobyl Pu account for the activity of $^{239+240}Pu$ in Polish soils. The $\%F_{241,ch}$ picture, however, indicates that Chernobyl is the overwhelming source of ^{241}Pu, especially in northeast Poland, where all samples except A1 224 exhibit >90% Chernobyl-derived ^{241}Pu. Significant $\%F_{241,ch}$ are also found for soils from southern Poland that have minimal Chernobyl contributions to the $^{239+240}Pu$ activity.

3.6. *^{241}Pu activity determinations using mass spectrometric and alpha spectrometric data*

Our results have shown that Chernobyl-associated ^{241}Pu is readily detected by this ICPMS approach. Ideally, ^{241}Pu activities would be measured directly with inclusion of a ^{242}Pu or ^{244}Pu spike at the oneset of the sample preparation, and we expect to use this approach in future studies. Nevertheless, it is also possible to calculate ^{241}Pu activities ex post facto by combining the $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and alpha spectrometric $^{239+240}Pu$ activities of Table 2:

$$A_{241} = A_{239}\left(^{241}Pu/^{239}Pu\right)(24\,110/14.4)(2.15) \tag{8}$$

$$AR_{240\,239} = \left(^{240}Pu/^{239}Pu\right)(24\,110/6563) \tag{9}$$

$$A_{239} = A_{239+240}\left[\frac{1}{(1 + AR_{240\,239})}\right] \tag{10}$$

In Eqs. (8)–(10), A_{239}, $A_{239+240}$, and A_{241} are the activities of ^{239}Pu, $^{239+240}Pu$, and ^{241}Pu, respectively; $AR_{240\,239}$ is the *activity ratio* of $^{240}Pu/^{239}Pu$; ($^{240}Pu/^{239}Pu$) and ($^{241}Pu/^{239}Pu$) are the atom ratios. The constants 24 110, 6563, and 14.4 are half-lives (years) of ^{239}Pu, ^{240}Pu, and ^{241}Pu, respectively; the constant 2.15 back-corrects A_{241} from 1 March 2002 to 1 May 1986.

The comparison, depicted in Fig. 5, shows that A_{241} calculated from Eqs. (8)–(10) agrees relatively well with the original liquid scintillation measurements from Table 2. The data are described by a line ($r^2 = 0.9532$): $A_{241,ICMPS+\alpha} = 1.129[A_{241,}$ LSC] − 21.167. The negative intercept arises from poorer agreement between

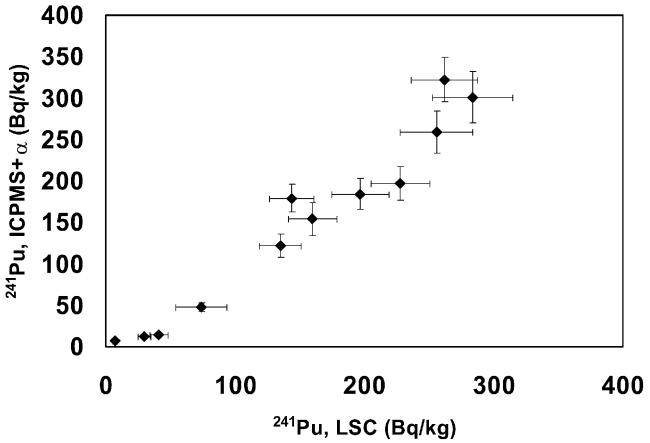

Fig. 5. Comparison between ^{241}Pu activities measured by liquid scintillation spectrometry and the procedure described in Section 3.6.

$A_{241,\mathrm{ICMPS}+\alpha}$ and $A_{241,\mathrm{LSC}}$ for low-activity samples, with the latter being significantly higher. Regardless, our ^{241}Pu method of Eqs. (8)–(10) independently confirms the trends observed in A_{241} by Mietelski et al. (1999), who used both LSC and ^{241}Am ingrowth procedures.

4. Conclusions

^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios in Polish forest soils show clear evidence of non-global fallout $^{239+240}$Pu originating from the 1986 Chernobyl disaster. The isotopic composition of Pu in Polish soils is described by two-component mixing between global fallout and Chernobyl emissions. The ''Chernobyl effect'' is most pronounced in soils from northeastern Poland, an area that evidently received significant non-volatile fallout from the Chernobyl plume. Different methods of apportioning $^{239+240}$Pu activity indicate >50% Chernobyl contributions in several samples from northeastern Poland. Although the maximum $^{239+240}$Pu activities in Polish soils are not unusual compared to worldwide activities of global fallout $^{239+240}$Pu, the addition of Chernobyl fallout has measurably added $^{239+240}$Pu to soils in Poland. The 1986 Chernobyl accident is the overwhelming source of ^{241}Pu in northeastern Poland. Chernobyl ^{241}Pu is also detectable in southern Poland, in areas that do not exhibit unusual ^{238}Pu/$^{239+240}$Pu activity ratio or ^{240}Pu/^{239}Pu atom ratio signatures. The environmental distribution of Chernobyl-derived ^{241}Pu warrants future attention, since the addition of ^{241}Pu from Chernobyl is very significant in comparison to previously present global fallout ^{241}Pu. The addition of small amounts of Chernobyl Pu is detectable by relatively large increases in ^{241}Pu/^{239}Pu atom ratios and ^{241}Pu activity. Mass spectrometric methods (e.g. RIMS,

TIMS, AMS, and ICPMS) are expected to play an increasingly important role in future studies of Pu in northern and eastern Europe.

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