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Isotopic Pu, U, and Np Signatures in Soils from Semipalatinsk-21, Kazakh Republic and the Southern Urals, Russia

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ABSTRACT

Mass spectrometry measurements of Pu, U and Np isolated from soils contaminated by the 1957 accident at the Mayak nuclear complex in the Southern Ural mountains ('Kyshtym accident') and from soils collected at and near the Former Soviet Union (FSU) test site at Semipalatinsk-21 are reported. The results provide a coherent isotopic data set suggesting (1) that Pu recovered from irradiated uranium fuels processed at Mayak formed the source material for Pu devices tested at Semipalatinsk-21; (2) that ^{237}Np in the breached Mayak storage tank resulted, principally, from enrichment of this radionuclide in waste streams during the processing of low burn-up uranium fuels to recover both Pu and U and (3) the presence of ^{236}U at both sites may be useful in tracing inputs of this, and other transuranic radionuclides, to nearby river systems that flow to the Arctic Ocean. Published by Elsevier Science Ltd.

INTRODUCTION

Recently, Yamamoto *et al.* (1996*a*, *b*) presented data on residual radioactivity in soils from the Former Soviet Union's (FSU) nuclear test site at Semipalatinsk-21 and environs (now in the Kazakh Republic) including the isotopic composition of Pu found there. Concurrently, we had measured

the isotopic composition of transuranic radionuclides in soils from and near Semipalatinsk-21 as well as in soils collected from the vicinity of Kyshtym in the Ural mountains. This latter site was heavily contaminated by (1) an accident at the Mayak fuel reprocessing complex, Chelyabinsk Province, in late 1957 (Trabalka *et al.*,1980*a*, *b*; Aarkrog *et al.*,1992); and, (2) wind-blown contamination from Lake Karachay, a high-level waste disposal site at Mayak, in 1967 (Aarkrog *et al.*, 1992). Our interest in making these measurements was to obtain baseline information on the isotopic signatures of the transuranic radionuclides at these locations to better interpret similar isotopic measurements being made in the Arctic Ocean Basin. Because Semipalatinsk-21 borders the Irtysh River (Fig. 1) which is a tributary of the Ob River, runoff from the landscape to the Irtysh (over decadal times scales) could supply long-lived radionuclides to the Arctic Ocean via the Ob. In addition, discharges of radioactive waste from Mayak directly to the Techa River (Fig. 1) is known to have occurred during the early

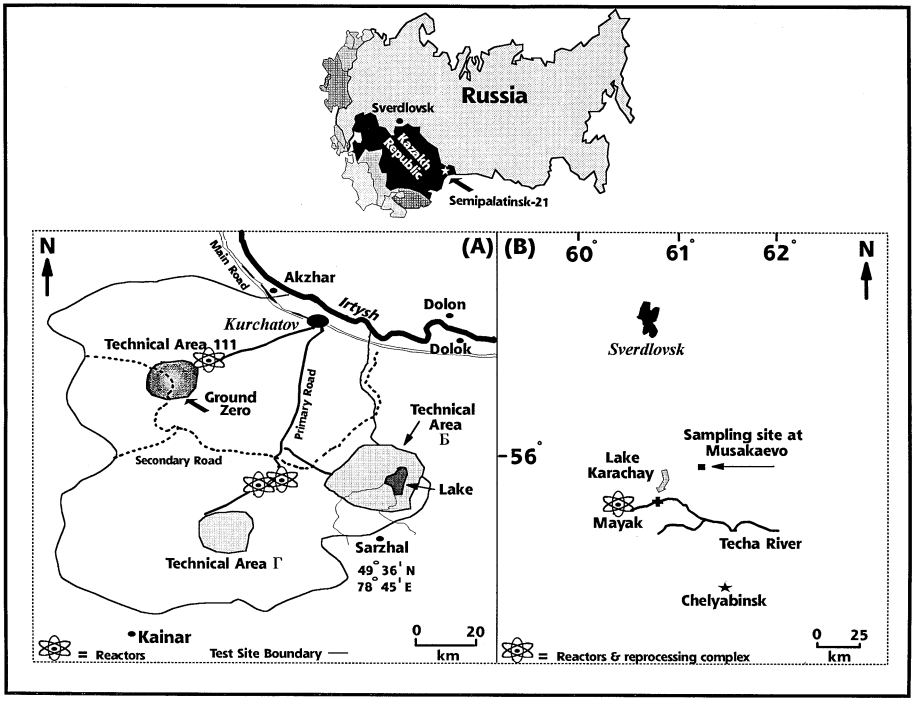

Fig. 1. Sampling site locations for Semipalatinsk-21 and Musakaevo. The reactors at Semipalatinsk-21 (A) are research reactors; the reactors at Mayak (B) are production reactors. Technical Area Б is the site of the 'Bolopan' samples collected by Yamamoto *et al.* (1996) representing ejecta from an underground explosion in 1965. (A) modified from Shebell and Hutter (1996); (B) modified from Aarkrog *et al.* (1992).

operating history of the complex (Trapeznikov *et al.*, 1993; Khotuleva *et al.*, 1993; Molchanova *et al.*, 1994). Subsequent migration of radionuclides from the Techa to the Iset and thence to the Arctic Ocean, via the Ob, has already been postulated (Trapeznikov *et al.*, 1993).

We report here the first isotopic measurements of transuranic radionuclides (Pu, Np, and U) in soils contaminated by the 1957 accident at Mayak as well as complimentary isotopic measurements of these radionuclides in soils collected at and near Semipalatinsk-21. Taken together, the data provide the necessary composition information, especially for Pu isotopes, to permit 'first-order' mixing calculations for estimating the fraction of Pu from these sources in environmental material containing global-fallout Pu.

MATERIALS AND METHODS

Soil contaminated by the 1957 Mayak accident was collected at Musakaevo (Fig. 1) by the Institute of Plant and Animal Ecology in Zarechney, Russia on 1 October 1991 and represents the 0–5 cm soil horizon. Soil samples (0–5 cm) from Semipalatinsk-21 (Fig. 1) were collected by scientists from the Department of Energy's Environmental Measurements Laboratory (EML) as part of an International Atomic Energy Agency (IAEA) special task force study charged with a preassessment of the prevailing radiological conditions at Semipalatinsk-21 and western areas in Kazakhstan (Shebell and Hutter, 1996). At Semipalatinsk-21, three cores (8·9 cm diameter) were taken at the apexes of an equilateral triangle (distance from center = 3 m) and sectioned to different depths. Equal depth intervals from each core were combined, mixed by hand, and approximately 50% of the material was returned to EML. We chose to analyze the 0–5 cm horizon from these cores; prior to removing aliquots from the curated samples they were blended for approximately 1 h on a rotary mixer to increase homogeneity.

Because the mass spectrometry facility at the Pacific Northwest National Laboratory (PNNL) is dedicated to low-level analyses, sample sizes were chosen to keep total actinide atom concentrations near 10^{10} atoms per sample. This necessitated the analysis of samples whose dry weights ranged between ~1 to 3 g. The samples were dry ashed at 600°C for 16 h to remove organic matter and were then dissolved in a mixture of HCl and HF to destroy silicious matrices in the soil and to dissolve any refractory transuranic radioelements. The residue from dissolution was then fumed to dryness, 3 times, with 6 N HCl to remove residual HF. The residue was then dissolved, with heat, in 6 N HCl containing boric acid to solubilize trace

quantities of rare earth and actinide fluorides. The final solutions were diluted to either 50 or 100 ml in volumetric flasks which then served as 'stock' solutions for the various analyses.

To determine the absolute amounts of actinides, aliquots from the stock solutions were processed with known quantities of ^{244}Pu, ^{236}Np, and ^{233}U (nominally 5×10^6 atoms) which served as yield determinants through the actinide isolation and purification process. The ^{244}Pu tracer was prepared from SRM-996 (Pu-244 Spike Assay and Isotopic Standard) issued by the National Institute of Standards and Technology (NIST). The ^{233}U was prepared by dissolution of a small quantity of isotopically pure metal supplied by Oak Ridge National Laboratory that was then standardized against NIST Uranium Oxide SRM-950a. The ^{236}Np was standardized, mass spectrometrically, against a calibrated ^{237}Np solution (proportional alpha counting) using a half-life of $(2{\cdot}14 \pm 0{\cdot}01) \times 10^6$year.

At Argonne National Laboratory (ANL) samples from Semipalatinsk-21 were treated with strong acid to determine the leachable fraction of the Pu and ^{241}Am. Each sample was treated three times with hot (80–90°C), 6 N HCl for 24 h. The leachates were combined, evaporated to $\sim$30 ml, and then centrifuged at high speed to isolate any residual particulate matter from the leachate. The supernate was then transposed to an $\sim$8 N HNO_3 solution prior to chemical isolation of the actinides. The leached residue was dissolved in HF and processed as a separate sample to determine the fraction of refractory material in the soil. NIST-traceable ^{242}Pu and ^{243}Am tracers were used to quantify recovery through the chemical processing and subsequent α-spectrometry measurements of ^{241}Am, ^{238}Pu, and $^{239+240}$Pu.

The chemical processing protocols, mass spectrometer source preparation, and thermal ionization mass spectrometry (TIMS) instrument have been summarized elsewhere and will not be repeated here (Beasley *et al.*, 1997). The chemical procedures used at ANL to isolate and purify actinides in environmental samples are described in Nelson and Orlandini (1986).

For the TIMS analyses, process blanks did not exceed $\sim 10^4$ atoms per sample for either the Pu or Np, a value below the detection limit of the PNNL mass spectrometer. However, trace quantities of ^{234}U, ^{235}U and ^{238}U were detected in the process blanks (from their presence in the ultra-pure reagents used in the analysis) but were 2 to 3 orders of magnitude lower than the atom levels measured in the samples themselves. Blank levels for the α-spectrometry measurements were also insignificant compared to those measured in the samples themselves.

To ensure that the soils from Musakaevo and Semipalatinsk-21 contained no ^{233}U or ^{244}Pu that would compromise quantitation at the TIMS

TABLE 1

Mass spectrometric determinations of actinide element isotopes in Soil (0–5 cm) contaminated by the 1957 accident at mayak, Chelyabinsk province (7·5 km SE of 56°N, 61°E at Musakaevo)

	Atom Ratio ± 1σ uncertainty[a]				
	$^{236}U/^{239}Pu$ (10^{0})[c]	$^{237}Np/^{239}Pu$ (10^{0})	$^{240}Pu/^{239}Pu$ (0^{0})	$^{241}Pu/^{239}Pu$[b] (10^{3})	$^{242}Pu/^{239}Pu$ (10^{-4})
Aliquot # 1[d]	0·312 ± 0·009	0·0717±0·0025	0·0283±0·0001	0·226±0·008	0·798±0·034
Aliquot # 2[e]	0·311±0·009	0·0737±0·0033	0·0281±0·0001	0·235±0·005	0·632±0·019
	Concentration ±1σ uncertainty (atoms g^{-1})				
	^{236}U[f] (10^{10})	^{237}Np (10^{10})	^{239}Pu (10^{11})	^{240}Pu (10^{9})	^{241}Pu (10^{7})	^{242}Pu (10^{7})
Aliquot #1[d]	5·28±0·12	1·21±0·04	1·69±0·03	4·78±0·08	3·82±0·14	1·35±0·09
Aliquot # 2[e]	4·87±0·12	1·15±0·03	1·57±0·02	4·40±0·06	3·68±0·10	0·99±0·08

[a] Relative uncertainties in atom ratios are less than those of atom concentrations as they are independent of uncertainties associated with yield determinant recoveries

[b] Decay corrected to 1 January 1995.

[c] Power of 10 by which each column entry should be multiplied to obtain measured isotope ratios.

[d,e] Values shown represent the mean of duplicate analyses for all isotope ratios and concentrations listed.

[f] ^{236}U concentration $= (5{\cdot}28 \pm 0{\cdot}12) \times 10^{10}$ atoms g^{-1}.

measurement step, aliquots of the stock solutions were processed and analyzed without the addition of these tracers. In neither case did we observe detectable levels of these radionuclides.

Finally, to test the homogeneity of the sample from Musakaevo, we prepared two samples of differing weights (1·09 and 2·59 g) as described above and ran duplicate aliquots from each. Table 1 lists the atom ratios and absolute abundances of the transuranic radionuclides measured. The data do suggest a slight inhomogeneity between the two samples analyzed which is particularly noticeable in the ^{242}Pu data. However, the degree of inhomogeneity is small and has no effect on the conclusions we draw from the data.

RESULTS AND DISCUSSION

Table 2 shows the atom ratios and absolute atom abundances of the transuranic radionuclides measured at Semipalatinsk-21 near Ground Zero (GZ) on the test site and at two off-site villages, Akzhar and Kainar (Fig. 1). The GZ area was the site of 87 atmospheric and 26 surface tests conducted there between 1949 and 1962. In addition, some 346 underground tests were conducted on the site, at Technical Areas Г and Б (Fig. 1), that continued until 1989 (Shebell and Hutter, 1996; Yamamoto *et al*., 1996). Table 3 compares the absolute activities of $^{239+240}$Pu, ^{241}Am, and the ^{238}Pu/$^{239+240}$Pu activity ratios for the different Semipalatinsk-21 sampling sites and shows the partitioning of these entities in strong acid leachates and the residue following leaching. As has been shown at the Nevada Test Site (NTS; Krey and Bogen, 1987), transuranic (and other radionuclides) can be made refractory at the high temperatures characteristic of nuclear detonations. Crustal material entrained during the detonations can fuse with vaporized components of the devices to produce difficultly acid-soluble residues. This is particularly evident for the GZ sample (Table 3) where $> 90\%$ of the $^{239+240}$Pu and ^{241}Am were present in a form resistant to strong acid treatment; at Akzhar and Kainar a greater portion of the $^{239+240}$Pu and ^{241}Am are solubilized by acid leaching.

It is clear that the absolute activity of $^{239+240}$Pu in the GZ soil aliquot analyzed at ANL is much greater than was measured in a separate EML soil aliquot at PNNL using TIMS. The total $^{239+240}$Pu in the ANL aliquot is $\sim$1360 Bq kg^{-1} (Table 3) while that in the EML aliquot is $\sim$134 Bq kg^{-1} (Table 2). We have confirmed that this factor of 10 does not result from weight or dilution errors. Rather, it is due, we believe, to the presence of micron-sized particles of Pu (either as pure Pu, PuO_2, or highly enriched, fused crustal material) in the sample. For example, the presence of

TABLE 2
Mass spectrometric determinations of actinide element isotopes in soil (0–5 cm) contaminated by nuclear device testing at and near Semipalatinsk-21

	Atom ratios ±1σ uncertainty[a]				
	$^{236}U/^{239}Pu$ (10^{0})[c]	$^{237}Np/^{239}Pu$ (10^{0})	$^{240}Pu/^{239}Pu$ (10^{0})	$^{241}Pu/^{239}Pu$[b] (10^{-3})	$^{242}Pu/^{239}Pu$ (10^{-4})
G.Z[d] 50·43°N, 77·83°E	0·0244±0·0009	0·0208±0·0013	0·0438±0·0001	0·499±0·008	0·789±0·026
Akzhar, 50·79°N, 78·45°E	0·0654±0·0066	0·1129±0·0038	0·0685±0·0004	0·944±0·029	7·93±0·23
Kainar, 49·21°N, 77·40°E	0·188±0·020	0·288±0·011	0·1026±0·0007	1·184±0·044	17·15±0·39
	Concentration ±1σ uncertainty (atoms g^{-1})				
	^{236}U (10^{9})	^{237}Np (10^{9})	^{239}Pu (10^{11})	^{240}Pu (10^{9})	^{241}Pu (10^{7})	^{242}Pu (10^{6})
Ground Zero	3·09±0·10	2·63±0·16	1·27±0·03[e]	5·52±0·11[e]	6·34±0·20	9·68±0·72
Akzhar	0·064±0·006	0·110±0·003	0·0097±0·0002	0·067±0·001	0·092±0·003	0·77±0·03
Kainar	0·069±0·007	0·106±0·001	0·0037±0·0001	0·038±0·006	0·044±0·002	0·63±0·02

[a] Relative uncertainties in atom ratios are less than those of atom concentrations as they are independent of uncertainties associated with yield determinant recoveries.
[b] Decay corrected to 1 January 1995.
[c] Power of 10 by which each column entry should be multiplied to obtain measured isotope ratios.
[d] Ground Zero; sample was taken 1·1 km south of G.Z.
[e] Absolute activities of $^{239+240}$Pu in this sample are calculated to be ~134 Bq kg^{-1}.

TABLE 3
Activities and activity ratios of selected actinide elements in soils at and near Semipalatinsk-21

Location	*Wt.* (*g dry*)	$^{239+240}Pu$ (*Bq kg*$^{-1}$) (*L*)[a]	$^{239+240}Pu$ (*Bq kg*$^{-1}$) (*R*)[b]	^{241}Am (*Bq kg*$^{-1}$) (*L*)	^{241}Am (*Bq kg*$^{-1}$) (*R*)	^{238}Pu / $^{239+240}Pu$ (*L*)	^{238}Pu / $^{239+240}Pu$ (*R*)
G.Z.[c]	0·2	64±(1)[d]	1295±(0·05)	7·3±(0·05)	70 ±(0·03)	0·020±0·002	0·037±0·001
Akzhar	5·0	0·55±(9)	1·3±(3)	0·17±(20)	0·17±(9)	0·029±0·005	0·020±0·003
	0·5	0·42±(12)	0·47±(11)	—	—	0·020±0·010	0·020±0·010
	0·5	0·50±(7)	0·55±(9)	0·19±(18)	0·23±(37)	0·040±0·010	0·030±0·010
Kainar	5·0	0·57±(12)	0·28±(6)	0·23±(14)	0·02±(22)	0·031±0·005	0·050±0·007
	0·5	0·67±(5)	0·17±(10)	0·25±(14)	0·08±(20)	0·060±0·010	0·060±0·020

[a] Leachate.
[b] Residue from leachate.
[c] See Table 1 for exact location coordinates.
[d] Number in parenthesis is the percent uncertainty at 1σ.
— Not determined.

a *single*, 3-μm diameter spherical particle of refractory $^{239}PuO_2$ ($\rho = 11{\cdot}46\ g\,cm^{-3}$; CRC, 1991) in a 0·2 g soil sample would, if completely solubilized, scale to an activity of $\sim$1720 Bq kg^{-1}.

Because the sources of the transuranic radionuclides at Musakaevo and Semipalatinsk-21 differ, the results from both sites are better discussed separately.

Musakaevo

Two lines of evidence lead us to believe that the transuranic radionuclides in the Musakaevo soil originate almost exclusively from processed, low burn-up reactor fuel. This is evident from the fact that ^{237}Np atom concentrations are elevated with respect to ^{236}U and ^{239}Pu. For example, the thermal neutron cross sections for the reactions ^{235}U (n, γ) ^{236}U, ^{236}U (n, γ) ^{237}U and ^{237}U (n, γ) ^{238}U are $\sim$100, $\sim$5, and $\sim$400 barns, respectively (Lederer and Shirley, 1978); the decay of ^{237}U to ^{237}Np occurs by β^- particle emission with a half-life of 6.75 days. Consequently, ^{237}Np concentrations in low burn-up fuel are not pronounced because (1) the irradiation times used to produce Pu of high ^{239}Pu content (low $^{240}Pu/^{239}Pu$ ratios) are not long; (2) the transformation of ^{237}U in the thermal neutron flux of the reactor is substantial; and (3) early ^{235}U enrichments in fuels used for Pu production were not high ($\leqslant 1\%$ for the Hanford graphite-moderated production reactors; Gerber, 1993). Moreover, reactor burn-up codes using natural uranium-fueled, graphite-moderated reactors (ORIGN 2; Croft, 1980) predict that when $^{240}Pu/^{239}Pu$ atom ratios reach 0·028 (Table 1), $^{237}Np/^{239}Pu$ atom ratios approach 0·003. Our measured $^{237}Np/^{239}Pu$ atom ratios at Musakaevo ($\sim$0·073; Table 1) exceed this value by more than a factor of 20.

We believe the preponderant ^{237}Np enrichment we observe in the Musakaevo soil arises from the enrichment of ^{237}Np in the processed wastes following chemical recovery of Pu and U at Mayak. For example, the production reactors at Hanford Washington (nine in number) irradiated approximately 1×10^5 metric tons of uranium fuel between 1944 and 1987 (DOE, 1996); eight of the production reactors were shut down in 1971 followed by the last reactor (the dual-purpose N reactor) in 1987. Of the total uranium fuel processed, only $1{\cdot}5 \times 10^3$ metric tons of U (mostly from the earlier 8 production reactors) are estimated to reside in on-site, high-level Hanford waste tanks (DOE, 1987) indicating that $> 98\%$ of the U in the irradiated fuel was recovered. Accepting a similarly high U recovery for irradiated fuels processed at Mayak argues for higher atom concentrations of ^{237}Np (relative to U) in stored wastes than would be predicted solely from the irradiation histories of those fuels.

It is also probable, however, that the high-level wastes released during the Kyshtym accident contained not only wastes from the processing of low burn-up uranium fuels used to produce weapons-grade Pu ($^{240}Pu/^{239}Pu$ atom ratio = 0·028; Table 1) but also some additional waste from processing highly enriched ^{235}U fuels, viz., irradiated experimental research fuels intended for use in reactor-powered vessels. Reactor cores with high ^{235}U enrichments (> 50%) produce elevated levels of ^{236}U and ^{237}Np, with fast neutron capture in ^{238}U [^{238}U (n, 2n) ^{237}U, $\sigma = \sim 0{\cdot}1$ barn; Soodak, 1958)] contributing to the production of ^{237}Np. Research by the FSU in nuclear propulsion for naval vessels began in 1953 and the first nuclear-powered submarine from this program was launched in 1958 (Cochran *et al.*, 1989). Testing of these experimental reactors, and the processing of their fuels, would have occurred during this period. However, wastes from this source would have been quantitatively smaller than those associated with Pu weapons production through 1957.

Decay correcting the mean of our 1 January 1995 $^{241}Pu/^{239}Pu$ atom ratios (0·000231; Table 1) to 29 September 1957, the time of the Mayak accident ($T_{1/2}$ ^{241}Pu = 14·4 year), gives a ratio of 0·00138 or ~0·0014. We can compare this ratio with early, post-shot Pu ratio measurements made at the Nevada Test Site (1951) for devices whose yields ranged between 1.2 and 31 kt (Operation Buster-Jangle; Hicks and Barr, 1984). Where mean $^{240}Pu/^{239}Pu$ atom ratios were 0·031 $\pm$ 0·006 (compared to the Musakaevo soil value of 0·0283; Table 2), $^{241}Pu/^{239}Pu$ ratios were 0·0010 $\pm$ 0·0001, in good agreement with our decay-corrected Musakaevo value. Because the isotopic signatures of Pu in a low-yield nuclear device are changed only slightly at detonation (thermal neutron fluxes are not large), we take this comparison as reasonable confirmation of the comparability of the fuel irradiation cycles of both the US and Soviet Union during the early-to-mid-1950s.

The contribution of Mayak-derived Pu to the soil at Musakaevo has previously been estimated at 96% (Aarkrog, 1995). The isotopic Pu data indicate that this fraction may be closer to 97–98%. Again, graphite-moderated reactors using natural or low-enriched ^{235}U fuels produce $^{242}Pu/^{239}Pu$ ratios near 0·00002 when $^{240}Pu/^{239}Pu$ ratios attain values between 0·02 and 0·03 (ORIGIN 2; Croff, 1980). Our measured $^{242}Pu/^{239}Pu$ ratio in the Musakaevo sample averages near 0·00007 (Table 1), a value higher than expected, indicating an additional source of Pu. The present-day $^{242}Pu/^{239}Pu$ ratio in integrated global fallout above 55° N latitude has recently been measured at 0·0041 $\pm$ 0·0006 (Beasley, 1997), comparable to that previously reported by Krey *et al.* (1976). Thus, it requires only a 1·5% global fallout input to our Musakaevo sample to provide the 'excess' ^{242}Pu we measure over that expected in low burn-up fuel.

It is instructive to compare our measured $^{240}Pu/^{239}Pu$ ratios from the Mayak accident with those measured by Smith *et al.* (1995) in sediments of Chernaya Bay (Arctic Ocean), the site of several low-yield underwater tests in the 1950s. These sediments showed $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios of 0·030 and 0·0012, respectively, where the latter ratio was decay-corrected to 1957, the time testing occurred. Both isotopic ratios compare favorably with the ratios measured in the Mayak wastes (decay-corrected to 29 September 1957) and argue that the Pu in these sediments were subjected to inconsequential thermal neutron fluxes beyond those experienced during its production.

Finally, we cannot estimate the contribution of ^{236}U, ^{237}Np, or Pu isotopes to the soil at Musakaevo from the resuspension event at Lake Karachay because we know of no reports that list the existing isotopic composition of the transuranic elements in either Lake Karachay water or resuspended lakeshore sediments at the time of the event.

Semipalatinsk-21

Figure 2 shows the relationships we observed between Pu isotopes and between ^{237}Np and Pu isotopes at Semipalatinsk-21, Akzhar, and Kainar. We have also included data from Musakaevo and the isotopic data from Semipalatinsk-21 reported by Yamamoto *et al.* (1996*b*) for completeness. From our measurements, we conclude that the Pu measured in soils at Akzhar and Kainar are mixtures of Pu released from Semipalatinsk-21 and integrated global fallout; the data fall on a concordant mixing line for all of the isotopes measured including that of the Pu measured in the Musakaevo soil [dotted line, Fig. 2(A)]. Using the mixing equations described in Krey *et al.* (1976), and the isotopic data from Table 2 (also transformed to activities using half-lives of ^{239}Pu and ^{240}Pu equal to $2{\cdot}4119 \times 10^4$ and 6.564×10^3 year, respectively), we calculate that the fraction of test-site derived Pu activity at Akzhar is ~76%, while that at Kainar is ~48%. The elevated $^{237}Np/^{239}Pu$ atom ratio we observed at Kainar is due, we believe, to the presence of increased fallout at this site from a ^{235}U device. We base this conclusion on the fact that while all of the Pu isotopes at Kainar are lower than those measured at Akzhar, the ^{236}U and ^{237}Np atom concentrations are virtually identical to those measured at Akzhar resulting in enhanced $^{236}U/^{239}Pu$ and $^{237}Np/^{239}Pu$ atom ratios (Table 2).

The $^{241}Pu/^{239}Pu$ ratios measured by Yamamoto *et al.* in soils from Ground Zero falls below our mixing line, but the crater ejecta ratios at Bolopan (Technical Area B; Fig. 1) are nearly identical to those we measure at Akzhar. However, the Bolopan data cannot be interpreted as

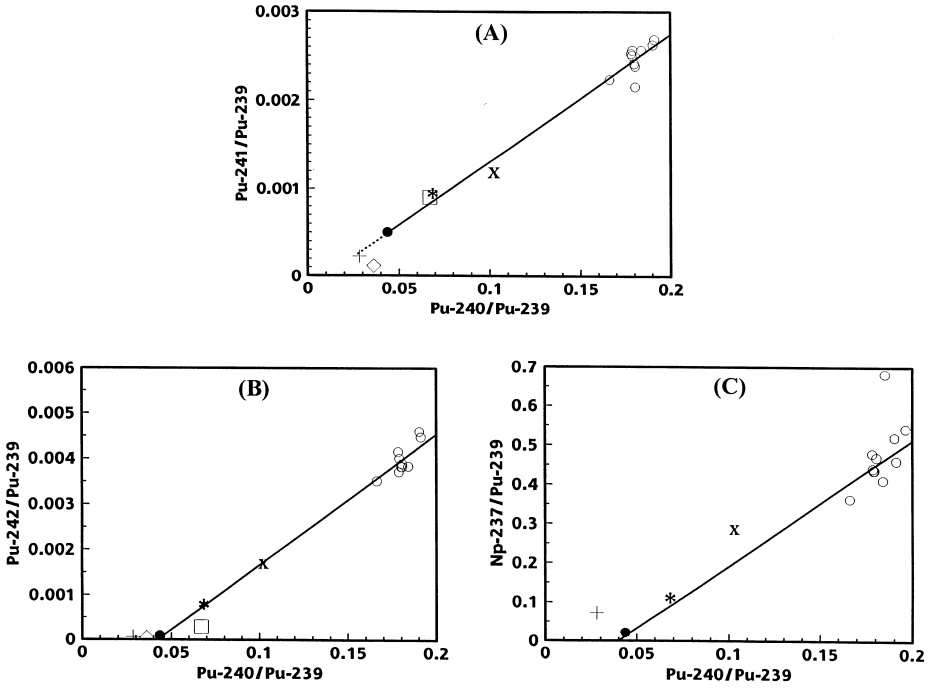

Fig. 2. Isotopic relationships of transuranic radionuclides isolated from soils at Musakaevo and Semipalatinsk-21. Sampling legend: + Musakaevo (Mayak); ● GZ (Ground Zero); ∗ Akzhar; × Kainar. ◇ Ground Zero; □ Bolopan (Semipalatinsk-21; Yamamoto *et al.*, 1996). The observed excess Np-237 at Musakaevo (C) is due to enrichment of this isotope in the Mayak wastes (see text) while at Kainar (C), the excess is most probably due to debris from a uranium device that also deposited elevated concentrations of U-236 at this site. The integrated global fallout values (○) were obtained from measurements made on aliquots of 30 cm deep soil cores collected in 1970 at Reykjavik (Iceland), Oslo (Norway), Bergen (Norway), Roskilde (Denmark), Barrow, Palmer, and Fairbanks (Alaska) as discussed in Beasley *et al.* (1997). The extension of the mixing curve (·····) intersected the Musakaevo sample (+) indicating that Pu of this composition was used for the majority of the Pu devices detonated at the test site.

a mixture of test and fallout debris because of the nonconcordance observed for the $^{242}Pu/^{239}Pu$ ratio in this sample [Fig. 2(B)].

Table 4 shows a comparison of the activity levels of selected actinides we measured at Semipalatinsk-21 and those reported by Yamamoto *et al.* (1996*a*). In all cases, significant differences are evident. We think that these disparities result from (1) differences in depositional inventories across the test site; (2) differences in the sampling depths employed in collecting the soils; and (3) to radionuclide inhomogeneities in the soils themselves.

TABLE 4
Comparison of absolute activities of ^{237}Np, $^{239+240}$Pu, and ^{241}Am in soils collected at and near ground zero, semipalatinsk-21[a]

^{237}Np ($Bq\,kg^{-1}$)		$^{239+240}Pu$ ($Bq\,kg^{-1}$)		^{241}Am ($Bq\,kg^{-1}$)	
Yamamoto *et al.*	This work	Yamamoto *et al.*	This work[b]	Yamamoto *et al.*	This work
75·9±3·2[c]	0·027±0·002	27 900±400	1359±1	520±10	77±0·06

[a]Samples collected in this work were 1.1 km from Ground Zero while those of Yamamoto *et al.* (1996*a*) were taken at the epicenter of Ground Zero.
[b]Except for the ^{237}Np from TIMS measurements, values shown are summed fromTable 3 for both leachate and residue.
[c]Uncertainties shown are at 1σ.

Samples collected at Ground Zero by Yamamoto *et al.* (1996*a*) were taken over the depth interval 0–3 mm while samples at Bolopan were collected over the 0–5 cm soil horizon. The lower specific activities (Bq kg^{-1}) we measure at GZ (Table 4) are most likely due to inclusion of a greater percentage of unlabeled soil in our samples (0–5 cm collection depth) and/or the interception of several 'hot' particles in the samples collected by Yamamoto *et al.* However, over a 40-year period, natural processes do redistribute surface material to depth as has been demonstrated in environmental research programs too numerous to cite here. For this reason, we think it more probable that sampling to depths of 5 cm in the soil column provides a more representative sample than does sampling to only millimeter-constrained depths, especially those intended for isotopic analysis. The two data sets do emphasize, however, that any future attempts at deriving radionuclide inventories for the entire test site will require an extensive soil collection to account for geographical inhomogeneities in the fallout distribution, soil collections to depths of at least 10 cm, and total dissolution of the soil samples to solubilize refractory radionuclides.

Our measurements of ^{238}Pu, $^{239+240}$Pu and ^{241}Am (Table 3) are consistent with conclusions drawn from the isotopic Pu measurements. In no case do we observe ^{238}Pu/$^{239+240}$Pu activity ratios as high (~0·45) as those seen by Yamamoto *et al.* (1996*a*) in the crater ejecta at Bolopan confirming quite localized deposition from this event. Rather, our ^{238}Pu/$^{239+240}$Pu activity ratios are consistent with a combined input of material from low-level device testing and that from SNAP-9A material introduced into the northern hemisphere in the mid-1960s (Krey, 1967). These ratios are also

consistent with those measured offsite by Yamamoto *et al.* (1996*a*). The $^{239+240}$Pu activities we measure at both Akzhar and Kainar do indicate the presence of refractory Pu of test-site origin. However, while we observe refractory ^{241}Am in the soils at Akzhar, the ^{241}Am in soils at Kainar appear to be completely acid-leachable. At present, we have no convincing explanation for this observation.

CONCLUSIONS AND RECOMMENDATIONS

From the isotopic data presented above, we believe that early releases of Pu from the nuclear complex at Mayak (1950–1960) are best characterized as having ^{240}Pu/^{239}Pu atom ratios of 0·028. We recommend that this value be used as one end member in calculations that partition Pu in environmental samples known to have been impacted by transuranic releases from Mayak that also contain integrated global fallout (^{240}Pu/^{239}Pu atom ratio $\approx$0·18). For samples suspected of containing fallout debris from low-yield tests at Semipalatinsk-21, an end-member ^{240}Pu/^{239}Pu atom ratio of 0·044 is recommended. In addition, confirmation of the presence of fallout debris from this source should be corroborated using chemical techniques that identify the presence of refractory Pu in the samples.

In a more speculative vein, the presence of ^{236}U and ^{237}Np at Mayak and Semipalatinsk-21, in conjunction with Pu isotopic measurements, may be useful in tracing transuranic radionuclide transport away from these sites and into nearby river systems. For example, we have measured ^{236}U in a sample of Ob River water collected above Salekhard in 1993 ($\sim 1 \times 10^8$ atoms l^{-1}; Beasley, 1997) confirming an upriver source for this radionuclide. Whether the origin of the ^{236}U can be traced to above-ground releases from Mayak (Ob River), Tomsk-7 (Ob River) or Semipalatinsk-21 (Irtysh River) — or a combination of all three — would be of interest. And while remote, the releases of both soluble ^{236}U and ^{237}Np (and other soluble radionuclides) to groundwaters from the extensive underground testing in Technical Area B at Semipalatinsk-21, with subsequent transport to the Irtysh River, cannot be entirely ignored.

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