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CHARACTERIZATION OF AIRBORNE PLUTONIUM-BEARING
PARTICLES FROM A NUCLEAR REPROCESSING PLANT

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CHARACTERIZATION OF AIRBORNE PLUTONIUM-BEARING PARTICLES FROM A NUCLEAR REPROCESSING PLANT*

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Abstract

The elemental compositions, sizes, structures, and ^{239}Pu contents were determined for 558 plutonium-bearing particles isolated from airborne particles collected at various locations in the exhaust from a nuclear fuel reprocessing facility. These data were compared with data from natural aerosol particles. Most of the collected particles were composed of aggregates of crustal materials. 3.6 percent of the particles were organic and 1.7 percent were metallic, viz., iron, chromium, and nickel. High enrichment factors for titanium, manganese, chromium, nickel, zinc, and copper were evidence of the anthropogenic nature of some of the particles. Plutonium contents of most particles were very low (less than one femtobecquerel of ^{239}Pu). Plutonium concentrations were determined by the fission track counting method. Only one particle contained sufficient plutonium for detection by electron microprobe analysis. This was a $1\text{-}\mu\text{m}$ diameter particle containing 73% PuO_2 by weight (estimated to be 170 fCi of ^{239}Pu) in combination with Fe_2O_3 and mica. The plutonium-bearing particles were generally larger than natural aerosols. The geometric mean diameter of those collected from the mechanical line exhaust point where plutonium is converted to the metal, was larger than that of particles collected from the wet cabinet exhaust ($12.3\text{ }\mu\text{m}$ vs. $4.6\text{ }\mu\text{m}$). Particles from the mechanical line also contained more plutonium per particle than those from the wet cabinets. The amount of plutonium per particle decreased with the distance of each sampling point from the mechanical line which is considered the major source of plutonium contamination in the reprocessing facility.

Introduction

Nuclear fuel reprocessing facilities at the Savannah River Plant release to the atmosphere minute quantities ($<1\text{ mCi/yr}$) of ^{239}Pu in particulate form. To provide information about the chemical and physical form of these particles, samples were collected from nine locations in the two systems which exhaust air from the plutonium finishing operation (JB-Line) in Building 221-F. Particles bearing plutonium were identified, isolated from other collected particles, and characterized as to size, elemental composition, and radioactive properties.

Sampling Locations

Particles were collected from air in both exhaust systems in a nuclear fuel reprocessing facility at the Savannah River Plant. A schematic diagram of these systems is given in Figure 1. System I takes room air from inside wet cabinets (where plutonium is in solution) and from work areas and exhausts it via the JB-line stack.¹ System II takes air from the mechanical line (where plutonium is handled in metallic form) and exhausts it via the 291-F stack.² In System I, samples were taken of unfiltered cabinet air from the fifth and sixth levels

FIGURE 1
EXHAUST SYSTEMS FROM JB-LINE

* Work done under Contract No. AT(07-2)-1.

(Sampling Points 29 and 30, respectively), of filtered air from both locations (Sampling Point 27), and of unfiltered room air from the fifth level (Sampling Point 23), and of air at the 156-foot level of JB-Line stack (Sampling Point 28). In System II, samples were taken of mechanical line air from just beyond the first high-efficiency, particulate air (HEPA) filters located in back of the cabinets (Sampling Point A or 31); of the combined air from the mechanical line, air sample exhaust, furnace off-gas vessel vent, process vacuum system, and air dryer system after the second HEPA filter (Sampling Point B or 26); of the air leaving the sand filter which also contained air from the support laboratory off-gas system of Building 772-F, the fuel dissolving and extraction process vessel vent system and Building 221-F canyons containing the process vessels (Sampling Point C); and of air from the 50-foot level in the 291-F stack where air from the sand filter mingles with that from the uranium recovery A-Line and other sources (Sampling Point D). Air was sampled almost continuously at all locations (except at Sampling Point A) during June 1975 for System I and October 1975 for System II. The level of radioactivity at Sampling Point A was so high that samples were collected only during the first two days.

Only 22 particles could be found on filters used at Sampling Point C and D during October 1975. These points were sampled again from the middle of May to the end of September 1977 with the collection of 163 additional particles. Thus, a total of 121 particles were analyzed from System I (16 from sampling point 23; 68 from point 29; and 38 from point 30) and 417 from System II (125 from Sampling Point A; 107 from Point B; 114 from Point C; and 71 from Point D). These figures do not include 20 particles which contained no elements with atomic numbers greater than 9 and were assumed to be organic.

Methods and Materials

Particle Collection

Particles were collected by drawing a fraction of exhaust air through membrane filters. These filters were polycarbonate films 47 mm in diameter with 0.1- μ m diameter pores supported in a polycarbonate aerosol holder.* Air was drawn through the holder by a small diaphragm pump at a rate of four liters per minute to give a face velocity at the filter of 3.8 cm/sec. Since samples were collected from exhaust ducts having varying linear velocities, the sampling technique was anisokinetic. At the above sampling flow rate, the total efficiency for particle collection by the processes of impaction, diffusion, and interception, calculated according to Spurney,³ is 100% for all particles with diameters of 0.001 μ m (the diameter of gas molecules) or larger.

Arrangement of the air sampling system is shown in Figure 2. To determine the fraction of the exhaust sampled, integrated air flow was measured with a dry type test meter** in series with the diaphragm pump. When nitrogen dioxide was present, exhaust gas was passed through two gas drying towers between the filter and the pump. The first tower contained indicating *Drierite*[†] to remove moisture from the air and save the *Ascarite*^{††} in the second tower. The self-indicating

FIGURE 2
ARRANGEMENT OF SAMPLE COLLECTION EQUIPMENT

* The aerosol holders and membrane filters were produced by Nuclepore Corporation, Pleasanton, California, and obtained from them or Bio-Rad Laboratories, Richmond, California.

** Manufactured by the American Meter Division of Singer.

† Trademark of W. S. Hammond Drierite Company.

†† Trademark of Arthur H. Thomas Company.

Ascarite, in turn, absorbed nitrogen dioxide to protect the pump and the dry test meter. A small flowmeter was mounted on the exhaust side of the dry test meter to give an indication of the instantaneous flow rate through the system. Air from the meter was fed back into the exhaust system to prevent its release to the service area.

Film Preparation

Figure 3 shows the procedure for converting the particle-containing filter membrane to a polycarbonate film. After air was sampled, the radioactivity retained on each filter was measured before it was handled in the laboratory. Each filter was then dissolved in a 40% (v/v) solution of 1,2-dichloroethane in dichloromethane.

The clear polycarbonate solution containing the particles was poured onto a clean, 50-mm (two-inch) square glass plate. One edge of a second 50-mm square glass plate was used to spread the solution evenly over the surface of the first plate. A 50-mm square acrylic support with a 45-mm diameter hole was placed on top of the wet film. The support and plate combinations were placed in covered petri dishes for 16 hours while the films continued to dry.

The glass plates were then removed by dipping the support and plate combinations in distilled water and prying the supports from the glass with tweezers.

Fission Fragment Track Production

The cast polycarbonate film was irradiated in a thermal neutron fluence of about 9×10^{14} neutrons per cm^2 . Films were arranged for irradiation by stacking the supports on top of each other thus sandwiching each film between two supports. Wrapped with each stack were preweighed Type 302 stainless steel disks. The induced radioactivity from 27-day ^{51}Cr in these disks was later measured to determine the thermal neutron fluence to which the particles were exposed.

The packaged stacks were irradiated in a light water-cooled, enriched uranium-fueled standard pile with graphite reflectors.⁴

To make the fission fragment tracks visible with an optical microscope, the polycarbonate film was etched for ten minutes in 6N NaOH at 52 to 55°C.

Alpha Track Production

To identify the fissionable material in each particle, the alpha particle emission rate was measured by coating the polycarbonate film with Kodak Type NTB nuclear-track emulsion (Kodak catalog number 164 4425). Under darkroom lighting, a 4-oz jar of emulsion was immersed in a water bath maintained at 40°C until the emulsion melted. The polycarbonate films were coated with emulsion by holding the supports containing the films vertically by one corner and dipping them into the clear molten emulsion for about one second. The coated films were then maintained at 28°C and about 80% relative humidity until the emulsion cooled and gelled (about 30 minutes).

To determine the alpha particle emission rate for each aerosol particle, the polycarbonate films were stored for one week before being developed. Spun

FIGURE 3
PROCEDURE FOR PREPARING POLYCARBONATE FILMS

aluminum *Desiccators** containing 60 grams of indicating *Drierite* were used to contain the films during this exposure. These were stored in a refrigerator between 4 and 5°C.

At the end of the exposure period, the alpha particle tracks in the emulsion were developed and all substances other than tracks were removed from the emulsion.

The film was prepared for track counting by placing the acrylic support on a 50-mm square, 1.0-mm thick polycarbonate block. Those particles having tracks were located under a microscope using a magnification of 105X. When found, the fission fragment and alpha particle tracks were counted using a magnification of 1000X.

This identification procedure was used to distinguish particle-bound plutonium from uranium. Highly enriched uranium mixtures will give a number of fission fragment tracks comparable to that of the plutonium mixtures. Even if there should be enough uranium to produce fission fragment tracks, mixtures of these isotopes would not produce alpha particle tracks. One femtocurie (fCi) of ^{239}Pu will produce about 22 alpha particles in a week and, when irradiated with a fluence of 8.64×10^{14} thermal neutrons/cm², will produce about 40 fission fragments. In a mixture of low-irradiation plutonium, the number of fission fragments produced will be increased to 53 with between 28 and 33 alpha particles depending on the age of the mixture. Only about half of these particles will produce tracks, yet this radiographic technique is much more sensitive than electron microprobe analysis, which is not sensitive to less than 10 fCi¹.

Particle Isolation

After a particle had been identified and the tracks counted, the particle was excised from the film in a polycarbonate square. At a magnification of 105X, two parallel cuts were made through the emulsion-coated film on either side of the particle using an ultra microlance. The film was then rotated through 90° and two more cuts made forming a square (see Figure 4a). The cut square was then probed in one corner by a tungsten needle, lifted from the film, and placed on a glass microscope slide (see Figures 4b, 4c, and 4d).

The emulsion layers were then removed from the polycarbonate square by placing a cover glass on top of the square. Water was introduced between the cover glass and slide using a glass microbrush. The emulsion was then removed by gently moving the cover glass a few mm from side to side (see Figure 4e); this rolled the swollen emulsion from the surface of the film, but not from the fission fragment tracks themselves. The cover glass was carefully lifted from the glass microscope slide, taking care not to lose the polycarbonate square containing the particle.

Particle Mounting

To mount a particle, the polycarbonate square was placed in a selected grid location on a beryllium sample mounting block** (Figure 4f). These sample mounting blocks were 25 mm in diameter and 13 mm thick and fit the standard electron microprobe sample holders, which grip the sides and provide the necessary electrical contact. The top surface of the block was highly polished and contains a grid

* Trademark of Fisher Scientific Company.

** Walter C. McCrone Associates, Inc. catalog number XIII-403.3.

FIGURE 4
PROCEDURE FOR MOUNTING PARTICLE FOR FISSIONABLE MATERIAL IDENTIFICATION

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network of 1-mm squares inscribed on the surface. The squares were numbered in mirror image fashion both vertically and horizontally through the center.

The polycarbonate square was then dissolved and washed back from the particle using dichloroethane from a glass microbrush. Dichloroethane from the brush was dispensed on the beryllium block just in front of the polycarbonate square until the square was engulfed in the solution. The microbrush was then used to push the solution back from the particle. Gelatin replicas of the fission fragment tracks remained with the particles.

A Polaroid picture of each particle was made at a magnification of 556X to identify the particles after the gelatin had been removed.

The gelatin with each particle was oxidized by exposure to an oxygen plasma for three hours in a low-temperature asher.*

To maintain control of particles after the gelatin track replicas were oxidized, each particle was located and photographed again using Polaroid film and a magnification of 556X. An arrow was marked on the film pointing to the particle, so there would be no mistake in what was intended for analysis.

The size of each particle was estimated from these Polaroid pictures taken after oxidation of the completely denuded particles. An average of the smallest and largest dimensions of the photographed particle were measured in mm and divided by the magnification.

Analysis

The plutonium-bearing particles, mounted on beryllium blocks, were analyzed with an electron microprobe. The analyses were made at Arizona State University in Tempe, Arizona, with a Cemea MS46 electron microprobe equipped with four crystal, wave-length-dispersive spectrometers (take-off angle of 18°) and an energy-dispersive analyzer.

Analytical data included measurements of x-ray intensities and estimates of particle size and shape. These data, along with estimated average densities, were used in the FRAME computer program⁵ as modified for particles work by Armstrong.⁶ These calculations gave the composition of each particle in both elements and oxide weight percents. Oxygen was not measured as such; elements were simply assumed to be present in the oxide form.

Grouping of Data by Enrichment Factors

The results were expressed in terms of "enrichment factors" (dimensionless ratios of elemental concentrations), which enabled the intercomparison of the compositions of plutonium-bearing particles with other atmospheric aerosols and the intracomparison among particles collected from different sampling points. A definition of enrichment factors and an explanation of their development and application in this work is given in the Appendix to this report.

To compare the chemical composition of the particles collected from Systems I and II with each other and with the average for global crustal aerosol, the

* Manufactured by International Plasma Corporation.

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particle analyses were grouped according to the level of the enrichment factors. Four groups were established for each element using the elemental concentration data in Table A-1 of the Appendix. The first group contained those particles which contained no detectable amounts of the element sought. The second group contained detectable amounts with enrichment factors less than one standard deviation below the geometric mean enrichment factor, $\bar{EF}_g/s_g$. The third group contained particles with enrichment factors between the lower and upper limits of one standard deviation from the geometric mean enrichment factor, $\bar{EF}_g/s_g$ and $\bar{EF}_g \cdot s_g$, respectively. The fourth group contained enrichment factors greater than one standard geometric mean enrichment factor, $\bar{EF}_g \cdot s_g$. The third column of Table I gives the percent of the particles analyzed which gave positive analyses for each element. The fourth, fifth, and sixth columns of Table I contain the percent of those having positive analyses which had enrichment factors less than, between, and more than the lower and upper limits of the geometric standard deviation.

To compare the chemical composition of particles collected at the various sample points in System II with each other and global crustal aerosol (Table A-I), this process was repeated and the results are listed in Table II.

Particles having no detectable amounts of an element were not counted with those with enrichment factors less than the lower limit for the geometric standard deviation (s_g) because there can be no zero or negative concentration of enrichment factor values in log-normal frequency distributions. Thus, the size of the three groups are expressed as the percent of the particles giving positive analyses, rather than the percent of the total number of particles.

Particle Evaluation by Size

In this study, particles were selected for analysis on the basis of their being recognizable by their radiating fission fragment tracks under a 160 X dissecting microscope used for their excision from the polycarbonate film. The film was first scanned and the location of the particles marked. A proportion of the particles were then excised without regard for the number fission fragment tracks present. Thus, there was some bias against particles having less than five tracks. The selection of particles for analysis, however, was not biased by physical size. The size of the particles was not measured until after the particles had been mounted and the polycarbonate film containing the tracks dissolved. Since the distribution of the number of tracks per particle appears to be log normal, the size distribution of the analyzed particles is indicative of the size distribution of particles in the aerosol carrying most of the plutonium.

Cumulative frequency plots were constructed for particles from Systems I and II. Particles in each system were first ranked in order of their approximate diameter in μm from the smallest to the largest. A list of the number of particles having successively larger diameters was made. A cumulative total of the number of particles at increasing diameter segments was calculated and then normalized by dividing by the total number of particles from each system. This gave the fraction of the particles having a diameter equal to or smaller than any particular diameter. Table III lists the particle diameters in μm ; and, in Columns 2, 3, 4, 5, and 6, the fraction of the particles having diameters equal to or less than each diameter measured in System I and Sampling Points A, B, C, and D in System II, respectively. These fractions are also plotted on the logarithmic probability graph given in Figure 5.

For comparison, a cumulative frequency plot was also made of the size distribution of particles in natural atmospheric aerosols.

FIGURE 5
SIZE DISTRIBUTION PLOTS FOR NATURAL AND COLLECTED PARTICLES

Table I. Comparison of Analyses of Particles From Systems I and II.

Element	System	Positive Analyses, %	% of Positive Analyses ^a		
			Less Than ^b	Within ^c	Greater Than ^d
Si	I	100	47	24	29
	II	99	29	30	41
Al	I	84	0	100	0
	II	88	0	100	0
Fe	I	93	14	35	51
	II	79	36	33	31
Ca	I	70	53	30	17
	II	52	41	40	19
Na	I	70	13	72	15
	II	54	8	81	10
K	I	90	56	30	14
	II	63	35	41	24
Mg	I	51	24	59	17
	II	39	38	52	10
Ti	I	74	20	17	65
	II	31	12	13	76
P	I	1	0	17	83
	II	12	4	8	88
Ba	I	0.5	0	0	100
	II	0.5	0	0	100
S	I	17	47	47	5
	II	70	28	60	13
Cl	I	34	13	67	21
	II	40	2	82	16
Cr	I	53	0	18	82
	II	29	0	9	91
Ni	I	56	2	25	73
	II	9	0	3	97
Zn	I	64	4	41	55
	II	45	5	52	43
Co	I	1	0	0	100
	II	0.2	0	0	100
Sc	I	36	12	37	51
	II	7	6	29	65
W	I	1	0	0	100
	II	0.5	0	0	100
Cd	I	0.2	0	0	100
	II	0.2	0	0	100

a. The percent of the positive analyses less than, within, and greater than one geometric standard deviation of the global geometric mean enrichment factor.

b. $EF < EF_g/s_g$.

c. $EF_g/s_g \leq EF \leq EF_g \cdot s_g$.

d. $EF > EF_g \cdot s_g$.

Table II. Comparison of Analyses of Particles From Sampling Points A, B, C, and D of System II.

Element	Sampling Point	Positive Analyses, %	% of Positive Analyses ^a		
			Less Than ^b	Within ^c	Greater Than ^d
Si	A	99	35	33	32
	B	98	8	24	69
	C	100	36	31	33
	D	99	40	31	29
Al	A	79	0	100	0
	B	94	0	100	0
	C	89	0	100	0
	D	96	0	100	0
Fe	A	98	31	22	46
	B	100	40	39	21
	C	58	33	41	21
	D	49	46	34	20
Ca	A	56	20	44	36
	B	77	54	38	9
	C	41	45	40	15
	D	27	53	32	16
Na	A	55	18	60	22
	B	90	4	94	2
	C	39	5	82	14
	D	24	6	94	0
K	A	76	20	48	31
	B	73	46	44	10
	C	55	35	32	33
	D	37	54	27	19
Mg	A	63	33	58	9
	B	48	35	55	10
	C	17	47	42	11
	D	21	60	27	13
Ti	A	42	12	6	83
	B	27	10	24	66
	C	30	14	11	74
	D	15	9	18	73
P	A	2	0	50	50
	C	3	0	0	100
	D	1	0	0	100
Mn	A	7	13	0	88
	B	30	3	9	88
	C	5	0	0	100
	D	6	0	25	75
Ba	A	1	0	0	100
	B	1	0	0	100
S	A	58	30	54	17
	B	93	21	69	10
	C	66	24	61	15
	D	61	47	44	9

Table II., Continued

Element	Sampling Point	Positive Analyses, %	% of Positive Analyses ^a		
			Less Than ^b	Within ^c	Greater Than ^d
Cl	A	43	4	47	49
	B	72	1	99	0
	C	27	0	97	3
	D	10	14	86	0
Cr	A	27	0	6	94
	B	58	0	15	85
	C	13	0	0	100
	D	14	0	0	100
Ni	B	27	0	3	97
	C	4	0	0	100
	D	7	0	0	100
Zn	A	53	14	35	51
	B	88	0	69	31
	C	22	4	24	72
	D	6	0	75	25
Co	B	5	0	0	100
Sc	C	1	0	0	100
Cu	A	22	7	33	59
	B	3	0	0	100
	C	1	0	0	100
W	A	1	0	0	100
	B	1	0	0	100
Cd	D	1	0	0	100

a. The percent of the positive analyses less than, within, and greater than one geometric standard deviation of the global geometric mean enrichment factor.

b. $EF < \overline{EF}_g / s_g$.

c. $\overline{EF}_g / s_g \leq EF \leq \overline{EF}_g \cdot s_g$.

d. $EF > \overline{EF}_g \cdot s_g$.

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Table III. Comparison of Size Distributions of Particles From Systems I and II With Natural Aerosols^a.

Diameter (D), μm	Fraction With Diameter $\leq D$					Natural Aerosol
	System I	Sampling Point A	Sampling Point B	Sampling Point C	Sampling Point D	
0.4	0.03			0.01	0.01	
0.5	0.04			0.02		
0.9	0.07			0.04	0.06	
1.1				0.09	0.08	0.25
1.2				0.10		0.42
1.4				0.11		0.64
1.7				0.14	0.11	
1.8	0.28	0.02		0.17		0.83
2.2	0.30			0.32	0.21	0.91
2.5				0.34	0.23	
2.7	0.35	0.04	0.01	0.37	0.24	0.949
3.0				0.42	0.31	
3.3				0.43	0.32	
3.6	0.53	0.10	0.06	0.46	0.34	0.979
3.9		0.11				0.983
4.0			0.07	0.51	0.38	
4.4				0.52	0.41	
4.5	0.54	0.13	0.10			0.989
5.0			0.11	0.55	0.48	
5.4	0.62	0.20	0.18	0.60		0.994
5.8			0.20	0.59		
6.1			0.22	0.61	0.56	
6.3		0.23	0.26			0.996
6.7			0.27	0.64	0.58	
7.0				0.67		
7.2	0.67	0.33	0.35	0.68		0.997
7.4				0.68		
7.8			0.36	0.70		
8.0	0.68	0.34	0.37	0.71	0.59	0.998
8.6			0.39		0.63	
9.0	0.75	0.40	0.46	0.74	0.69	0.999
10.0		0.41	0.48	0.78	0.75	
10.8	0.79	0.44	0.60	0.81		
11.7		0.46	0.61	0.82	0.79	
12.6	0.83	0.54	0.62	0.83	0.80	1.000
13.5		0.55	0.66		0.82	
14.4	0.84	0.58		0.89		
14.9			0.67		0.83	
16.2	0.88	0.61	0.71			
17.1		0.62		0.89	0.89	

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Table III., Continued

Diameter (D), μm	Fraction With Diameter $\leq D$					Natural Aerosol
	System I	Sampling Point A	Sampling Point B	Sampling Point C	Sampling Point D	
18.0	0.92	0.64	0.75	0.90		
20.7		0.70	0.81	0.91	0.92	
21.6	0.93	0.71	0.82			
23.4		0.74	0.85	0.930	0.930	
24.3		0.75	0.86			
25.2	0.94	0.78	0.87		0.972	
26.9	0.95	0.81	0.91	0.939		
27.9		0.83	0.92			
28.8			0.93	0.956	0.986	
30.6		0.86	0.935			
31.5		0.87		0.974		
32.4		0.88	0.944			
33.5		0.89	0.963			
34.2	0.959	0.94	0.972	0.982		
35.1				1.000	1.000	
36.0	0.975	0.944	0.981			
39.6		0.968	0.991			
41.4	0.983		1.000			
50.4	0.992					
53.9		0.992				
59.4	1.000					
62.9		1.000				

a. The percent of the positive analyses less than, within, and greater than one geometric standard deviation of the global geometric mean enrichment factor.

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A very simple function that has been used extensively in atmospheric research to express particle size distribution in both natural and polluted atmospheres is

$$\frac{dN}{dD} = aD^{-b} \quad (1)$$

where N is the number concentration or total number of particles per unit volume having diameters from the lower limit of definition of aerosols up to diameter D in μm . From the relationships

$$dD = D d(\ln D) \quad (2)$$

and

$$\ln D = \ln 10 \cdot \log D \quad (3)$$

the more useful expression

$$\frac{dN}{d(\log D)} = (\ln 10)aD^{-c} \quad (4)$$

is obtained where $c = b - 1$, and $dN/d(\log D)$ is called the number distribution. Junge⁷ found c to be about 3 over the size range $-0.7 < \log D < 1.5$ or $0.2 < D < 32 \mu\text{m}$. Integrating the first equation between D_0 and D ($D_0 < D$) gives

$$N = \left[\frac{aD^{-c}}{c} \right]_{D_0}^D = \frac{a}{3} \left[\frac{1}{D_0^3} - \frac{1}{D^3} \right] \quad (5)$$

Instead of expressing the distribution as the number of particles per unit volume, it can be expressed as a fraction, F, of the total number of particles or

$$F = \frac{N}{N_T} = 1 - \left[\frac{D_0}{D} \right]^3 \quad (6)$$

where N_T is the total number of particles when $D = \infty$, and $N_T = a/3D_0^3$. To obtain a reasonable distribution, only those particles which could be easily seen with an optical microscope were included. Thus D_0 was assumed to be $1 \mu\text{m}$, and Equation 6 can be expressed as

$$F = 1 - \frac{1}{D^3} \quad (7)$$

The frequency distribution for natural aerosols with particles diameters between $1 \mu\text{m}$ and D, calculated from this expression, is given in Column 7 of Table III and plotted in Figure 5.

To see how closely the distribution of particle diameters resembles a log-normal distribution, the assumption was made that the observed diameters represent a sample of a population having a log-normal distribution. The geometric mean diameter, $\bar{D}_g$, and geometric standard deviation, s_g , were calculated from these data using equations similar to those given earlier for the geometric mean enrichment factor and geometric standard deviation. These values are given in Table IV. Values for the upper 68.27% limit for the diameters were calculated from the product of $\bar{D}_g$ and s_g . The best fit log-normal probability curves were plotted on the

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logarithmic probability graph in Figure 5 by drawing straight lines through co-ordinates for $\bar{D}_g$ and $\bar{D}_g \cdot s_g$ on the 50.00 and 84.14% cumulative percent abscissae, respectively.

To determine the degree of asymmetry, the skewness (SK) of these frequency distributions was calculated using the relationship

$$SK = 3 \left(\frac{\ln \bar{D}_g - \ln d_{med}}{\ln s_g} \right) \quad (8)$$

where d_{med} = the median diameter. A perfect log-normal distribution has a skewness of zero. If a distribution has a higher tail to the right than to the left, it is positively skewed.

Table IV. Distribution of Particle Diameters in Systems I and II.

System	Sample Location	Data Points, N	Geom Mean Diameter, $\bar{D}_g$	Geom Std Deviation, s_g	Skewness, SK
I		121	4.64	2.92	0.71
II	A	125	12.27	2.24	0.04
II	B	107	10.82	1.93	0.34
II	C	114	4.48	2.75	0.37
II	D	71	5.43	2.69	0.23

Particle Evaluation by Plutonium Content

Another characteristic studied was the distribution of plutonium among the particles as indicated by the observed number of fission-fragment tracks in the surrounding polycarbonate.

The track distribution among particles from both systems was evaluated in the same way as the particle diameters. The fraction of the particles with the number of tracks equal to or less than a selected number, T, are given for Sampling Points A, B, C, and D in Table V. Figure 6 is a logarithmic probability plot of cumulative percent of particles from each of these sampling points. Figure 7 is a similar plot for particles from four locations in System I. The calculated geometric mean for the number of fission-fragment tracks per particle. The geometric standard deviation, and the skewness for particles from each sampling point are given in Table VI. Best fit log-normal probability curves for each distribution are plotted in Figures 6 and 7. For the comparison of the track distributions for particles from the various sampling points in System I with those from System II, the probability curve for the track distribution for particles from Sampling Point A in System II is plotted with the distributions from System I in Figure 7.

$$* 50.00 + \frac{68.27}{2}$$

FIGURE 6
DISTRIBUTION OF THE NUMBER OF TRACKS PER PARTICLE FOR
PARTICLES COLLECTED FROM SAMPLING POINT A, B, C, AND D IN SYSTEM II

FIGURE 7
DISTRIBUTION OF THE NUMBER OF TRACKS PER PARTICLE
FOR PARTICLES COLLECTED FROM THE MECHANICAL LINE
(SAMPLING POINT A), WET CABINETS, AND ROOM AIR

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Table V. Distribution of Fission Tracks Among Plutonium-Bearing Particles Collected From Sampling Points A, B, C, and D.

Number of Tracks	Fraction With Tracks $\leq T$			
	Sample Point A	Sample Point B	Sample Point C	Sample Point D
1	0.04			
2	0.05			
3	0.09			
4	0.13			0.01
5	0.15		0.06	0.03
6	0.19	0.01	0.09	
7	0.21		0.11	
8	0.26		0.13	0.06
9	0.31	0.03	0.15	0.10
10	0.34	0.04	0.20	0.13
11	0.36		0.24	0.21
12	0.38		0.26	0.25
13	0.40	0.05	0.32	0.28
14	0.44	0.07	0.38	0.32
15	0.45	0.07	0.44	0.42
16	0.47	0.08	0.48	0.46
17	0.50	0.11	0.49	0.58
18	0.51	0.15	0.54	0.63
19	0.54	0.17	0.56	0.69
20	0.59	0.21	0.59	0.70
21	0.60	0.22	0.63	0.72
22	0.63	0.26	0.66	0.75
23	0.64	0.31	0.70	0.77
24	0.68	0.37	0.72	0.82
25	0.70		0.75	
26	0.72	0.39	0.78	
27	0.74	0.40	0.82	
28	0.75	0.44	0.87	0.83
29	0.76	0.45	0.89	0.85
30	0.78	0.48	0.90	0.86
31	0.79	0.50	0.92	0.89
32	0.81	0.52	0.93	
33	0.82	0.56	0.947	0.92
34	0.84	0.58		0.93
35	0.85	0.59		0.944
36	0.86	0.60	0.956	
37		0.61	0.965	0.958
38	0.87	0.62		
39	0.88			
40	0.89	0.63		0.972

Table V., Continued

Number of Tracks	Fraction With Tracks $\leq T$			
	Sample Point A	Sample Point B	Sample Point C	Sample Point D
41		0.65		
42	0.90	0.66		
43		0.68		
44	0.91	0.69		
46	0.91			
47		0.73		
48	0.92	0.75		
49	0.93	0.76		
50	0.945	0.77		0.986
51	0.950			
52		0.78		
54	0.955		0.991	
55		0.80		
57		0.81		
58		0.84		
59		0.85		
60	0.960	0.89		
63		0.90		
65			1.000	
68		0.91		
70		0.92		
72	0.965			
73		0.93		
75	0.970			
80	0.980	0.93		1.000
82		0.953		
84		0.972		
98		0.981		
100	0.990	0.991		
150	0.995	1.000		
200	1.000			

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Table VI. Distribution of Fission Tracks Among Plutonium-Bearing Particles from Various Sources in Systems I and II.

Source	Data Points, N	Geom Mean of No. of Fission Tracks, $\bar{T}_g$	Geom Std Deviation, s_g	Skewness, SK	Geom Mean Activity Particle, fCi
<u>System I</u>					
Unfiltered 5th Level Wet-Cabinet Air	15,987	3.76	2.56	-0.20	0.09
Unfiltered 6th Level Wet-Cabinet Air	7,042	3.32	2.99	-0.51	0.08
5th Level Room Air ^a	53	1.00	8.40	-0.98	0.02
Filtered Wet-Cabinet Air ^a	98	0.87	4.14	-0.29	0.02
<u>System II</u>					
Sampling Point A Air	200	14.74	2.69	-0.43	0.36
Sampling Point B Air	107	32.38	1.78	0.23	0.79
Sampling Point C Air	114	16.50	1.75	-0.22	0.40
Sampling Point D Air	71	17.01	1.65	0.24	0.41

a. Values determined graphically.

Discussion

The most abundant elements in average crustal rock (and soil) are oxygen (46.60%), silicon (27.72%), aluminum (8.13%), iron (5.00%), calcium (3.63%), sodium (2.83%), potassium (2.59%), magnesium (2.09%), and titanium (0.44%).⁸ With the exception of oxygen, which was not detected by electron microprobe analyses, these elements are also found in most inorganic particles (Tables I and A-1). This supports the idea that most plutonium-bearing particles are airborne crustal material to which minute quantities of plutonium have become attached.

Of particular interest is the quantity of ²³⁹Pu contained on these particles. One femtocurie (1 fCi = 10⁻¹⁵ Ci) of ²³⁹Pu irradiated under the conditions described here should produce 41 fission-fragment tracks. The minimum detection limit for electron microprobe analysis of plutonium is about 0.2 picograms or about 10 fCi of ²³⁹Pu,¹ which is equivalent to 410 fission-fragment tracks. Because of this relatively low sensitivity of electron microprobe analysis, plutonium could be detected by this method in only one of the 558 particles selected for analysis, even though all the particles produced fission-fragment tracks. This single particle was a small, 1- μ m-diameter particle, collected from unfiltered wet-cabinet exhaust. It contained 73% PuO₂ by weight (equivalent to 170 fCi of ²³⁹Pu) in combination with Fe₂O₃ and mica.

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Of the major crustal elements listed in Table I, silicon and iron were the most ubiquitous being found in most particles. The enrichment factor distribution for these elements, however, does not fall within the log-normal distribution for crustal material. For the enrichment factors of an element to match the log-normal distribution of crustal material in aerosols, there should be about 16% of the enrichment factors of less than one geometric standard deviation, 68% within one geometric standard deviation of the mean, and another 16% above one geometric standard deviation. This lack of conformity may result from the low values for the geometric standard deviations of the enrichment factors for these elements in aerosols.

Only the enrichment factors for sodium and chlorine fall within the log-normal distribution for crustal material. This may be due to the relative high solubility of compounds of these elements and, in the case of chlorine, the high value for the geometric standard deviation.

Particles from System I contain a greater variety of elements than those from System II and thus all but four elements are contained on a higher proportion of particles from System I than from System II. The most striking example was nickel. While 56% of the particles from System I contained nickel, only 9% of those in System II did. The major crustal elements (those in Table A-1 comprising 0.4% or more of crustal material) are contained on over half the particles from System I and with the exception of magnesium in particles from sampling Points C and D and titanium are also contained on over half the particles from System II. Some of the minor elements (those comprising 0.1% or less of crustal material) are present in over half the particles, viz, nickel, chromium, and zinc in particles from System I and sulfur, chromium, and zinc in particles from sampling point B of System II. The chromium and nickel may have come from the 304L stainless steel alloy of cabinets and exhaust ducts or the *Hastelloy*-C alloy in the wet cabinets. However, few of the particles contained the proper ratio of chromium-to-nickel found in either alloy. Also, if *Hastelloy*-C contributed the nickel in the particles, some molybdenum should also have been detected.

Of the elements which are present on less than 10% of the particles, all but copper on particles from System II have high enrichment factors. This indicates that the minor constituents of crustal material are not uniformly distributed among particles but are concentrated on a few particles where they represent a major constituent.

The plutonium-bearing particles were larger than natural aerosol particles collected at relatively low altitude (<2.3 km) as seen in Figure 5. Those particles collected from sampling points A and B of System II were larger than those from System I, with geometric mean diameters two or three times those of particles from other locations.

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Particles from all parts of System II also contained on the average more plutonium per particle than those from System I. As seen in Table VI, the geometric mean of the activity in System I, containing only HEPA filters, was a factor of 10 to 100 less than that of System II, which uses a large sand filter before the air is exhausted to the atmosphere. The geometric mean of measured activity per particle released to the atmosphere was 0.4 fCi.

A comparison of the mean diameters of particles collected from different sampling points, given in Table IV, with the mean number of fission fragment tracks for particles from the same location, given in Table VI, indicate a possible relationship between particle size and plutonium content. Correlation coefficients between the cube of the particle diameter and the number of fission fragment tracks from each particle from sampling Points B, C, and D were calculated. These are given in Table VII. These coefficients differ significantly from that expected from a random sample from a population of paired variables having a correlation coefficient of zero. Thus, even though the points on a plot of particle diameter cubed versus number of fission fragment tracks appears scattered, there is a significant correlation between the quantity of plutonium in particles collected from Sampling Points B, C, and D in System II and the particle volume. (Tracks with particles collected at other sampling points, where only ^{239}Pu could be found, were counted but not recorded for each particle. Only where a ratio of alpha particle to fission fragment tracks was needed to distinguish plutonium bearing particles from those having other fissionable materials were the track counts recorded).

Table VII. Correlation and Coefficient of Alienation for the Cube of the Diameter and the Number of Fission Fragment Tracks for Particles From Sampling Points B, C, and D of System II.

Sampling Point	Number of Particles	Correlation Coefficient
B	107	0.69
C	114	0.29
D	71	0.36

Summary

Plutonium-bearing particles collected from a nuclear reprocessing plant exhaust were found to be aggregates of crustal material. High enrichment factors for metals were evidence of the anthropogenic nature of some particles. The radioactivity of the plutonium associated with individual particles was very small (~ 0.4 fCi).

The results of this work indicate the need for further study of the behavior of these plutonium-bearing particles following their release to the atmosphere and subsequent interaction with the environment.

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Appendix: Use of Elemental Enrichment Factors to Express Particle Compositions

Background

Two recent developments in aerosol studies have provided valuable tools for the analysis of particle composition data. The first is the use of ratios of elemental concentrations called "enrichment factors" to compare aerosol compositions. Begun in the early seventies, this technique has gained wide acceptance in the last few years⁹⁻¹³. The second development is the availability of data on the composition of natural aerosols. Rahn⁹ published a compilation of 104 data sets of trace elements in aerosols along with the geometric mean and geometric standard deviation of the enrichment factors for each of the elements. These data sets were from sampling sites ranging from highly industrialized temperature zones to the tropics and poles, and represent all continents except South America, as well as various marine locations. As a framework from which to view much of the order in atmospheric aerosols, Rahn used the concept of aerosol-crust enrichment factors for the elements. This concept has been applied to analyzing data collected in this study to provide for (a) the intercomparison of the compositions of plutonium-bearing particles with atmospheric aerosols compiled by Rahn and (b) the intracomparison among particles collected from different sampling points.

Microprobe Analyses of Particles

To be comparable, results of microprobe analyses must be expressed as elemental ratios. The reason for this is that not all elements which may be present in an aerosol are detected by microprobe analysis. The microprobe used in this study is quantitative only for elements with atomic numbers greater than 10. It is only semi-quantitative for oxygen (the most abundant element in crustal material) as well as other major elements of low atomic number such as hydrogen, fluorine, and carbon. Atmospheric aerosols are known to contain in addition to elements and oxides, carbonaceous material such as sooty carbon and organics and water-soluble ionic material such as sulfate, nitrate, and ammonium ions. Thus elemental weight percents, normalized to 100 based on the elements detected cannot be compared. Even the addition of a hypothetical oxygen concentration, calculated on the supposition that all elements are present as oxides of known valence, will still not account for the organic fraction of particles. However, a ratio of the concentrations of one element to another will normally be relatively unaffected by the concentrations of other elements which may be present and thus can be used for comparisons even when a complete analysis of all the elements in an aerosol or single particle is not available.

Enrichment Factors

A dimensionless ratio of elemental concentrations, called the enrichment factor, has been defined as

$$EF(X) = \frac{(X/Ref)_{\text{aerosol}}}{(X/Ref)_{\text{source}}} \quad (A-1)$$

where $EF(X)$ is the enrichment factor of element X in an aerosol relative to some source material. X/Ref is the ratio of the concentration of element X to the concentration of the reference element, Ref , in both the aerosol and the source material.

Source Material

Elemental ratios in aerosols or in single particles are normalized by dividing them by ratios of the same elements in a standard source material to obtain the enrichment factors. If a particle is composed of the same material as the source, the enrichment factor will be 1.00 for all elements. If the ratio of an element to the reference element is greater or less than the same ratio in the source material, the enrichment factors will be greater or less than 1.00, and the particle is said to be either enriched or depleted, respectively, in that element.

The most commonly-used crustal source material for continental enrichment-factor calculations is globally-averaged crustal rock. (For marine enrichment-factor calculations, sea salt is used.) Because the composition of plutonium-bearing particles are compared with data reported by Rahn,⁹ the same crustal-rock composition used by him (that reported by Mason)⁸ was selected as the source material composition for this work. Column 2 of Table A-I gives the elemental concentrations in globally-averaged crustal rock for those elements found in plutonium-bearing particles.

Reference Element

Of the various elements which seem to be reliably crust-derived in aerosols, aluminum is generally considered to be the most suitable reference elements. (When sea salt is the source material, the nearly universal choice is sodium.) Aluminum is a major element (81,300 ppm in rock), well-determined by a variety of analytical techniques, and has a minimum of specific pollution sources.

Thus for this work, enrichment factors for element X in most particles were calculated using

$$EF(X) = \frac{(X/Al)_{\text{particle}}}{(X/Al)_{\text{rock}}} \quad (A-2)$$

with aluminum as the reference element and average crustal rock as the source material. However, 18 particles from System I and 48 from System II contained no aluminum. Thus the enrichment factors had to be based on silicon rather than aluminum where

$$EF(X) = \frac{(X/Si)_{\text{particle}}}{(X/Si)_{\text{rock}}} \cdot \frac{(\overline{Si}/Al)_{\text{g aerosol}}}{(\overline{Si}/Al)_{\text{rock}}} = 0.79 \frac{(X/Si)_{\text{particle}}}{(X/Si)_{\text{rock}}} \quad (A-3)$$

(The second set of ratios is the geometric mean of the global aerosol-crust enrichment factor explained in the next section.)

Using these two relationships, the enrichment factors were calculated from the elemental weight percents obtained for 115 particles in System I and 415 particles in System II. Six small (0.5 to 3.6 μm diameter) iron particles in System I and two particles [$\sim 15 \mu\text{m}$ diameter containing K, Cr, and Fe (1:3:3)] from Sample Point A of System II contained neither aluminum nor silicon and were thus not included in the study.

TABLE A-I. Elemental Concentrations in Average Crustal Rock and Geometric Mean Enrichment Factors of Various Aerosols

Element	Conc., ppm	Geometric Mean Enrichment Factors					
		Global EF _g /s _g	Global EF _g	Global EF _g *s _g	Remote Marine EF _g	Remote Conti- nental EF _g	Urban EF _g
Si	277,200	0.62	0.79	1.01	0.7	0.7	0.79
Al	81,300	1.00	1.00	1.00	1.0	1.0	1.00
Fe	50,000	1.05	2.06	4.06	2.5	1.5	2.2
Ca	36,000	1.15	2.84	7.04	8.0	1.5	2.9
Na	28,300	0.64	4.44	30.8	10 ² - 10 ³	0.4	1.81
K	25,900	0.99	1.98	3.98	6.0	1.5	1.63
Mg	20,900	0.64	2.38	8.90	10 ¹ - 10 ²	0.7	2.0
Ti	4,400	1.01	1.39	1.92	1.2	1.2	1.63
P	1,050	0.79	2.63	8.71	-	-	2.6
Mn	950	1.45	3.91	10.5	3.0	2	3.2
Ba	425	2.61	5.50	11.6	-	~2	4.8
S	260	228.0	608.0	1620.0	-	-	490.0
Cl	130	100.0	740.0	5470.0	10 ⁴ - 10 ⁵	40.0	300.0
Cr	100	2.50	8.11	26.3	20.0	6	6.2
Ni	75	8.74	31.9	116.0	100.0	50	10.8
Zn	70	79.7	257.0	832.0	400.0	80	300
Co	25	0.91	3.52	13.6	4.0	1.5	4.6
Sc	22	0.59	1.17	2.34	0.8	0.8	0.60
Cu	55	34.0	102.0	304.0	150.0	20.0	149
U	1.8	0.92	2.87	8.93	-	-	2.87
W	1.5	4.89	19.1	74.3	-	-	11.0
Cd	0.2	274.0	1920.0	13,400.0	5000.0	2000.0	940.0

Comparative Aerosol Data

To compare the elemental composition of plutonium-bearing particles with that of atmospheric aerosols, enrichment factors calculated for elements in these particles were grouped according to data supplied by Rahn⁹ for aerosols. In his report, trace element concentrations in aerosols from 104 published and unpublished data sets were used to calculate enrichment factors. From the enrichment factors in each data set, the geometric mean enrichment factor ($\overline{EF}_g$) and geometric standard deviation (s_g) of the logarithmic frequency distributions of enrichment factors were calculated for each element using the following formulae:

$$\overline{EF}_g = \exp \left[\frac{1}{N} \sum_{i=1}^N \ln EF_i \right] \quad (A-4)$$

and

$$s_g = \exp \left\{ \left[\frac{1}{N-1} \sum_{i=1}^N (\ln EF_i - \ln \overline{EF}_g)^2 \right]^{1/2} \right\}$$

where N = the number of data points

EF_i = the enrichment factor of the i th point.

The geometric mean enrichment factors obtained by Rahn⁹ for 19 elements are given in Table A-1 for global, remote marine, remote continental, and urban aerosols. The geometric means of the global aerosol enrichment factors include data from all points and may be weighted too heavily toward cities, but they can serve as a useful first approximation to a general aerosol. The urban enrichment factors are geometric means for 29 cities. The enrichment factors for remote continental and remote marine areas were read from the enrichment-factor plots and are therefore somewhat subjective.

To obtain the lower and upper limits for 68.27% of the enrichment factors closest to the geometric mean, values for $\overline{EF}_g/s_g$ and $\overline{EF}_g \cdot s_g$, respectively, were calculated using global values. (When describing concentrations at selected statistical levels remote from a mean, the s_g is a multiplier or divider of the $\overline{EF}_g$, whereas its counterpart Gaussian standard deviation functions as an increment to the arithmetic mean. This is a consequence of the fact that multiplying and dividing values is equivalent to adding and subtracting their logarithms.) The results from these calculations are also given in Table A-I.

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