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Journal of Marine Research

Volume 29, Number 1

*Plutonium-239 in and over the Atlantic Ocean*¹

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ABSTRACT

Plutonium-239 has been found in over-ocean aerosols in about the same ratio to Strontium-90 as that reported over land. In seawater, Pu-239: Sr-90 ratios are shown to be less than half of those in over-ocean aerosols, confirming geochemical separation of these nuclides in the ocean. It is suggested that the sedimentation of Pu-239 may be more involved with biological processes than has been found for Ce-144 or Pm-147.

Introduction. Plutonium isotopes, Pu-239 in particular, have always been significant components of world-wide nuclear fallout and minor components of some nuclear powerplant wastes. Most of the literature dealing with the introduction of plutonium to nature has been collected by Joseph et al. (1970) and briefly summarized by Volchok and Krey (1970); plutonium in fallout has been routinely monitored for some years, and the data have been reported regularly (Anonymous 1968-1970). A careful review of the literature by Volchok et al. (1970) revealed only one report of plutonium concentrations in seawater, that being by Pillai et al. (1964). During preparation of this re-

1. Contribution No. 2114 from the Woods Hole Oceanographic Institution.

Accepted for publication and submitted to press 15 July 1970.

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port, however, we became aware of the studies by Miyake and his coworkers (Miyake and Sugimura 1968; Miyake et al. 1970). Our study of plutonium in the oceans, like theirs, was prompted by concern over the small body of data available and by the knowledge that the long half-life of Pu-239 will make its use as a geochemical tracer practicable for generations to come. Consequently, for about a year we have been measuring Pu-239 routinely in seawater, in over-ocean aerosols, in marine sediments, and in some samples of marine organisms.

It seems timely to present a preliminary report of the data so far collected on water and aerosols because our findings do not confirm an important conclusion by Pillai et al. (1964): Pu-239 in seawater does, in fact, appear to be separated from both Sr-90 and Cs-137.

Methods. Our programs and techniques for the collection of seawater, of aerosol samples over the ocean, and of marine sediments have been discussed elsewhere (Bowen and Sugihara 1965, Bowen et al. 1968, Volchok et al. 1970, Noshkin 1969 and manuscript, Burke 1968). Wong, Noshkin, and Bowen (1970) have reported details of our radiochemical procedure for plutonium, which we summarize briefly: plutonium radio-isotopes, with Pu-236 added as a yield monitor, are collected with the hydroxide precipitate used to separate lanthanides, antimony, and iron from samples of each of the matrices to be analyzed; in 8N HNO₃, the plutonium isotopes are retained on columns of Dowex 1 after the other nuclides and carriers have been eluted, using successive washes of 8N HNO₃ and concentrated HCl. Plutonium is then eluted from the column with NH₄I in concentrated HCl and finally electroplated onto stainless-steel planchets before being measured by alpha-particle spectrometry, using a silicon solid-state detector and multichannel analyzer. Because of contamination of the detector with americium-241 (used by the manufacturer for its calibration of the detector), we have been unable to measure Pu-238 at the low levels found in our samples. The background levels encountered are as follows: at 5.75 mev (line used to monitor Pu-236) 0.0073 ± 0.0009 cpm; at 5.48 mev (line most suitable for Pu-238) 0.0265 ± 0.0016 cpm; at 5.15 mev (line used for Pu-239) 0.0007 ± 0.0003 cpm. Our counting efficiencies have approximated 38%; the Pu-236 tracer ranges about 0.3 cpm in final samples, and the Pu-239 levels are rarely useable below 0.01 cpm. The detector contamination, therefore, contributes insignificantly to the measurements of Pu-236 and Pu-239, but it overwhelms the range of Pu-238 levels encountered by us in water and aerosol samples. We have confirmed that the detector contamination is in fact americium-241; this was done from an accumulated 10,000-minute background, from the position of the 5.48 mev alpha peak, plus identification of alpha peaks characteristic of U-233, Th-229, Ac-225, Fr-221, and At-217, all daughters of Am-241; the only other alpha peaks present are small contributions (20 counts per

10,000 min. or less) from radon or thoron and their daughters. We are attempting to obtain an uncontaminated detector that will enable us to measure Pu-238 in environmental samples.

To collect enough counts for acceptable statistics, environmental specimens such as those described here have required counting times of 24 to 72 hours per sample.

Results. In Table I we have set out a small number of aerosol analyses for Pu-239 and Sr-90. These should be compared with the much larger series reported by the AEC Health and Safety Laboratory (Anonymous 1968-1970).

In Table II we have set out our data for Pu-239 in seawater samples (collected in the Atlantic Ocean at various places, times, and depths) together with the ratios of Pu-239 to Sr-90, to Cs-137, or to both. Also included are the results from four samples analyzed as blanks. Of these blanks, the New Mexico Oil Well Brine (from a Devonian formation) has proved to be free of all artificial environmental radionuclides (Bowen 1970, Volchok, personal communication); its use and the use of the artificial distilled-water-reagent blank is an obvious radiochemical precaution. The water from the Coney Island Aquarium Well is rich in Sr-90 (Volchok 1968), but we have found it to be free of Cs-137 and of Ce-144 and Pm-147; by analogy we would expect it to be free also of plutonium, an element that is likely to be lost by adsorption of most of its chemical forms (Coleman 1965); by a sort of circular argument into which one is often forced, the insignificant observed values of Pu-239 have confirmed our expectations.

Discussion. Pillai et al. (1964) concluded that "... plutonium apparently has not appreciably fractionated from strontium and cesium in this oceanic surface water." We believe that neither their data nor ours are consistent with this conclusion.

Consider first the data of Pillai et al. Note that this stated conclusion was based on samples taken in 1964; they compared a mean ratio of 0.8% Pu-239 : Sr-90 in surface ocean water with a mean ratio of 1.0% Pu-239 : Sr-90 obtained from measurements on samples taken at Richmond, California; however, if they had used Volchok's (1969) ratio $1.5 \pm 0.5\%$ as the "most reasonable value" in 1964, their conclusion would have been very different. Note also that samples collected early in 1964 reflected the very high fallout increments reported for the two previous years (Bowen et al. 1969); their samples, therefore, could have represented the results of only minimal times of action of any separation processes that are active in seawater.

Now consider our data. Our own aerosol data (Table I), after discounting the one inexplicably low value for Pu-239, have yielded a mean ratio of 1.3% Pu-239 : Sr-90. This figure agrees surprisingly well with Volchok's (1969)

Table I. Plutonium-239 and Strontium-90 in over-ocean aerosols.

Collection dates	Position				Pu-239 dpm/samp.*	Sr-90 dpm/samp.*	Pu-239/Sr-90 ‰
	Start		Finish				
	Lat.	Long.	Lat.	Long.			
30-VI to 3-VII-67	45°20'N	14°55'W	43°24'N	24°30'W	0.35 ± 0.04	33.0 ± 0.3	1.06 ± 0.12
14-VII to 18-VII-67	43°21'N	29°20.7'W	43°59'N	41°00'W	0.051 ± 0.029	7.4 ± 0.4	0.7 ± 0.4
18-VII to 21-VII-67	43°59'N	41°00'W	46°01'N	52°06'W	0.023 ± 0.008	1.6 ± 0.3	1.44 ± 0.57
30-III to 3-IV-68	12°N	41°W	13°N	24°W	1.14 ± 0.08	71.3 ± 0.5	1.60 ± 0.11
28-V to 31-V-68	10°S	13°E	01°S	05°E	0.05 ± 0.02	3.5 ± 0.3	1.34 ± 0.53
24-IV to 29-IV-68	26°46'S	14°47'E	09°S	13°30'E	0.02 ± 0.03	21.9 ± 0.3	(0.09 ± 0.14)
8-X to 11-X-68	06°N	12°W	23°N	35°W	0.19 ± 0.03	16.8 ± 0.5	1.13 ± 0.18
Average (omitting # 6)							1.30 ± 0.07

* Analysis of only a fraction (usually about one-half) of each filter.

Table II. Plutonium-239 in seawater.

Collection date	Position		Depth (m)	Pu-236 recovery (%)	Pu-239 dpm/1000 kg	Pu-239/Sr-90 (%)	Pu-239/Cs-137 (%)
	Lat.	Long.					
V-1963	44°00' N	41°00' W	Surf.	25	2.2 ± 0.6	0.63 ± 0.17	0.55 ± 0.16
XI-1967	56°30' N	51°00' W	"	28	1.4 ± 0.4	0.51 ± 0.15	0.43 ± 0.13
II-1968	07°39.3'N	41°07.5'W	"	43	0.7 ± 0.2	0.51 ± 0.15	0.92 ± 0.27
X-1968	28°31.1'S	07°34' E	"	13	0.4 ± 0.4	0.27 ± 0.27	0.29 ± 0.3
XII-1968	27°47' N	67°35' W	" B	18	1.5 ± 0.5	0.42 ± 0.14	0.32 ± 0.11
"	"	"	" D	22	2.6 ± 0.7		0.59 ± 0.16
XII-1968	31°49' N	"	"	9	1.7 ± 0.6	0.60 ± 0.21	0.37 ± 0.13
VI-1969	36°23' N	70°03' W	" E	43	2.3 ± 0.5	0.95 ± 0.21	0.98 ± 0.29
"	"	"	" X	43	0.9 ± 0.3	0.39 ± 0.13	0.33 ± 0.12

II-1968	07° 39.3' N	41° 07.5' W	100	43	0.6 ± 0.2		0.35 ± 0.12
VI-1968	00° 01.5' N	03° 45' E	30	36	0.5 ± 0.2	0.45 ± 0.18	0.39 ± 0.18
VI-1968	00° 09' N	17° 20' W	30	6	1.1 ± 0.6	0.92 ± 0.5	0.65 ± 0.4
"	"	"	75	5	0.3 ± 0.3	0.30 ± 0.30	0.22 ± 0.24
X-1968	28° 31.1' S	07° 34' E	100	57	0.7 ± 0.4	0.47 ± 0.27	0.42 ± 0.26
XI-1968	18° 11.9' S	07° 35.7' E	100	28	0.7 ± 0.3		0.67 ± 0.3
XII-1968	27° 47' N	67° 35' W	50	25	2.8 ± 0.7	0.99 ± 0.25	0.66 ± 0.18
"	"	"	100	8	2.7 ± 0.8	0.78 ± 0.23	0.72 ± 0.24
"	"	"	300	7	1.7 ± 1.4	0.56 ± 0.47	0.39 ± 0.32
V-1969	39° 58' N	06° 42.6' E	400	31	1.5 ± 0.3		0.87 ± 0.17
VI-1969	37° 01' N	00° 03' E	100	11	7.7 ± 1.2		1.94 ± 0.30
"	"	"	400	17	0.7 ± 0.2	0.37 ± 0.11	0.49 ± 0.37
VI-1963	00° 03' S	34° 53' W	500	18	0.0 ± 0.4	—	—
VI-1968	00° 09' N	17° 20' W	700	22	4 ± 3	30 ± 34	—
XI-1968	18° 11.9' S	07° 35.7' E	500	5	4 ± 4		130. ± 130.
XI-1968	25° 14' N	67° 37.5' W	500	23	1.5 ± 0.5		0.75 ± 0.25
"	"	"	1000	45	0.2 ± 0.1		2 ± 1
XII-1968	31° 49' N	63° 33.5' W	500	20	5.2 ± 1.2	1.86 ± 0.43	1.54 ± 0.42
"	"	"	700	27	1.7 ± 0.6	1.28 ± 0.45	1.04 ± 0.41
"	"	"	1500	12	0.4 ± 0.3	1.18 ± 0.92	1.0 ± 0.8
"	"	"	2000	1	0.2 ± 0.3	0.95 ± 1.43	1.0 ± 2.2
"	"	"	4500	6	-0.2 ± 0.2	—	—
V-1969	39° 58' N	06° 42.6' E	1000	42	0.4 ± 0.2		0.63 ± 0.32
VI-1969	37° 01' N	00° 03' E	1000	24	0.6 ± 0.2	1.50 ± 0.51	1.67 ± 0.57
"	"	"	2200	32	0.6 ± 0.2		1.94 ± 0.64

Blanks

New Mexico oil-well brine	34	-0.005 ± 0.010	per sample
Distilled water-reagent blank	34	0.017 ± 0.015	" "
Coney Island Aquarium well	42	-0.01 ± 0.02	" "
" " " "	48	0.01 ± 0.02	" "

recommended value of 1.5%; and our data are well within the ranges exhibited over the northern hemisphere stations summarized by Volchok and Krey (1970) or for those over Tokyo reported by Miyake et al. (1968). It is too early to attach any significance to the fact that we have no over-ocean Pu-239: Sr-90 ratios greater than 2% compared with the high frequency of such ratios overland, especially since the spring of 1968 (Volchok and Krey 1970).

Considering the measured concentrations of Pu-239 and the ranges of the observed Pu-239: Sr-90 ratios, there is very good agreement between our data from seawater analyses (Table II) and those published by Pillai et al. (1964) and by Miyake's group (Miyake and Sugimura 1968, Miyake et al. 1970). We had, in fact, expected higher mean values for the Pacific because of its load of close-in fallout at the various test sites.

For convenience in this discussion, the Pu-239 measurements of seawater tabulated in Table II have been divided in four groups: surface-water samples (9), samples from depths of 30 to 400 m (12), samples from depths of 500 m and more (13), and blanks (4). The four blank analyses confirm that we had little difficulty with Pu-239 contamination. However, when comparing data, note that the blanks are reported as "dpm per sample" (30 to 55 l) whereas the sample analyses are reported (simply for convenience in writing) as "dpm per 1000 l" even though only 55-l aliquots were analyzed.

Consider first the surface samples. The mean Pu-239: Sr-90 ratio for these samples (0.56%) appears to be clearly different from that for our aerosol samples (Table I) or for Volchok's (1969) precipitation samples. It seems inescapable that Pu-239 has been moving out of the sea surface faster than has Sr-90; from the mean Pu-239: Cs-137 ratio of 0.53%, the same conclusion is evident with respect to Cs-137.

Next, consider the samples from depths of 30 to 400 m. Compared with the surface samples, these show slightly higher mean ratios (0.61% vs Sr-90 and 0.65% vs Cs-137), but the variance within the two groups of samples makes this difference wholly insignificant. The data are consistent with either of two hypotheses: (i) the rates of mixing within the upper 400 m of the ocean are fast compared with the rates of whatever other processes move plutonium; (ii) the downward vertical velocities of plutonium in the upper 400 m are so fast compared with the integration times represented by the concentrations measured that little or no separated plutonium remains in the 30-to-400-m layer. For reasons discussed below, we tend to favor the second hypothesis.

The third group of samples, from depths of 500 m and more, is different; in the first two groups, no Pu-239: Sr-90 ratio exceeded 1%, but in the third group only one value was less than 1%; disregarding the one ratio that was over 100%, the mean ratio was 1.3%. In the case of Pu-239: Cs-137, again disregarding the one extremely high value, the mean ratio was 1.35%.

The consistently low ratios for surface and shallow water (compared with the delivered ratio inferred from aerosol and precipitation data) as well as the higher mean ratio for samples collected at depths of 500 m and more are consistent with only the hypothesis that plutonium in the ocean does in fact separate from Sr-90 and Cs-137 and moves downward in the water column at rates greater than those typical of the "soluble" fallout nuclides. Miyake and Sugimura (1968) also observed lower-than-expected Pu-239:Sr-90 ratios in two samples of surface water collected in 1967 in the northwestern Pacific; they measured Pu-239, at concentrations within their surface-water range, in one sample from 1000 m and another from 3000 m. Without being categorical, Miyake et al. (1970) have implied that the low Pu-239:Sr-90 ratios found in their surface samples resulted from a more rapid downward penetration of Pu-239 than of Sr-90. An association of plutonium with sinking particles is, of course, a behavior that would have been predicted for it in seawater, judging by its position in the actinide series of elements and by the relative ease of hydrolysis of its three and four valent ions (Coleman 1965).

In Fig. 1 we show the concentrations of Pu-239, Sr-90, and Cs-137 derived from samples taken in a vertical profile in the Sargasso Sea, December 1968; all of these data appear in Table II. This profile, with its maximum Pu-239 concentration at 500 m, is strikingly similar to the vertical profiles of concentration of Ce-144 or Pm-147 described by Sugihara and Bowen (1962) and Bowen and Sugihara (1965). By inference, then, we might expect that Pu-239, like the lanthanides, will be useful in tracing sedimentary particulate matter and in studying the mixing processes within sediment columns. The data of Pillai et al. (1964) seem to indicate that there may be a greater biological involvement in the sedimentation of plutonium than in the sedimentation of the lanthanides. The available data, including our own (Wong, Noshkin, Surprenant, and Bowen 1970), are too few for a comparison of the mean concentration factors for Pu-239 vs Ce-144, for instance, but do make the hypothesis an attractive one.

The presence of "excess" Pu-239 in most samples from depths of 500 m or greater (group 3 in Table II) is certainly consistent with the hypothesis that biological sedimentation is of major importance in moving plutonium. The release of Pu-239 would be expected when bacterial degradation of biogenic particles occurs during the downward migration. Since formed phosphates are such good collectors of plutonium *in vitro* (Coleman 1965), it is tempting to suggest that this may be an important mechanism for the biological concentration of plutonium; in that case, then, an increase in the Pu:Sr ratios would be expected to parallel (with depth) the increase in "inorganic phosphate" released by the degradation of particulate biogenic phosphate taken from the surface layers. We are pursuing this question by examining in greater detail the water column between 500 and 1000 m, and by analyzing marine-plankton and marine-sediment profiles.

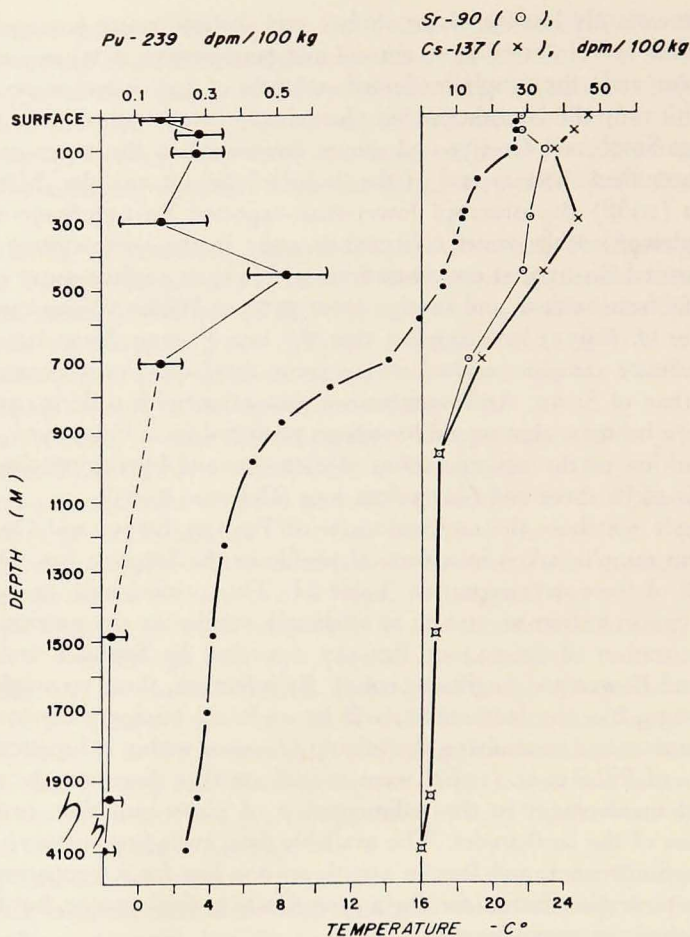


Figure 1. Vertical profile of concentrations of Pu-239, Sr-90, and Cs-137 from a station on 11 December 1968 at $31^{\circ}49'N$, $63^{\circ}33.5'W$ in the Sargasso Sea. Depths calculated from unprotected reversing thermometer readings; temperature profile from accompanying Nansen-bottle cast.

A full account of the Sr-90, Cs-137, and lanthanide concentrations in these and related samples is being prepared. That account will be accompanied by pertinent hydrographic data and by chlorinity measurements that confirm the successful operation of the large-volume water sampler (Bodman et al. 1961).

Acknowledgments. It is a pleasure to acknowledge the radiochemical help of our coworkers Miss L. Surprenant and A. G. Gordon; in sample collecting we have had helpers too numerous to list here. H. L. Volchok has criticized

and encouraged our writing. The program at the Woods Hole Oceanographic Institution has been supported by the U. S. Atomic Energy Commission under contract AT(30-1)-2174.

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