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^{241}Pu AND ^{241}Am IN SEDIMENTS FROM COASTAL BASINS OFF CALIFORNIA AND MEXICO

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In sediments deposited in the coastal basins off the western North American continent since the early 1960's, there is more ^{241}Am activity than one would predict if its presence was solely due to the decay of ^{241}Pu that was produced during the testing of weapons in 1961-62 (taken as July 1, 1962 for calculations). This excess can be accounted for by the decay of ^{241}Pu, if pre-1962 fallout (fallout from the pre-moratorium testing) has been continuously introduced into the recent sediments along with fallout from post-moratorium testing. This hypothesis is supported by the plutonium depth profiles which do not reflect direct fallout from the atmosphere, as characterized by two peaks corresponding to the two major weapons testing periods, but continuously increasing plutonium and americium concentrations from 1954 to 1974. Thus, the nuclides may be coming from a large reservoir that has accumulated and mixed fallout since 1952. Such a concentration gradient for all of the nuclides requires their immobilization in the sediment after deposition.

1. Introduction

^{239}Pu from nuclear weapons testing fallout over the past three decades is the dominant alpha transuranic activity in the environment today. Assuming no further large-scale atmospheric releases, the global inventory of ^{241}Am activity produced from the decay of fallout ^{241}Pu will be about 70% of ^{239}Pu in approximately 70 years. This results from the relatively short half-lives of ^{241}Pu ($T_{1/2}$ = 14.4 years) [1] and ^{241}Am ($T_{1/2}$ = 433 years) [1] compared to ^{239}Pu ($T_{1/2}$ = 24,260 years), and the high ^{241}Pu/$^{239+240}$Pu activity ratio of 14–16 in fresh bomb debris [2,3]. An initial survey for ^{241}Pu in oceanic samples has been made by Livingston et al. [4]. We report herein on ^{241}Pu and ^{241}Am concentrations in coastal sediments off California and Baja California.

In order to better understand the behaviors of transuranics in coastal marine systems, ^{241}Pu and ^{241}Am were assayed in California and Baja California basin sediments in which we had already measured $^{239+240}$Pu and ^{238}Pu [5]. These California Basin sediments are anoxic and not bioturbated. Hence, they are attractive for these studies. There are several compelling reasons to determine ^{241}Pu in these sediments. First of all is the establishment of whether the ^{241}Pu/$^{239+240}$Pu activity ratio reflects (1) direct atmospheric fallout of debris from weapons tests, (2) the introduction of older fallout materials that has accumulated on soil debris and transported to surface ocean waters by winds or rivers, or (3) the resuspension of marine sediments from other areas. Previously, we had pointed out that the $^{239+240}$Pu concentrations in these anoxic basin sediments continuously increase from strata deposited in the early

1950's to those recently accumulated, suggesting very sizeable current inputs of these transuranics. Preliminary work on ^{241}Am also indicated a relatively high ratio of ^{241}Am/$^{239+240}$Pu in near-surface sediments, i.e., recently deposited, whereas one would expect a low ratio if the transuranics came from fallout of recent weapons tests. A significant introduction of old material to the presently depositing sediments thus appeared possible. Secondly, the possible fractionation of plutonium from americium through diffusional processes in the sediments is worthy of consideration.

2. Methods

The determination of ^{241}Pu in environmental samples has been made either directly by mass spectrometry or by ingrowth of the daughter, ^{241}Am, from its parent ^{241}Pu with alpha spectrometry. The first method suffers from the inaccessibility of the instruments to environmental scientists and in some cases may lack the sensitivity at very low numbers of atoms ^{241}Pu even though the ^{241}Pu/$^{239+240}$Pu activity ratio is greater than 1. The second method involves the chemical separation of ^{241}Am from the Pu after waiting several years for its growth from ^{241}Pu. By this method the Pu and Am are stripped from the counting planchet upon which the Pu was originally plated, and spiked with ^{243}Am. The Am is then separated from Pu, replated and assayed by alpha spectrometry. This method has been applied to various marine and terrestrial samples [4,6,7]. However, due to the low Pu activity of these environmental samples, long counting periods are required to measure the ^{241}Am that has grown in. Counting errors of approximately 10% resulted from these low activities.

We have recently developed a low background liquid scintillation counter for the assay of alpha and beta particles. For the direct determination of the ^{241}Pu beta (E_{max} = 0.021 MeV) the instrument is capable of measuring 10^{-15} g ^{241}Pu. The detector has an efficiency of 35–40% and a background of 1 cpm in the ^{241}Pu spectral energy region in the presence of the scintillant. The efficiency for Pu alphas is 100% with a background of 0.4–0.5 cpm. The instrument

and the ^{241}Pu measurement will be described in detail in a forthcoming paper.

Measurements of ^{241}Pu were made on sediments taken from the Santa Barbara Basin off southern California and the Soledad Basin off Baja California. One Santa Barbara Basin core was collected in September, 1973; two other cores collected in May, 1974 yielded the surface samples designated in the tables as "A" and "B". Soledad Basin samples were recovered off Baja California in October, 1973. The direct measurement of ^{241}Pu were compared with those based on ^{241}Am ingrowth. The Pu which was previously deposited on platinum planchets from June, 1974 to January, 1975 was removed by heating with 8N HNO$_3$ for two days and taken to dryness subsequent to spiking with ^{243}Am. On some of these samples, the planchets were recounted for Pu and Am isotopes by alpha spectrometry for verification of the complete removal of these two transuranics. The sample was then dissolved in 3 ml of 1N HNO$_3$ and extracted with 10 ml of a scintillation mixture (5 g terphenyl + 0.05 g POPOP in 800 ml spectrographic grade toluene) containing 0.5 ml HDEHP ((di(2-ethylhexyl) phosphoric acid)). The presence of the Am in the aqueous fraction did not interfere with the liquid scintillation counting of the ^{241}Pu and the total alphas of plutonium.

The ratio ^{241}Pu/$^{239+240}$Pu and the absolute ^{241}Pu activity are determined in the following way. Two independent measurements are made by liquid scintillation techniques: the ^{241}Pu beta activity and the total alpha activity. By the alpha measurement the alphas emitted by the different isotopes of plutonium cannot be distinguished from one another. The $^{239+240}$Pu activity is ascertained by multiplying the ratio $^{239+240}$Pu/total alpha activity, determined by alpha spectroscopy, by the total alpha activity, determined by liquid scintillation counting. The absolute ^{241}Pu activity is calculated by multiplying the ^{241}Pu/$^{239+240}$Pu ratio, determined by scintillation counting, by the $^{239+240}$Pu activity determined by alpha spectroscopy.

The ^{241}Am ingrowth from ^{241}Pu is obtained subsequent to ^{241}Pu counting. The scintillation mixture is transferred quantitatively from the counting vial to a separatory funnel and the aqueous phase containing the Am is separated from the Pu fraction. The Am fraction is re-extracted again with 0.5 ml HDEHP in

10 ml of toluene. When the aqueous phase is clear, it is transferred to a small beaker, adding several drops of $HClO_4$ and taken to dryness. By this method, Pu contamination is minimized. The Am is plated [8] and counted by alpha spectrometry.

The [241]Am was sought in the sediment samples in the following way. The original Am fraction, which was initially spiked with [243]Am, and 10 mg of yttrium carrier were separated from the Pu, U and Fe [5]. It was further purified by $Pb(NO_3)_2$ precipitation with HNO_3 eliminating lead isotopes and the alkaline earth elements [9]. The nitric acid supernatant containing Am, lanthanides and actinides was extracted with DDCP (dibutyl N, N-diethyl carbamyl phosphonate) [10].

DDCP has been demonstrated to extract Am, Pu and Th with high yields but the behaviors of Th and Pu in the back extraction with $2M$ HNO_3 are not described. It was found using [234]Th and [242]Pu tracers that plutonium and thorium are not stripped from the DDCP with $2M$ HNO_3. Thus, the DDCP extraction procedure is an effective decontamination step for [241]Am (alpha energy, 5.5 MeV) from [238]Pu (alpha energy, 5.5 MeV) and [228]Th (alpha energy, 5.4 MeV). The Am fraction was evaporated to dryness and separated on a Bio Rad Ag-1 column using ethanol, methanol, and HNO_3 mixture [11]. The Am was eluted with $6M$ HNO_3, evaporated to dryness and plated onto stainless steel [8].

Fig. 1. Pu and Am isotopes in basin sediments. Time frame is based upon ^{210}Pb geochronology [5]. The [210]Pu values are corrected for decay to the date of collection. The [241]Am/[241]Pu ratios are given in percent.

3. Results and discussion

Concentrations of [241]Pu and [241]Am, and the ratios [241]Am/[241]Pu and [241]Am/[239+240]Pu in Santa Barbara Basin and Soledad Basin sediments are shown in Fig. 1 and Table 1. The [241]Pu activities are corrected to the date of collection for Fig. 1 and Table 1 and to July 1, 1962 for Table 1 and Table 2. There are evident increasing activities of [241]Pu and [241]Am with decreasing ages of the strata up to the late 1960's deposits where they leveled off through the most recent (1974) deposits. This result is similar to that found previously for [239+240]Pu [5].

The [241]Am/[241]Pu and the [241]Am/[239+240]Pu ratios (Fig. 1 and Table 1) show very constant values with depth in the sediment (or time). This indicates environmental sour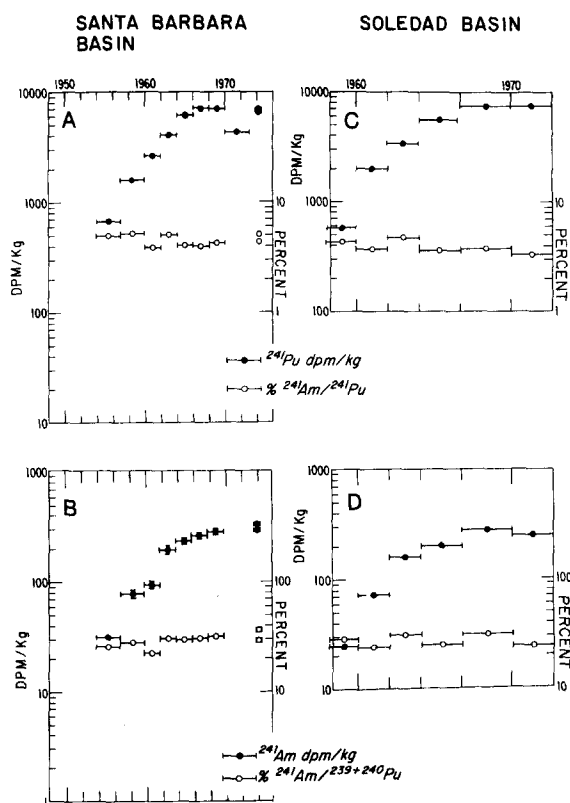ces for these transuranics in which accumulations over long time intervals have taken place, i.e., the major inputs from U.S.A. and U.S.S.R. tests in the late 1950's and 1960's are the dominant contributions and are contained along with entries from more recent but lower intensity tests (Fig. 2). If direct fallout of these nuclides from the stratosphere governed the sediment concentrations, then profiles similar to Fig. 2 would be expected. Herein we have compelling evidence that the transuranics entering these deposits represent a mixture of remobilized crustal debris which accumulated these metals over the time period before their incorporation in the deposits with a smaller amount of direct fallout. The immediate source of this crustal debris, wind or river transported material or resuspended shelf and slope sediments, as yet cannot be identified.

The [241]Pu/[239+240]Pu activity ratios found in these

TABLE 1

^{241}Pu and ^{241}Am concentrations, and ^{241}Am/^{241}Pu and ^{241}Am/$^{239+240}$Am ratios in Santa Barbara and Soledad Basins

Years of deposition	Collection date	Depth (cm)	$^{239+240}$Pu (dpm/kg)	^{241}Am (dpm/kg)	$\frac{^{241}Am}{^{239+240}Pu}$	^{241}Pu (dpm/kg) (by liquid scintillation)	$\frac{^{241}Am}{^{241}Pu}$	$\frac{^{241}Pu}{^{239+240}Pu}$ (by liquid scintillation)	$\frac{^{241}Pu}{^{239+240}Pu}$ (by ^{241}Am ingrowth)	^{241}Pu (dpm/kg) (by liquid scintillation)	$\frac{^{241}Pu}{^{239+240}Pu}$ (by liquid scintillation)	$\frac{^{241}Pu}{^{239+240}Pu}$ (by ^{241}Am ingrowth)
						(^{241}Pu corrected to date of collection)				(^{241}Pu corrected to July 1, 1962)		
Santa Barbara Basin												
SBB-A	(5/1974)	surface	928 ± 16	337 ± 23	0.36	6740	0.050	7.3 ± 0.2	6.4 ± 1	11,880	12.8	11.0
SBB-B	(5/1974)	surface	1027 ± 32	297 ± 27	0.29	6890	0.043	6.7 ± 0.3	6.5 ± 1	12,220	11.9	11.1
1970–1973	(9/1973)	0 –1.2	534 ± 21	n.d.	n.d.	4190	–	7.9 ± 0.3	6.9 ± 0.6	7210	13.5	11.8
1968–1970	(9/1973)	1.2–2.1	887 ± 31	290 ± 13	0.33	6920	0.042	7.8 ± 0.5	7.1 ± 0.6	11,890	13.4	12.2
1966–1968	(9/1973)	2.1–3.0	864 ± 19	270 ± 11	0.31	6980	0.039	8.1 ± 0.4	–	11,920	13.8	–
1964–1966	(9/1973)	3.0–3.8	790 ± 20	240 ± 10	0.30	6010	0.040	7.6 ± 0.2	6.0 ± 0.7	10,350	13.1	10.3
1962–1964	(9/1973)	3.8–4.8	642 ± 19	200 ± 17	0.31	4000	0.050	6.2 ± 0.2	5.6 ± 0.6	6870	10.7	9.6
1960–1962	(9/1973)	4.8–5.6	420 ± 7	97 ± 6	0.23	2560	0.038	6.1 ± 0.2	–	4370	10.4	–
1957–1960	(9/1973)	5.6–6.6	277 ± 5	80 ± 6	0.29	1560	0.051	5.6 ± 0.2	4.4 ± 0.4	3240 *	11.7 *	9.1 *
1954–1957	(9/1973)	6.6–7.6	125 ± 3	32 ± 3	0.26	660	0.049	5.3 ± 0.2	5.4 ± 0.5	1580 *	12.7 *	12.9 *
Soledad Basin												
1970–1973	(10/1973)	0 –1.3	1043 ± 27	247 ± 25	0.24	7430	0.033	7.1 ± 0.2	6.7 ± 0.6	12,730	12.2	11.5
1967–1970	(10/1973)	1.3–2.9	905 ± 20	278 ± 17	0.31	7430	0.037	8.2 ± 0.3	7.7 ± 0.7	12,760	14.1	13.2
1965–1967	(10/1973)	2.9–4.2	809 ± 14	200 ± 20	0.25	5640	0.036	7.0 ± 0.4	7.3 ± 0.7	9630	11.9	12.6
1962–1965	(10/1973)	4.2–5.2	527 ± 15	161 ± 7	0.31	3400	0.047	6.5 ± 0.2	7.1 ± 0.7	5850	11.1	12.2
1960–1962	(10/1973)	5.2–6.2	300 ± 7	73 ± 10	0.24	1980	0.037	6.6 ± 0.2	5.9 ± 0.5	3420	11.4	10.1
1958–1960 **	(10/1973)	6.2–7.1	85 ± 4	25 ± 4	0.29	580	0.043	6.8 ± 0.5	–	1165 *	13.7 *	–

* The following samples were decay-corrected for ^{241}Pu to the midpoint of the deposition years:

Santa Barbara Basin: 1957–1960, ^{241}Pu corrected to July 1, 1958.

1954–1957, ^{241}Pu corrected to July 1, 1955.

Soledad Basin: 1958–1960, ^{241}Pu corrected to July 1, 1959.

** This sample was reanalyzed for $^{239+240}$Pu, ^{241}Pu and ^{241}Am. This accounts for the difference from the $^{239+240}$Pu in Koide et al. [5].
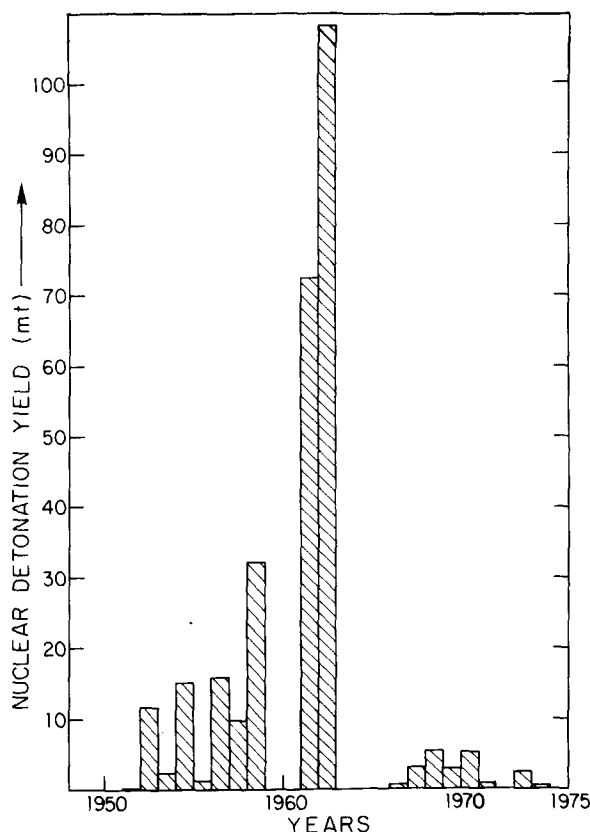
Fig. 2. Nuclear weapons testing as a function of time. Data from Carter and Moghissi [12].

sediments averaged 6.9 at the time of collection (12.4 corrected for decay of ^{241}Pu to July 1, 1962 *) as determined by ^{241}Pu liquid scintillation and approximately 8% lower by the ^{241}Am ingrowth method. However, the average counting error by alpha counting method was approximately 10% due to the low activities of ^{241}Am that had grown in since the electrodeposition of plutonium. More important is the agreement of the decay-corrected average ratio of 12.4 with the ratios of 14–16 of fresh bomb debris [2,3]. Livingston et al. [4] arrived at a representative ratio of 13–14 for the 1961–1962 U.S.S.R./U.S.A. tests and the 1967 Chinese Test. A ratio of 13.9 obtained

* The ^{241}Pu is corrected for decay to July 1, 1962 on the basis that the most extensive production of ^{241}Pu in the northern hemisphere was made up to this date.

when their average Buzzard Bay sediment samples are corrected to July 1, 1962.

If ^{241}Pu activities measured by liquid scintillation are corrected to July 1, 1962 and used to calculate [4] the amount of ^{241}Am ingrowth in the sediments at the time of collection, then ingrowth ^{241}Am counts for approximately 60% of the ^{241}Am that was measured in the sediments (Table 2). It is possible that this excess ^{241}Am may have been produced during the weapons tests, or there has been a fractionation of ^{241}Pu from the ^{241}Am in the water column if the ^{241}Pu preferentially stays in solution. However, we will assess an alternative explanation for the deficiency of ^{241}Am based on an additional input of ^{241}Pu back to November 1, 1955, a mid-point between the weapons tests November 1, 1952 to November 1, 1958. These tests were not taken into account in our calculation for the ^{241}Am values derived from ^{241}Pu since July 1, 1962. As an approximation, we assume that 32% of the total nuclear bomb yield and of the plutonium production came from the early nuclear bomb tests (1952–1958) (carried out primarily by the U.S.; Fig. 2 and Carter and Moghissi [12]). We correct 32% of ^{241}Pu at July 1, 1962 back to November 1, 1955. Then the total contribution of ingrowth ^{241}Am calculated from 1952 and 1961 series of weapons tests to the time of collection approaches more closely the values measured for ^{241}Am (Table 2). This interpretation necessitates that the Am and Pu are immobilized subsequent to deposition and the ^{241}Am present is primarily an ingrowth product of bomb fallout ^{241}Pu. Further, we recognize that the transuranic fluxes are latitude dependent. Thus the bomb yields may not give precise fluxes of transuranic nuclides at any given site [13,14].

Although the ^{241}Am is present in recent sediments at high levels as a result of ingrowth, the ^{241}Pu introduced from the early 1950's has decayed to less than 30% of the original values and thus the ^{241}Am activities in sediments off the California coast will continue to increase.

There is a radical difference between the ^{241}Pu concentrations in the sediments compared to that which would be expected from the direct and sole entry of fallout debris. In the latter case, the maxima corresponding to high levels of testing in the 1950's and 1960's would be evident. They are not. Instead, there is a continuously increasing ^{241}Pu

TABLE 2

^{241}Pu and ^{241}Am in basin sediments

	^{241}Pu (dpm/kg) corrected to July 1, 1962	^{241}Am (dpm/kg) measured	^{241}Am ** (dpm/kg)	^{241}Am **/^{241}Am	^{241}Am *** (dpm/kg)	^{241}Am ***/^{241}Am
Santa Barbara Basin						
SSB-A surface	11,880	337	170	0.5	270	0.8
SSB-B surface	12,220	297	175	0.6	278	0.9
1968–1970	11,890	290	163	0.6	261	0.9
1966–1968	11,920	270	164	0.6	262	1.0
1964–1966	10,350	240	142	0.6	227	1.0
1962–1964	6870	200	94	0.5	150	0.8
1960–1962	4370	97	60	0.6	96	1.0
1957–1960 *	3240 *	80	55	0.7		
1954–1957 *	1580 *	32	30	0.9		
Soledad Basin						
1970–1973	12,730	247	176	0.7	107	1.2
1967–1970	12,760	278	176	0.6	105	1.0
1965–1967	9630	200	133	0.7	79	1.1
1962–1965	5850	161	81	0.5	48	0.8
1960–1962	3420	73	47	0.6	28	1.0
1958–1960 *	1165 *	25	19	0.8		

* ^{241}Pu decay corrected midpoint. See Table 1, *.

** ^{241}Am calculated from ^{241}Pu when decay corrected to July 1, 1962.

*** This ingrowth ^{241}Am was calculated to the time of collection assuming that the ^{241}Am at July 1, 1962 (column 1) is a mixture of which 32% is decay corrected back to November 1, 1955, midpoint from November 1, 1952 to November 1, 1958 and the remainder decay corrected to July 1, 1962. The 0.32/0.68 is based on the nuclear detonation yield distribution from the first series of atmospheric tests (1952 to the moratorium in 1958–1959) compared to the second series of tests primarily in 1961 and 1962. See Fig. 2.

concentration with time up to the late 1960's and subsequently leveling off. This suggests inputs from reservoirs which have accumulated the fallout debris since its introduction. The reservoir may be soil debris or resuspended sedimentary particles in seawater or a combination of the two. At present we cannot identify the reservoir more decisively.

Similarly, the ^{210}Pb of the sediments, used for the determination of the deposition rate, has a variety of sources: direct fallout from the atmosphere following production from ^{222}Rn fallout from the atmosphere on particulates; river-borne particulates; production within the water column and sediments from ^{226}Ra; and the redeposition of sediments from other sites. But of importance, is the observation that the sedimentation rate, ascertained by unsupported ^{210}Pb, is in concord with that obtained by varve counting [15].

Acknowledgement

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