Activity Ratios of $^{241}\text{Pu}/^{239+240}\text{Pu}$ and $^{238}\text{Pu}/^{239+240}\text{Pu}$ in Fall-out Samples Collected in the Period of 1961-1968

T. MATSUNAMI and T. MAMURO

Department of Health Physics and Instrumentation, Radiation Center of Osaka Prefecture, 704 Shinke-cho, Sakai-shi, Osaka-fu, Japan 593

(Received November 13, 1980)

Fallout plutonium/Plutonium isotopic ratio/Hot particle

INTRODUCTION

Beta-ray emitting nuclide $^{241}\text{Pu}$, which transforms into alpha-ray emitting nuclide $^{241}\text{Am}$ ($\alpha$-ray energy: 5.49 MeV (85%), 5.44 MeV (13%); half-life: 458 y), is released in nuclear explosions together with three alpha-ray emitting plutonium isotopes, namely, $^{238}\text{Pu}$ ($\alpha$-ray energy: 5.50 MeV (72%), 5.46 MeV (28%); half-life: 86.4 y), $^{239}\text{Pu}$ ($\alpha$-ray energy: 5.16 MeV (88%), 5.11 MeV (11%); half-life: 24,390 y) and $^{240}\text{Pu}$ ($\alpha$-ray energy: 5.17 MeV (76%), 5.12 MeV (24%); half-life: 6,580 y).

Analysis of the proportion of $^{241}\text{Pu}$ in environmental plutonium samples is important both because of the increasing concern over the radiotoxicity of its daughter $^{241}\text{Am}$, and because the short half-life of $^{241}\text{Pu}$ (13.2 y) offers promise of its use for identification of origins of plutonium released into the environment on the basis of the fact that plutonium released from atomic power plants and that originating from nuclear explosions show different activity ratios of $^{241}\text{Pu}/^{239+240}\text{Pu}$.\(^1\)

Twelve to nineteen years ago, we extracted plutonium from two kinds of radioactive fallout samples, namely, highly radioactive fallout particles (hot particles) which were collected shortly after nuclear explosions and rain water samples, and electroplated it on stainless steel plates. The specimens thus prepared were subjected to alpha-ray spectrometry to measure the activity ratio of $^{239+240}\text{Pu}$.\(^2\) Some of these specimens are preserved even now. Recently they were again subjected to alpha-ray spectrometry. By comparing the old and new alpha-ray spectra, the activity ratios of $^{241}\text{Pu}/^{239+240}\text{Pu}$ at the sampling time were estimated.
Table 1. Activity ratios of $^{239+240}$Pu and $^{239+240}$Pu found in old fallout samples collected in the period of 1961-1968

| Sample | Date of sampling | Date of chemical separation | Date of the first measurement | Date of the second measurement | Time interval (y) | Counting rate ratio* | $^{239+240}$Pu/239+240Pu | $^{241}$Pu/239+240Pu |
|--------|-----------------|-----------------------------|------------------------------|-----------------------------|-----------------|-------------------|---------------------|---------------------|
| P-1    | Oct. 1961       | June 1967                   | Aug. 1967                    | Nov. 1978                   | 5.67            | 0.17              | 0.293±0.007         | 0.316±0.007         | 0.208±0.042         |
| P-2    | Oct. 1962       | June 1967                   | Aug. 1967                    | Jan. 1979                   | 4.67            | 0.17              | 0.170±0.009         | 0.174±0.007         | 0.176±0.009         |
| P-3    | Oct. 1962       | June 1967                   | June 1968                    | Nov. 1978                   | 4.67            | 1.00              | 0.101±0.003         | 0.130±0.003         | 0.101±0.003         |
| R-1    | Oct. 1961       | July 1967                   | Jan. 1968                    | July 1979                   | 5.75            | 0.50              | 0.209±0.038         | 0.381±0.043         | 0.208±0.042         |
| R-2    | Aug.-Oct. 1962  | Mar. 1967                   | Oct. 1967                    | Apr. 1980                   | 4.50            | 0.58              | 0.112±0.011         | 0.262±0.014         | 0.106±0.012         |
| R-3    | Nov. 1962       | July 1967                   | Oct. 1967                    | Apr. 1980                   | 4.67            | 0.25              | 0.118±0.021         | 0.211±0.021         | 0.120±0.022         |
| R-4    | May-Sept. 1963  | July 1967                   | Apr. 1968                    | Sept. 1979                  | 4.00            | 0.75              | 0.030±0.003         | 0.191±0.007         | 0.016±0.003         |
| R-5    | Feb.-July 1964  | July 1967                   | Mar. 1968                    | Nov. 1979                   | 3.21            | 0.67              | 0.010±0.002         | 0.188±0.008         | 0.000±0.003         |
| R-6    | Aug.-Oct. 1964  | May 1965                    | Nov. 1967                    | Apr. 1980                   | 0.67            | 2.50              | 0.081±0.009         | 0.254±0.015         | 0.030±0.012         |
| R-7    | May 1965        | June 1965                   | Dec. 1967                    | Sept. 1979                  | 0.08            | 2.50              | 0.052±0.005         | 0.199±0.010         | 0.007±0.006         |
| R-8    | Dec. 1966       | April 1967                  | Jan. 1968                    | May 1980                    | 0.33            | 0.75              | 0.081±0.012         | 0.133±0.013         | 0.077±0.013         |
| R-9    | Mar. 1968       | April 1968                  | April 1968                   | Sept. 1979                  | 0.08            | 0.00              | 0.237±0.020         | 0.449±0.033         | 0.237±0.020         |

* Alpha counting rate ratio of 5.4-5.5 MeV peak to 5.1 5.2 MeV peak
** Activity ratio of $^{238}$Pu to $^{239+240}$Pu at sampling time
*** Activity ratio of $^{238}$Pu to $^{239+240}$Pu at sampling time
SAMPLES AND METHODS

The specimens that were remeasured are three hot particle samples (P-1 to 3) and nine rain water samples (R-1 to 9) as listed in Table 1. The hot particle samples were prepared in the following way. Hot particles of several microns in diameter originating from U.S.S.R. nuclear explosions of 1961 and 1962 were isolated under a microscope. They were dissolved, and plutonium was extracted from the solutions thus prepared and electroplated on a stainless steel plate. Sample P-1 was prepared from 63 hot particles collected in our laboratory in October 1961, sample P-2 from 30 hot particles collected also in our laboratory in October 1962 and sample P-3 from 81 hot particles which were collected at Nagaoka in October 1962 by Prof. Kobayashi of Niigata University. Rain water samples R-1 and R-7 were prepared both from rain water collected at single rain fall, and the rest rain water samples were prepared from rain waters collected at several rain falls (10 to 100 liters).

The first alpha-ray spectrometry was made with a gridded ionization chamber, and the second with a surface barrier type of silicon detector. In Figs. 1 and 2 are illustrated the old and new alpha-ray spectra of sample P-3, respectively.

The alpha-ray energies of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ are not now differentiable by alpha-ray spectrometry. Also, the alpha-ray energies of $^{241}\text{Am}$ and $^{238}\text{Pu}$ are not differentiable. Now, let the alpha counting rate ratio of ($^{238}\text{Pu}$ + $^{241}\text{Am}$) to ($^{239}\text{Pu}$ + $^{240}\text{Pu}$) obtained in the first spectrometry and that obtained in the second spectrometry be expressed by $P$ and

![Fig. 1. Alpha-ray spectrum of sample P-3 collected with a gridded ionization chamber in June, 1968.](image1)

![Fig. 2. Alpha-ray spectrum of sample P-3 collected with a Si detector in November, 1978.](image2)
Q, respectively. By setting the time of sampling to be the origin of time, the time of chemical separation of plutonium to be $T_1$, the time of the first alpha-ray spectrometry to be $T_1 + T_2$, and the time of the second alpha-ray spectrometry to be $T_1 + T_2 + T_3$, we find, after assuming that the plated plutonium was free of $^{241}$Am at the time of chemical separation,

$$X = \frac{P}{\lambda_1} \left[ \frac{\{\exp(-\lambda_1T_2) - \exp(-\lambda_2T_2)\}}{\exp(-\lambda_1(T_1 + T_2))} \right] \frac{\{Q - P \exp(-\lambda_3T_3)\}}{\{\exp(-\lambda_2T_3)\}} \exp(-\lambda_2(T_1 + T_2))$$

where $X$ and $Y$ are the activity ratios of $^{238}$Pu/$^{239+240}$Pu and $^{241}$Pu/$^{239+240}$Pu at the time of sampling, respectively, and $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the disintegration constants of $^{238}$Pu, $^{241}$Pu and $^{241}$Am, respectively.

**RESULTS AND DISCUSSION**

In Table 1 are shown the values of $X$ and $Y$ which were calculated from the measured values of $P$ and $Q$. In Figs. 3 and 4 are plotted the activity ratios of $^{238}$Pu/$^{239+240}$Pu and $^{241}$Pu/$^{239+240}$Pu at the time of sampling in relation to the time of sampling.

![Fig. 3. Activity ratios of $^{238}$Pu to $^{239+240}$Pu found in fallout samples.](image-url)
It is generally recognized that the typical value of the activity ratio of $^{238}\text{Pu}/^{239+240}\text{Pu}$ in nuclear debris from nuclear explosions is about 0.03.\textsuperscript{3, 4, 5} Rain water samples R-4 to 7 have activity ratios near this value. The large values found in samples R-8 and R-9 are evidently ascribed to the release of $^{238}\text{Pu}$ from the burnup of the SNAP-9A over Indian Ocean in 1964.\textsuperscript{6} The activity ratios of $^{238}\text{Pu}/^{239+240}\text{Pu}$ found in hot particle samples P-1 and 2 are apparently larger than those found in rain water samples R-1 to 3 which were collected at the same place nearly in the same periods. This suggests that $^{238}\text{Pu}$ is more enriched in hot particles compared to $^{239}\text{Pu}$ and $^{240}\text{Pu}$ than in finer particles. Rain water samples R-1 to 3 have appreciably higher activity ratios of $^{238}\text{Pu}/^{239+240}\text{Pu}$ than the typical ratio, 0.03, and a possible explanation for this is that these rain water samples abundantly contained fallout particles of relatively larger size.

It is seen in Fig. 4 that the activity ratios of $^{241}\text{Pu}/^{239+240}\text{Pu}$ found in rain water samples are not so different from sample to sample as those of $^{238}\text{Pu}/^{239+240}\text{Pu}$ are. Livingston et al. pointed out that the typical value of the activity ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ found in fallout samples is 13 to 14.\textsuperscript{11} Our rain water samples except R-8 show also such values.

Hot particle samples P-1 to 3 show considerably lower values of $^{241}\text{Pu}/^{238+240}\text{Pu}$ ratio than the rain water samples. In hot particles $^{241}\text{Pu}$ is apparently depleted compared to $^{239}\text{Pu}$ and $^{240}\text{Pu}$, being just reversed to the case of $^{238}\text{Pu}$.

Sample R-8 was prepared from the rain water that was collected shortly after the fifth Chinese nuclear explosion of December 1966 and thus thought to have contained much fresh nuclear debris from this explosion. Sample R-8 shows an appreciably low
activity ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ compared to the other rain water samples. This appears to suggest that this rain water contained abundantly fallout particles of larger size originating from the explosion.

Rain water samples R-1 to 3, which were prepared from the rain water that was thought to contain abundantly fallout particles of relatively larger size, have considerably higher activity ratios of $^{239}\text{Pu}/^{238+240}\text{Pu}$ than the typical ratio, 0.03. On the contrary, their activity ratios of $^{241}\text{Pu}/^{239+240}\text{Pu}$ are near the typical ratio, 13 to 14. At present this cannot be explained.

The dependence of the thermal fractionation on particle size is naturally thought to be different among the four plutonium isotopes, due to the differences in the nuclide production reactions and in the half-lives of the precursor nuclides appearing just after detonation.\(^{7,8,9,10}\) Further investigation from such a point of view is necessary in order to understand the dependence of the plutonium isotopic ratios on particle size.

REFERENCES

1. H.D. Livingston, D.L. Schneider and V.T. Bowen (1975) $^{241}\text{Pu}$ in the marine environment by a radiochemical procedure. *Earth and Planetary Science Letters*, 25: 361-367.
2. T. Mamuro and T. Matsunami (1969) Plutonium-238 in fallout. *Science*, 163: 465-467.
3. J.H. Harley (1980) Plutonium in the environment-a review. *Journal of Radiation Research*, 21: 83-104.
4. Y. Miyake, Y. Katsuragi and Y. Sugimura (1968) Deposition of plutonium in Tokyo through the End of 1966. *Papers in Meteorology and Geophysics*, 19: 267-276.
5. Y. Miyake, Y. Sugimura, K. Saruhashi, K. Katsuragi and K. Hirose (1979) Plutonium and americium in the environment. *Proc. of 6th Intnl. Congr. of Radiation Research*, 940-948.
6. H.L. Volchok (1968) Fallout of Pu-238 from the SNAP-9A burnup. *United States Atomic Energy Commission, Health and Safety Laboratory Report*, No. 184, Part 1: 2-10.
7. R.S. Clark, K. Yoshikawa, M.N. Rao, B.D. Palmer, M. Thein and P.K. Kuroda (1967) Time interval between nuclear detonation and formation of single fallout particles. *Journal of Geophysical Research*, 72: 1793-1796.
8. T. Mamuro, T. Matsunami and A. Fujita (1968) Radionuclide fractionation in fallout particles from an air burst. *Health Physics*, 14: 223-239.
9. T. Mamuro, T. Matsunami, A. Fujita and K. Yoshikawa (1969) Radionuclide fractionation in fallout particles from a land surface burst. *Journal of Geophysical Research*, 74: 1374-1387.
10. M. Sakanoue (1974) Trans-plutonic elements in the environment. *Journal of the Atomic Energy Society of Japan*, 16: 372-375 (in Japanese).