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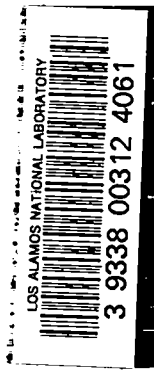

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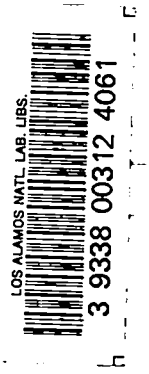

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NEPTUNIUM-237 PRODUCTION FROM ATMOSPHERIC NUCLEAR TESTING

by

D. W. Efurd, G. W. Knobeloch, R. E. Perrin, and D. W. Barr

ABSTRACT

Mass spectrometric measurements on neptunium and plutonium from two soil samples that are representative of global fallout have been completed. The $^{237}Np/^{239}Pu$ atom ratio is 0.7 ± 0.2. This ratio, when multiplied by the amount of plutonium in worldwide fallout, indicates that 3 t of ^{237}Np were produced by atmospheric testing to date.

I. INTRODUCTION

For several years the National Academy of Sciences has been conducting an exhaustive study of the risk associated with nuclear power. The study will encompass all facets of the industry, from mining to use of the uranium to final disposition of the fission products and actinides. The study's Steering Committee, chaired by Conyers Herring of the Bell Telephone Laboratories and Stanford University, is charged with preparation of the final report, including a chapter on storage or disposal of the by-products of fission. Recent re-evaluation of the relative health hazards (per unit mass) of various actinides has placed ^{237}Np near the top of the list, primarily because of its mobility.

To evaluate the health risk involved in the burial of actinides, including ^{237}Np, at least three questions are immediately apparent and should be addressed:

(1) How much ^{237}Np exists on the earth and in the atmosphere from past and present testing of weapons?

(2) Has this ^{237}Np had any observable health effects on people or caused any injury to the environment?

(3) What is the ^{237}Np rate of production in the existing and projected nuclear power industry?

Neptunium-237 ($t_{\frac{1}{2}} = 2.14 \times 10^6$ a) is the only remaining transuranic element in global fallout whose abundance has not been quantified. Holm and Nielsson[1] state, "By mass ^{237}Np can be expected in the environment in the same order as ^{239}Pu since the (n,2n)/(n,γ) reaction (ratio) for ^{238}U (in) a thermonuclear device can be as high as 0.5-1." Measurements of the neptunium and plutonium precursors ^{237}U and ^{239}U from filter papers exposed to atmospheric debris can be used to predict that the $^{237}Np/^{239}Pu$ atom ratio in global fallout is 0.71 ± 0.18. This study measured ^{237}Np concentrations in soil samples that were previously shown to be representative of global fallout. The average $^{237}Np/^{239}Pu$ ratio in these samples, multiplied by the total plutonium production from atmospheric testing, should give an accurate estimate of total ^{237}Np available for global dispersion.

II. SAMPLE COLLECTION AND ANALYSIS

Krey and Hardy of the US Department of Energy Environmental Measurements Laboratory (EML) furnished two 100-g soil samples contaminated by global fallout. These samples were collected by EML's standard operating procedure as a part of their ongoing program to measure plutonium in the environment.[2] Data obtained by EML for these two soil samples are shown in Table I. Table II shows the vertical distribution of ^{137}Cs, ^{90}Sr, and $^{239+240}Pu$ for a depth profile study at the North Eastham, Massachusetts sampling location.[3] In the soil sample collected at Stevens Hill, Pennsylvania, all the cesium, strontium, and plutonium are contained within the first 24 cm.* If one assumes that ^{237}Np is no more mobile than cesium, strontium, or plutonium, the two soil samples chosen for this study should also be suitable for determining the $^{237}Np/^{239}Pu$ atom ratio in global fallout.

Aliquots of each soil were spiked with ^{236}Np and ^{242}Pu. Dissolution of the samples was accomplished with HNO_3, HF, and $HClO_4$. The samples were dissolved in 1M HCl and transferred to 1-ℓ separatory funnels. Plutonium was

*From information provided by P. W. Krey, US Department of Energy, Environmental Measurements Laboratory, 376 Hudson Street, New York City, NY 10014 (1981).

TABLE I

RADIOCHEMICAL DATA FOR SOILS

	EML No.	
	S-2711	S-2328
Sampling location	Stevens Hill, Pennsylvania	North Eastham, Massachusetts
Sampling date	5/31/79	10/79
Depth	0-24 cm	0-30 cm
Dry soil/cm^2 (g)	23.91	37.12
pCi/kg dry soil:		
^{238}Pu	0.29 ± 10%	0.21 ± 17%
$^{239+240}Pu$	7.8 ± 5%	6.0 ± 5%
^{241}Am	2.2 ± 5%	1.6 ± 5%
^{137}Cs	430. ± 5%	300. ± 5%
Atom ratios		
$^{240}Pu/^{239}Pu$	0.182	0.180
$^{241}Pu/^{239}Pu$	0.0055	0.0051

reduced to Pu(III) with $FeCl_2$ and $NH_2OH \cdot HCl$. Np(IV) was extracted into a xylene solution 0.5M in 2-thenoyltrifluoracetone (TTA).[4] The TTA-xylene was washed three times with 1M HNO_3, and the Np(IV) was removed from the organic phase by stripping with three aliquots of 10M HNO_3. The neptunium was further purified in multiple sorptions from 10M HCl onto Dowex 1 x 8 ion exchange resins, followed by elution with 5M HCl.[5] Final cleanup of the neptunium was accomplished by placing the 5M HCl in a quartz test tube and drying, followed by addition of 1 drop of HNO_3 and 0.5 mℓ of $HClO_4$. The solution was fumed to dryness at 180°C.

TABLE II

1972 NORTH EASTHAM SOIL SAMPLES[a]

Depth (cm)	Total Radionuclide (%) ^{90}Sr	^{137}Cs	$^{239+240}Pu$
0-2[b]	22	70	52
2-4	32	14	21
4-6	13	4	8
6-8	8	3	7
8-10	5	1	3
10-12	3	1	2
12-14	3	1	2
14-16	3	1	1
16-21	5	2	3
21-26	2	<3	<1
26-31	2		
31-36	<2		
36-41			
41-46			
46-51			
51-56			

[a]Adopted from Hardy.[3]

[b]Includes surface vegetation.

After the extraction of the Np(IV), the Pu(III) was carried on LaF_3, washed three times with a solution of 3M HCl and 3M HF, and metathesized three times with NaOH. After the precipitate was dissolved in 7M HNO_3, the solution was passed through a Dowex AG 1 x 8, 100 to 200 mesh, anion exchange resin. The column was washed with three 5-mℓ aliquots of 7M HNO_3 and converted to the chloride form by washing with three 5-mℓ aliquots of 10M HCl. Plutonium was eluted from the column with 10M HCl-0.05M HI. The eluate was evaporated to

near-dryness and then fumed to dryness with a few drops of HNO_3. Next, the plutonium was dissolved in 10M HCl containing a few drops of 30% H_2O_2 and loaded on a pre-conditioned BIO·RAD AG MP-1, 50 to 100 mesh, macroporous anion column containing 0.1 mℓ of resin. The column was washed five times with the HCl-H_2O_2 solution and twice with five drops of 9M HNO_3. The plutonium was eluted with 48% HBr. The solution was fumed to near-dryness, a few drops of HNO_3 and 0.5 mℓ of $HCLO_4$ were added, and the solution was again fumed to dryness at 180°C. Blanks consisting of 10 g of quartz were analyzed with each set of soil samples. The blanks and the soil samples were treated identically.

Quartz test tubes containing the neptunium and plutonium samples were submitted for mass spectrometry analysis. The samples were dissolved in 100 μℓ of 1.5M HCl buffered with ammonia to a pH of 2.7. The solutions were loaded on rhenium mass spectrometer filaments, and neptunium or plutonium was electroplated from the solution onto the filament at 3.4 V for 20 minutes. After 25 μg of platinum were added as dinitratosulfatoplatinous acid in 1.5M HCl, the plating voltage was reduced to 3.0 V for 20 minutes. The filament was placed under a heat lamp, and 1 A was passed through the filament for 10 minutes.

Samples were analyzed on a 12-in., single-stage, thermal ionization mass spectrometer operated in the pulse counting mode. Counting data for plutonium were collected at 1450°C; neptunium was analyzed at 1550°C.

III. RESULTS AND DISCUSSIONS

Table III shows the $^{237}Np/^{239}Pu$ atom ratios obtained from analysis of the two soil samples. These data have been corrected for laboratory blanks. No plutonium was observed in the blanks above the detection limit of 5×10^6 atoms ^{239}Pu/g of quartz. The blank corrections for the neptunium ranged from 1 to 20%. The $^{237}Np/^{239}Pu$ ratios reported in Table III fall within the range predicted by Holm and Nilsson.[1] If one assumes that all four measurements are equally valid, a $^{237}Np/^{239}Pu$ ratio of 0.7 ± 0.2 is calculated to be representative of global fallout.

The amount of ^{237}Np produced by atmospheric testing can be estimated by multiplying the average $^{237}Np/^{239}Pu$ ratio of 0.7 ± 0.2, measured in this study, by the total plutonium production from atmospheric testing. Harley calculates that combined testing by all the nuclear powers through 1962 produced 400 kCi of $^{239+240}Pu$; he also estimates that testing by France and China contributed

TABLE III

NEPTUNIUM AND PLUTONIUM CONCENTRATIONS IN SOILS CONTAMINATED BY GLOBAL FALLOUT

Sample	Weight (g)	^{237}Np (atoms/g)	^{239}Pu (atoms/g)	$^{237}Np/^{239}Pu$
2711	10	2.2×10^8	3.6×10^8	0.6
2711[a]	12.5	1.4×10^8	---	0.7
2328	15	2.0×10^8	3.9×10^8	0.5
2328[a]	50	1.5×10^8	---	1.0

[a]Plutonium-239 was not measured on this sample. The $^{237}Np/^{239}Pu$ atom ratio was calculated from EML data, Table I.

an additional 5% to the global inventory between 1962 and 1969.[6] Golchert and Sedlet estimate that an additional 2.7% was deposited on the ground by 1977.[7] Leifer and Toonkel determined the $^{239+240}Pu$ stratospheric inventory for the northern hemisphere was 75 Ci in 1977; they gave no value for the southern hemisphere.[8] By summing the above values for plutonium production, one can estimate that approximately 430 kCi of $^{239+240}Pu$ were produced by atmospheric testing. The $^{240}Pu/^{239}Pu$ ratio in global fallout is 0.18 (Ref. 9). Therefore, approximately 4200 kg of ^{239}Pu and 750 kg of ^{240}Pu were produced. An estimate of 2940 ± 750 kg of ^{237}Np produced by atmospheric testing is derived by multiplying the average $^{237}Np/^{239}Pu$ ratio for the two soil samples studied by the amount of ^{239}Pu produced through atmospheric testing. This quantity is in excellent agreement with the value 3000 ± 750 kg that is derived by summing individual shot data.

It will be very difficult to determine if this ^{237}Np has caused any observable health effects in people or any injury to the environment. Plutonium measurements have been made in liver, lung, and other tissues from more than 1200 people who have been exposed to environmental levels of plutonium. Table IV shows the average plutonium concentration for lung and liver tissues collected by McInroy,[10] Cobb,[11] and Fisenne.[12] No study has ever shown conclusively that these levels of plutonium cause any measureable health effect. If it is assumed

TABLE IV

PLUTONIUM CONCENTRATION IN INDIVIDUALS EXPOSED TO GLOBAL FALLOUT

Investigator	No. of Autopsies	$^{239+240}$Pu (dpm/kg) Lung	Liver
McInroy et al.	705	0.42	1.57
Cobb et al.	519	0.52	2.22
Fisenne et al.	50	0.13	1.39

that the ^{237}Np/^{239}Pu atom ratio in global fallout is a first approximation of the ratio measured in human tissue samples, the predicted ^{237}Np concentration in liver tissue would be <0.02 dpm/kg of tissue. Data obtained during Cobb's study suggest that neptunium is excreted from the body more quickly than plutonium.[13] Therefore, it is possible to predict that the ^{237}Np concentration in the body is very low and that observable health effects attributable to the ^{237}Np body burden will be very difficult to measure.

Table V shows Essington's[14] representation of the activity of heavy elements in accumulated waste for the entire nuclear industry. This material is contained "on-site" at various locations. Because reactor waste is of a concentrated nature, in contrast to the world-wide dispersion of fallout debris, it is not possible to infer a direct relative risk for the two sources based solely on quantity. Release of ^{239}Pu or ^{237}Np in a relatively restricted, populated region could conceivably result in very large body burdens for the exposed individuals. No such event can be conceived for the already dispersed fallout.

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TABLE V

ACTIVITY OF HEAVY ELEMENTS IN ACCUMULATED WASTE FOR ENTIRE NUCLEAR INDUSTRY[a]

	Normalized to 1 for ^{239}Pu					
Isotope	1972	1976	1980	1986	1990	2000
^{237}Np	0.22	0.22	0.20	0.15	0.14	0.76
^{239}Np	11.5	11.	14.5	43.1	31.7	7.84
^{236}Pu	0.00092	0.00075	0.00056	0.0036	0.010	0.012
^{238}Pu	36.1	49.	55.6	167.	283.	361.
^{239}Pu	1.	1.	1.	1.	1.	1.
^{240}Pu	1.54	1.7	1.89	4.45	5.33	3.14
^{241}Pu	315.	300.	295.	403.3	367.	255.
^{242}Pu	0.0043	0.0044	0.0047	0.0099	0.011	0.011
^{243}Pu	---	---	---	---	---	---
^{241}Am	96.1	96.5	103.	178.	141.	77.2
$^{242}Am^{m}$	5.69	5.5	7.23	19.5	14.2	5.68
^{242}Am	5.69	5.5	7.23	19.5	14.2	5.68
^{243}Am	11.5	11	14.5	43.1	31.7	7.84
^{242}Cm	5637.	3020.	2624.	3183.	953.	278.
^{243}Cm	2.31	2.25	2.34	4.03	3.00	2.16
^{244}Cm	1561.	1510.	2441.	9813.	6464.	919.
^{245}Cm	0.23	0.23	0.50	2.64	1.92	0.33
^{246}Cm	0.046	0.046	0.072	0.49	0.35	0.063
^{247}Cm	---	---	---	---	---	---
TOTAL (Ci)	7.2×10^{5}	1.4×10^{7}	7.9×10^{7}	9.3×10^{8}	1.2×10^{9}	1.8×10^{9}

[a]Adapted from Perkins[15] by Essington and Fowler.[14]

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