Reports

Plutonium-238 in Fallout

Abstract. *The observed variation in the activity ratio of plutonium-238 to plutonium-239 plus plutonium-240 in rainwater in Japan over the period from 1961 through 1968 seems to indicate that the influence of the plutonium-238 released by the burnup of the nuclear auxiliary power generator (SNAP-9A) became noticeable within about 6 months and that variation in the isotope ratio with time is affected by nuclear debris produced in the latest explosions as well as by the plutonium-238 released from the SNAP-9A generator.*

Measurements of the α-ray spectra of plutonium were made on 22 samples of rainwater collected from 1961 through 1968, in an investigation of the variation of the activity ratios of ^{238}Pu to (^{239}Pu + ^{240}Pu) in rainwater in Japan with time. Similar measurements of the α-ray spectra were also made on highly radioactive fallout particles found and collected on a roof at our laboratory shortly after some Soviet and Chinese nuclear test explosions. All the particles subjected to the measurement were isolated from dust particles, and their diameters were measured. Some showed more than 50 nc of β-activity at the time of collection and measured up to 30 μ in diameter (*1*). Samples of both rainwater and airborne dust are likely to contain old debris in considerable proportion, even though collected shortly after a detonation; therefore analyses of these samples might lead to false conclusions on the compositions of long-lived nuclides in the fresh nuclear debris. Analyses of isolated radioactive particles may avoid such ambiguity. Our results on the rainwater samples and radioactive particles are discussed in connection with the release of ^{238}Pu from the burnup of a SNAP-9A (Systems for Nuclear Auxiliary Power) generator in April 1964.

The radioactive particles or the evaporated residues of the rainwater samples were dissolved by alkali fusion in a platinum crucible; from this solution Pu was separated by solvent extraction with a mixture of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and benzene (*2*), and then electroplated on a stainless steel plate 30 mm in diameter. Alpha-ray spectra were measured by means of a gridded ionization chamber connected to a 512-channel pulse-height analyzer (model ND 120, Nuclear Data, Inc.) (Tables 1 and 2). Figure 1 shows the activity ratios of Pu isotopes in rainwater samples and radioactive particles plotted against the collection times.

High values of the activity ratio of Pu isotopes (0.30, 0.17, and 0.10) were found in radioactive particles from Soviet explosions (Table 2). However, the ratios of radioactive particles from the Chinese explosions of 1964 to 1966 were considerably lower or negligibly low. The ratio of nuclear debris is naturally different from explosion to explosion, depending on the burst conditions and the bomb materials used.

The time variation of the activity ratio of Pu isotopes in Japan rainwater (*R*1–*R*22) is rather well reproduced in Fig. 1, even though our measurements were not based on monthly depositions, but on available rainwater samples. The low ratio obtained on sample *R*1 (0.01 ± 0.02) suggests that the ratio was very low before the reopening of the nuclear test explosions by the Soviets in autumn 1961. The ratio increased abruptly in autumn 1961 (*R*2) and decreased rapidly after the end of the test explosions (*R*3 and *R*4). After the latter half of 1962, however, it again increased, being affected by the nuclear debris produced in the explosions of 1962 by both the United States and the Soviets (*R*5 and *R*6). The ratio decreased rather sharply during 1963, reaching a minimum at the end of 1963, and again increased in the latter half of 1964. The ratio was comparatively constant in the period from the latter half of 1964 until the end of

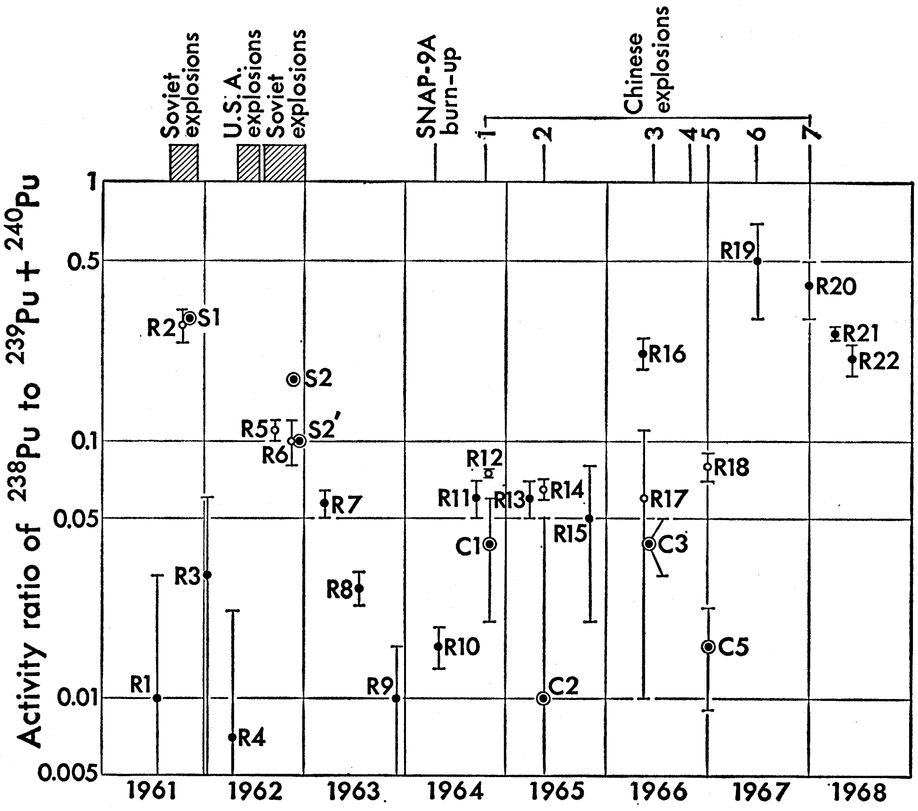

Fig. 1. Activity ratios of ^{238}Pu to (^{239}Pu + ^{240}Pu) in rainwater samples and radioactive particles plotted against time of collection. Open circles represent rainwater samples collected shortly after an explosion and found to contain some fresh nuclear debris; solid circles represent rainwater samples containing no fresh nuclear debris.

1965 and began to increase rather abruptly at the beginning of 1966, again showing a decreasing tendency since the end of 1967.

At present no satisfactory explanation can be given for the rapid decrease in the ratio during the first half of 1962 and during 1963. However, it is presumed that nuclear debris with an activity ratio of Pu isotopes in excess of 0.1 was produced in some of the explosions in 1961 and 1962, but that the ratio in the stratospheric debris as a whole was not increased noticeably. The rapid decrease in the ratio during the first half of 1962 and during 1963 seems to correspond to the subsidence of the tropospheric debris produced abundantly in 1961 and 1962.

Samples *R*11 and *R*12 were collected just before and after the first Chinese nuclear explosion (16 October 1964). The value of the ratio obtained on sample *C*1 (0.04 ± 0.02) suggests that the ratio of the nuclear debris produced in this explosion was rather low. Sample *R*12 contained some fresh nuclear debris, but its concentration of fresh debris was not so high; therefore its Pu content was considered to be mainly the result of old debris. Thus the ratio of *R*12 was nearly equal to that of *R*11. A quite similar situation holds also for samples *R*13 and *R*14, collected before and after the second Chinese explosion (14 May 1965), respectively. The abrupt increase in the ratio observed from late 1964 onward appears to be attributable to the influence of the ^{238}Pu released by the burnup of the SNAP-9A generator. Korsmayer (*3*) estimated that the satellite with the SNAP-9A generator reentered the atmosphere at an altitude of about 46 km over the Indian Ocean in the Southern Hemisphere. Our result seems to indicate that ^{238}Pu from the SNAP-9A generator became noticeable in rainwater in Japan within 6 months.

An abrupt increase in the plutonium ratio occurred in 1966 (*R*16). Samples *R*17 and *R*18 were collected shortly after the third and fifth Chinese explosions, respectively. The abnormally low values of the ratio for these two samples of rainwater may be the result of isotopic dilution by fresh nuclear debris; the low values of the ratio obtained on samples *C*3 and *C*5 sustain this explanation.

Samples *R*19 and *R*20 were collected shortly after the sixth and seventh Chinese explosions, respectively, but their concentrations of fresh nuclear debris were both extremely low. Therefore, the contribution of fresh debris to their Pu content was very low. Thus the ratios of samples *R*19 and *R*20 may be regarded as representative of the ratios in rainwater at those times. Volchok (*4*) observed that the increase in the ratio in the deposition at New York owing to ^{238}Pu from the SNAP-9A generator was rather gradual until the spring of 1966 and became abruptly marked during the spring of 1967. Our result for the same period substantially agrees with Volchok's observation.

Feely *et al.* (*5*) report that high-altitude air samples obtained prior to the reentry of the SNAP-9A generator showed a fairly constant ratio averaging about 0.03. Volchok (*4*) assumed that any sample with a ratio in excess of that value might be presumed to contain ^{238}Pu from the SNAP-9A generator and that the amount of ^{238}Pu from it might be determined by subtracting the indicated background amount. In order to estimate the deposition rate of ^{238}Pu from the SNAP-9A generator, this background ratio should be determined exactly. Our measured ratios of samples *R*9 and *R*10, about 0.02, may be regarded as the background ratio in Japan rainwater prior to the influence of ^{238}Pu from the SNAP-9A generator, but these values are somewhat low as compared with the background ratio of 0.03 (*5*) used by Volchok. According to our results, the ratio in rainwater was affected not only by ^{238}Pu from the SNAP-9A generator but also by the nuclear debris produced in the latest nuclear explosions. Consequently, there is

Table 1. Plutonium activities (^{238}Pu + ^{239}Pu + ^{240}Pu) of measured samples of rainwater and activity ratios of ^{238}Pu to (^{239}Pu + ^{240}Pu).

Sample			Pu (pc)	Activity ratio ^{238}Pu/ (^{239}Pu + ^{240}Pu)
No.	Collection time	Volume (liters)		
*R*1	3 May–14 September 1961	10.8	9.3×10^{-2}	0.01 ± 0.02
*R*2	9–11 October 1961	10.5	9.3×10^{-2}	.28 ± .04
*R*3	17 November 1961–8 February 1962	7.4	7.4×10^{-2}	.03 ± .03
*R*4	9–10 April 1962	19.8	1.6×10^{-1}	.007 ± .015
*R*5	9 August–5 October 1962	6.1	3.5×10^{-1}	.11 ± .01
*R*6	9–28 November 1962	4.3	1.6×10^{-1}	.10 ± .02
*R*7	9–13 March 1963	46.0	6.9×10^{-1}	.057 ± .007
*R*8	1 May–25 September 1963	10.0	7.3×10^{-1}	.027 ± .004
*R*9	1 October 1963–31 January 1964	6.7	3.8×10^{-1}	.010 ± .006
*R*10	6 February–19 July 1964	10.2	1.00	.016 ± .003
*R*11	21 August–17 October 1964	20.0	3.8×10^{-1}	.06 ± .01
*R*12	21 October–2 November 1964	28.0	1.22	.075 ± .003
*R*13	31 January–15 May 1965	7.6	2.3×10^{-1}	.06 ± .01
*R*14	20 May 1965	23.0	6.3×10^{-1}	.065 ± .006
*R*15	1 September–30 December 1965	8.3	8.4×10^{-2}	.05 ± .03
*R*16	7 May 1966	27.4	1.2×10^{-1}	.22 ± .03
*R*17	10 May 1966	57.0	4.0×10^{-2}	.06 ± .05
*R*18	31 December 1966–1 January 1967	27.2	3.0×10^{-1}	.08 ± .01
*R*19	22–23 June 1967	14.4	2.2×10^{-2}	.5 ± .2
*R*20	26–27 December 1967	9.1	3.9×10^{-2}	.4 ± .1
*R*21	16–26 March 1968	26.0	3.7×10^{-1}	.264 ± .015
*R*22	27 May 1968	117.5	1.5×10^{-1}	.21 ± .03

Table 2. Plutonium activities (^{238}Pu + ^{239}Pu + ^{240}Pu) of measured samples of radioactive particles and activity ratios of ^{238}Pu to (^{239}Pu + ^{240}Pu).

Sample				Pu (pc)	Activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu)
No.	Assumed date of explosion	Diameter (μ)	Particles (No.)		
*S*1	October 1961	5–10	63	2.31	0.302 ± 0.005
*S*2	October 1962	8–15	30	8.5×10^{-1}	.168 ± .007
*S*2′*	October 1962	4–12	81	3.41	.102 ± .002
*C*1	16 October 1964	8–15	110	1.2×10^{-1}	.04 ± .02
*C*2	14 May 1965	4–6	30	9.2×10^{-2}	.01 ± .04
*C*3	9 May 1966	8–15	170	3.3×10^{-1}	.04 ± .01
*C*5	28 December 1966	20–28	230	3.8×10^{-1}	.016 ± .007

* Collected at the Niigata University, Nagaoka.

some difficulty associated with defining and determining exactly the background ratio in rainwater.

Krey (*6*), who estimated the particle size distribution of ^{238}Pu from the debris of the SNAP-9A generator by an autoradiographic technique, concluded that the diameters of the particles ranged from 5 to 58 nm with an arithmetic mean of about 10 nm. Such small particle size explains the very slow increase in the ratio in deposition in the Northern Hemisphere, as predicted by Harley (*7*). Our results seem to indicate that the arrival of ^{238}Pu from the SNAP-9A generator in the Northern Hemisphere occurred appreciably earlier than expected. One possible explanation is that some larger particles were also produced by the generator burnup and that these subsided rather rapidly, resulting in the earlier transfer of debris from the Southern to the Northern Hemisphere. The fact that comparatively constant values of the ratio were obtained in the period from the latter half of 1964 to the end of 1965 seems attributable to isotopic dilution by nuclear debris produced in the 1964 and 1965 nuclear explosions, such as the first and the second Chinese explosions.

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Hydrocarbons of Blue-Green Algae: Geochemical Significance

Abstract. *The hydrocarbon compositions of 11 species of blue-green algae are simple and qualitatively similar. Three marine coccoids contain only monoenoic and dienoic C_{19} hydrocarbons. Hydrocarbons of the remaining eight species are C_{15} to C_{18}. Hydrocarbons of higher molecular weight (C_{20} or more) were not detected. Blue-green algae do not appear to be the source material for the long-chain (greater than 20 carbons) hydrocarbons found in ancient sediments.*

Because blue-green algae are primitive organisms with the ability to grow in environments that favor the preservation of organic matter, such as hypersaline or reducing environments, they are often suggested as source material for the organic matter associated with ancient sediments. We have studied the composition of the lipids of blue-green algae in order to determine relationships among them, and to define their potential as geological source material. The fatty acid compositions are simple (*1*). The hydrocarbon patterns are even simpler than the fatty acid patterns.

The conditions used to grow the pure cultures of algae are given in Table 1. *Trichodesmium* was collected from a large unialgal surface bloom which occurred near Port Aransas in the Gulf of Mexico. The sample used in this study is from the same bloom for which the fatty acid pattern was reported (*1*). The algal mat was part of an extensive blue-green community (nearly a pure culture) growing in a few centimeters of water on a mud flat near Port Aransas. The mat was collected prior to the dehydration which occurs later in the summer, and the algae appeared to be healthy.

The analytical procedure was designed to detect hydrocarbons containing from 14 to 34 carbon atoms. The cells were harvested by centrifugation or by a plankton net in the case of *Trichodesmium*. The moist cells were transferred to a separatory funnel and shaken with a few milliliters of methanol for 5 minutes. An equal volume of hexane was added and the mixture was shaken for 15 minutes. The hexane layer was transferred to a 10-ml flask and evaporated to 0.5 ml under a stream of dry nitrogen. The sample was placed on a silica gel column (Woelm activity I) which had been washed with hexane. The hydrocarbons were eluted with 50 ml of hexane. The hexane was evaporated to 0.5 ml with a nitrogen stream and set aside for analysis. The hydrocarbons were identified and measured by gas chromatography on columns of Apiezon L, SE-30, and FFAP. Standards of the saturated and monoenoic hydrocarbons were used to obtain retention times. Standard dienoic hydrocarbons were not available. The identifications of these polyunsaturated molecules are based on the shift in elution order on Apiezon L compared with FFAP and on the fact that hydrogenation of the samples yielded only a single saturated (C_{19}) hydrocarbon.

The hydrocarbon compositions of the blue-green algae were very simple (Table 2). The hydrocarbons constituted between 0.05 and 0.12 percent of the dry weight of the cells. The three marine coccoids contain only normal C_{19} molecules with one or two double bonds. The remaining organisms contain normal hydrocarbons in the C_{15} to

Table 1. Growth conditions of blue-green algae. All organisms were grown in test tubes with continuous gassing with 1 percent CO_2 in air. Illumination was 3300 lu/m^2 provided by fluorescent lamps. At harvest, cell concentrations were approximately 0.5 mg (dry weight) per milliliter.

Organism	Code name	Growth conditions	
		Temp. (°C)	Medium*
Trichodesmium erythaeum	Trico	†	Bloom
Coccochloris elabens	17A	39	ASP-2
Microcoleus chthonoplastes	BA-1	39	ASP-2
Nostoc muscorum G.‡	NM	30	C
Agmenellum quadruplicatum	PR-6	39	ASP-2
A. quadruplicatum	BG-1	39	ASP-2
Plectonema terebrans	SP-31	30	ASP-2
Oscillatoria williamsii	Mev	39	ASP-2
Lyngbya lagerhaimii	Mont	30	ASP-2
Anacystis nidulans ‡	Ana. n.	39	C
A. nidulans ‡	TX-20	39	Cg-10
Algal mat		†	

* For medium C, see (*5*); for medium ASP-2, see (*6*). † Natural. ‡ Culture was obtained from J. Graham, University of Texas, Austin. The other cultures are marine isolates of our laboratory (*6*). The Ana. n. cells were grown and lyophilized in Austin; TX-20 was grown in our laboratory on a different medium (*7*).