The Cycling of Transuranic Radionuclides
in the
Columbia River, its Estuary,
and the
Northeast Pacific Ocean

DOE/EV/70030--7

DE82 011218

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PROGRESS REPORT

T.M. Beasley

Principal Investigator

School of Oceanography
Oregon State University
Marine Science Center
Newport, OR 97365

February 1981 - December 1981

Prepared for the U.S. Department of Energy
under Contract DE-AM06 -76RL 02227
Task Agreement DE-AT06 -76EV 70030

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It
has been reproduced from the best available
copy to permit the broadest possible avail-
ability.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

This report summarizes progress from February, 1981 through December, 1981 in research dealing with the behavior of transuranic and other radionuclides in the Columbia River downstream from the Hanford Reservation. We have met all of the objectives outlined in last year's renewal proposal except one which is discussed below.

We have now essentially completed the analyses of all cores raised from the Columbia River between McNary Reservoir and the mouth of the river. This permits us to establish a budget for Pu and Am; for McNary Reservoir we plan to assign budgets for ^{152}Eu , ^{60}Co and ^{137}Cs as well, but these will require a few more analyses which will be done during the first quarter of 1982.

Over the past year, three papers describing our research were accepted for publication in scientific journals. A fourth paper, co-authored with colleagues from the Monaco Laboratory of the IAEA, has been accepted for publication in 1982 and deals principally with elucidating Pu uptake by starfish through food and water pathways. A final paper, summarizing our research on the Washington and Oregon continental shelves has been submitted for consideration. In all, this years accomplishments have been gratifying.

In addition to completing most of the tasks we outlined for ourselves, we participated in the analyses of four natural matrix standard reference materials for the National Bureau of Standards. This exercise required far more time than originally anticipated, but the outcome should be beneficial to the geochemical community in general and particularly to DOE contractors investigating environmental radioactivity. It seems appropriate to begin with this topic, since all conclusions about the behavior of radionuclides in the environment are based on the implicit assumption that measured concentrations of the activities are correct. Without

demonstrating that such measurements are sound, hypotheses and conclusions drawn from these data must be considered tenuous.

QUALITY CONTROL MEASUREMENTS

The National Bureau of Standards has prepared two samples of soil and sediment which contain varying amounts of artificial and natural radioactivity for inclusion in their natural matrix standards library. One of these, the Columbia River sediment sample, was collected by us for the Bureau from McNary Reservoir. Table 1 shows the four standards discussed here, their characteristics and the location of their collection.

Table 1. NATURAL MATRIX STANDARDS - NATIONAL BUREAU OF STANDARDS

<u>Sample Designation</u>	<u>Characteristics</u>	<u>Collection Site</u>
River Sediment	Sediment - low organic matter content- siliceous- moderate clay content- low-level transuranic and β, γ activities	Columbia River
Rocky Flats soil # 1	soil-low organic content- moderate transuranic activity of varying chemical/physical form- low β, γ activities	Rocky Flats, CO.
Lake Sediment (Gytijja)	sediment - high organic content- moderate transuranic activities- moderate β, γ activities.	Chalk River, Canada.
Peruvian soil	soil - low organic content - very low transuranic and $\beta \gamma$ activities	Peru

β, γ nuclides include ^{90}Sr -Y, ^{60}Co , ^{137}Cs , $^{152-154}\text{Eu}$. Not all nuclides are present in all samples.

At present, only two of the reference materials have been issued, and copies of the certification sheets are appended. Table 2 sets out our results in

comparison to those certified by NBS. The agreement is very satisfactory.

Table 2. COMPARISON OF ANALYTICAL RESULTS FOR NBS REFERENCE MATERIALS

Sample	River sediment		Rocky Flats Soil, #1	
Radionuclide	OSU [†] (dpm/kg)	NBS [*]	OSU (dpm/kg)	NBS
238-Pu	0.74±0.18	0.78±0.13	10.4±1.9	10.0±1.1
239,240 Pu	30.5±1.0	30.5±1.8	485±38	482±14
241-Am	8.3±0.5	9.0±1.9	73.4±5.3	75±5
60-Co	280±30	278±14	-	-
137-Cs	1883±72	1740±110	1137±51	1056±48
152-Eu	2060±100	1830±73	-	-

* certified values; error represents 99% confidence interval. Excludes hot particles for transuranic measurements in the Rocky Flats sample.

† values represent standard deviations about the mean of a large but variable number of measurements. Excludes hot particles for transuranic measurements in the Rocky Flats sample.

The Rocky Flats soil values for both Pu and Am were the subject of some controversy between the participating laboratories for several months. Disagreement centered both on the absolute amounts of transuranics in the sample and the variability evidenced both between and with approximately 90 gram aliquots of this material. Those laboratories who relied on "total" sample dissolution techniques invariably reported both higher mean transuranic concentrations as well as a greater range of values than did those laboratories who simply acid-leached the soil. By contrast, all participating laboratories achieved similar results in the analysis of the Columbia River sediment sample whether or not the sample

was acid-leached or totally dissolved. This latter finding argued that the yield determinants used by all laboratories had to be essentially correct and that the Pu and Am in the river sediment was more easily equilibrated with the added determinants than was the case for the Rocky Flats soil.

Ultimately it was shown that at least 8% of the Pu in the Rocky Flats soil is not mobilized by simple acid leaching (a treatment which is felt to be adequate for fallout-derived transuranics) and in addition that there are "hot particles" within the stock sample that are not equally distributed among the various aliquots available for purchase.

During the course of this exercise, it was necessary to demonstrate that our total dissolution techniques ($\text{HNO}_3 + \text{HF}$ solubilizations) would deliver quality Pu and Am results on soil samples where these radioelements were known to be in refractory forms. For this purpose, we obtained a soil sample from the Radiation and Environmental Sciences Laboratory (Idaho Falls) in which the Pu and Am had been made refractory by heating the soil to 900°C for 20 hours. The expected values for Pu-238 and Pu-239,240 were 13.6 ± 0.4 and 897 ± 72 dpm/kg, respectively; the mean of 10, five gram aliquots run by our procedures gave values of 13.4 ± 1.5 and 915 ± 39 dpm/kg, respectively for the plutonium radionuclides. Equally good agreement was found between the predicted and measured concentrations of Am-241.

Because of the disagreement between laboratories, it required about $2\frac{1}{2}$ months during this year to finalize all of the measurements we have performed on the four NBS samples to date. It must, however, be viewed as time well spent, as it continues to demonstrate that our measurements are of high quality. It should be noted that all of the transuranic and ^{137}Cs measurements which were made on these samples were done by the principal investigator; the laboratory assistants funded under this contract at that time were engaged in the analysis of Columbia River sediment cores.

While analyzing the NBS reference materials, it became apparent that low-level Co-60 measurements by GeLi γ -ray spectrometry required counting times that could not be justified by the resultant confidence limits associated with its determination. The cobalt radiochemical procedures which incorporate stable Co as a gravimetric yield determinant and provide sufficient decontamination from fission-product and naturally-occurring radionuclides are all tedious. Many employ H_2S and a fair number isolate the purified cobalt as potassium cobaltinitrite, a precipitate which is not always of constant composition and therefore not suitable for accurate determinations⁽¹⁾. During the summer tenure of Dr. C.D. Jennings, we developed an improved radiochemical separation for Co-60 which is rapid, provides excellent decontamination from fission-product and naturally-occurring radionuclides and recovers cobalt in high yield. We have prepared a manuscript for submission to Talanta, a draft of which is appended.

TRANSURANIC BUDGET FOR THE COLUMBIA RIVER-PRELIMINARY

Enough cores have now been analyzed to attempt a preliminary budget for Pu and Am in the Columbia River from the confluence of the Snake River at Pasco, WA to the river's mouth.

We can arbitrarily divide the river into four areas; the reach between the confluence of the Snake River and McNary Reservoir, the reach between McNary and Bonneville Dams, the reach from Bonneville Dam to river kilometer 50 at the head of the estuary and finally the estuary itself (Fig. 1). The greatest number of cores (36) analyzed from the river were raised from McNary Reservoir (Fig. 2), and these have been used to budget both Pu and Am in the reservoir between river kilometers 470 and 520. The area contained within this river reach is $\sim 100 \text{ km}^2$. The average Pu inventory in the sediments of this reach is 22 mCi/km^2

(1) Hahn, R.B. and Smith, D.L. (1961). Determination of radioactive cobalt in mixtures of radionuclides. Talanta, 7: 291-295.

Figure 1. Columbia River Study area.

Figure 2. Columbia River sampling sites.

giving a budget of 2.2 Ci of Pu-239,240. The mean Am-241/Pu-239,240 ratio in these sediments is 0.22, and therefore the Am-241 inventory is near 0.5 Ci. The low Am/Pu ratio in McNary sediments is due to the addition of Pu-239 by the old Pu production reactors. If account is taken of this contribution (20-25%), then the fallout Am/Pu ratio approaches 0.3, a value which is consistent with our measurements in other aquatic sediments.

Repeated attempts were made to raise cores between McNary Dam and John Day Dam without success. The sediment that was retrieved was coarse-grained sand whose activities were all uniformly low (~ 1 dpm/kg dry). For this river reach, we have assigned a maximum integrated inventory of 0.2 mCi/km^2 , which yields a total Pu-239,240 inventory of ~ 0.04 Ci. Since John Day Dam was not completed until April, 1968, it is not surprising that we did not encounter fine sediment accumulations there.

The pools behind both the Dalles Dam and Bonneville Dam, where fine sediments could be retrieved, showed integrated inventories which averaged near 10 mCi/km^2 . Upriver from these pools (above the confluence of the Deschutes and Wind Rivers, respectively), the sediments are again coarse-grained and of low activity giving inventories near 0.2 mCi/km^2 . Thus, from river kilometer 241 to 326, the Pu-239,240 inventory is estimated near 0.6 Ci.

Below Bonneville Dam to the head of the estuary (river kilometer 50), all cores analyzed had integrated inventories of $\approx 0.2 \text{ mCi/km}^2$. This entire reach of river is calculated to contain about 0.06 Ci of Pu-239,240.

Within the estuary itself, the majority of the bed sediments are comprised of 84% sand, 13% silt, 2% clay and 1% gravel. The clay and silt content of the mixture lead to somewhat higher inventories within the estuary than are seen in sediments directly upriver. Cores of estuarine textural composition typically exhibit integrated inventories near 1 mCi/km^2 . Where fine sediments accumulate to depths of ~ 1 meter (Youngs Bay), inventories approach 15 mCi/km^2 . However,

only about 10% of the estuary does accumulate such fine material in isolated locations. Consequently, the integrated inventory for the estuary is based primarily on the activities measured in the coarse-grained cores. As such, we calculate that there is approximately 1.5 Ci of Pu-239,240 contained in the sediments between the mouth of the river and river kilometer 50. Summation over the entire 520 kilometers of estuary and river bed gives a total Pu-239,240 inventory of 4.4 Ci. Except for McNary Reservoir sediments, it is reasonable to assign a Am-241/239,240 Pu ratio of 0.3 for all bed sediments, and therefore the Am-241 inventory over the same river reach is near 1.2 Ci.

These estimates are open to refinement as we prepare the data for publication, but there should be no substantial change in the values quoted for any portion of the river. If changes are made, they most likely will occur in our estimates of the transuranic burden in McNary Reservoir. On the Oregon side of the river, inventories were the highest of any observed throughout the river ($> 50 \text{ mCi/km}^2$). In many cases, our cores did not capture the entire radionuclide profile even though cores lengths were $> 80 \text{ cm}$. We are presently in the process of estimating what fraction of the total Pu inventory in these areas lies below our maximum sampling depth. Our first estimate suggests that at best, the total inventory of Pu may rise from an estimated 2.2 Ci to perhaps 3.0 Ci.

PUBLICATIONS

Appended to this years annual report are reprints and preprints of work published during the contract year or presently under journal review. Rather than discuss each paper separately, the summary below shows the status and major theme of each paper. As reprints become available, they will be forwarded to the proper DOE repository.

PUBLICATIONS SUMMARY

Title	Journal	Status	Topic
Hanford-derived Pu in Columbia River sediments.	Science 214: 913-915 (1981)	Published	Details the contribution of Hanford Pu production reactors to Pu inventories of river sediments.
Pu and Am in anoxic marine sediments: Evidence against remobilization.	Geochim. et Cosmochim. Acta. 45: 1917-1930 (1981)	Published	Questions hypothesis that Pu and Am are remobilized by organic complexones in marine sediments.
Pu and Am export to the northeast Pacific Ocean by Columbia River run-off.	Est. Coast. & Shelf Sci.	In Press (Dec. 1981)	Budgets annual and total transuranic export to coastal shelf off Washington and Oregon
Pu, ²⁴¹ Am and ¹³⁷ Cs ratios, inventories and vertical profiles in Washington and Oregon continental shelf sediments.	Geochim. et Cosmochim. Acta.	Submitted	Discusses budget of transuranics on continental shelves of Washington and Oregon, the processes controlling inventories and mobility of radionuclides.
Routes of Pu uptake and their relation to biomagnification in starfish.	Mar. Poll. Bull.	In press (1982)	Discounts previously advanced theory of Pu biomagnification in starfish.

It seems reasonable to re-state the original goals of our research project to judge our progress to date. In 1977, we set out to collect material from the river system to answer the following questions:

- 1) What are the standing inventories of transuranics and other radionuclides presently in the river reach between McNary Reservoir and the estuary?
- 2) Of this transuranic inventory, what amount (if any) can be attributed to the operation of the old, single-pass production reactors on the Hanford Reservation?
- 3) How much Pu and Am has been exported by this major river to the northeast Pacific Ocean?
- 4) What is the fate of the Pu exported by the river once it enters the ocean? What processes control its distribution and does the river export constitute a significant addition of Pu to the coastal zone?
- 5) Is there any evidence in this river system that the transuranics display unusual post-depositional mobility once deposited in sediments?
- 6) What are the transuranic burdens in the biotic components of the river system and how do they compare with those measured in purely oceanic regimes?

To date, we have answered the first five questions. The sixth remains to be addressed.

We had, in fact, intended to collect biological samples from McNary Reservoir, the river and the estuary this year, but circumstances prevented us from doing so. First, the boat we had intended to use, the R/V Sacajawea, has been laid-up for modifications for most of the fall months. A new diesel engine has been installed and work is presently proceeding to add offshore navigational capability and to improve the hydraulic system.

During the winter and spring months, volume flow in the river and inclement weather conditions preclude collecting infauna in the upper river; sampling is best done between July and November. We have therefore deferred the collection of fresh specimens until 1982. We are, however, presently exploring the possibility of analyzing museum samples of biota which may be available at Battelle-Northwest. We think this is important scientifically as we know of no such systematic approach dealing with transuranic concentrations in riverine food webs which has been published in the literature or which is presently underway elsewhere. We have received several enquiries concerning our published data of Pu in Columbia River sediments (one of which is attached to this report), which bear on this subject. As there are reasonably high inventories of Pu and Am in McNary Reservoir sediments, the concentrations of these radioelements in the infauna which reside there are worthy of study. Moreover, as the sediments there carry a unique $^{240}/^{239}$ Pu signature, it will be of interest to determine whether the biota carry an isotopic ratio comparable to that of the sediment and sediment pore waters or that of contemporary river water which should be quite different. Resident and anadromous fish populations should also be sampled and the Pu isotopic signature determined in selected tissues along with total transuranic concentrations.