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RADIONUCLIDES IN SEDIMENTS FROM THE
NORTHEAST ATLANTIC DISPOSAL SITE

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TABLE OF CONTENTS

Abstract	1
Introduction	1
Methods--Sample Collection	2
Cooperative Study with P. J. Kershaw and R. J. Pentreath, Fisheries Laboratory, Lowestoft, United Kingdom	2
Cooperative Study with M. van der Loeff, Netherlands Institute for Sea Research, Netherlands and J. Smith and M. Bewers, Bedford Institute of Oceanography, Canada	2
Intercalibration	3
Control Site Samples	3
Results and Discussion	6
Gamma Spectrometry	6
Plutonium Concentrations	7
Acknowledgments	13
References	13

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229

RADIONUCLIDES IN SEDIMENTS FROM THE NORTHEAST ATLANTIC DISPOSAL SITE

ABSTRACT

The concentrations and inventories of $^{239+240}\text{Pu}$ in sediments from within the boundaries of the low-level radioactive waste-disposal site in the northeast Atlantic are not significantly different from global fallout levels expected in deep-sea sediments from this region of the Atlantic. No man-made gamma-emitting radionuclides were above detection limits in the sediment samples analyzed. Further, there is no indication that past disposal practices have led to an area-wide contamination of the site with waste-related radionuclides.

INTRODUCTION

Deep sea disposal of packaged, low-level radioactive wastes has occurred at several sites in the northeast Atlantic. However, since 1977, disposal has been restricted to a single site $4 \times 10^3 \text{ km}^2$ within 10 nautical miles north and south of 46° N. ($45^\circ 50' \text{ N.}$ to $46^\circ 10' \text{ N.}$) and between 16° W. and $17^\circ 30' \text{ W.}$ A program of coordinated scientific studies was initiated in 1980 by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development to develop a site-specific model for predicting radiation exposures to man with a greater degree of accuracy. Task groups on physical oceanography, geochemistry, biology, modeling, and radiological surveillance were established to provide scientific input on the physical, geochemical, and biological processes controlling the behavior of radionuclides in the deep ocean and specifically at the disposal site. As part of this effort, we have undertaken cooperative studies with other investigators to better improve our understanding of the behavior of long-lived radionuclides in deep ocean sediments. Sediment core samples collected within and outside the disposal site during 1982 were provided for analysis. Here we discuss the available results for gamma-emitting radionuclides and plutonium determined in these samples.

METHODS--SAMPLE COLLECTION

COOPERATIVE STUDY WITH P. J. KERSHAW AND R. J. PENTREATH, FISHERIES
LABORATORY, LOWESTOFT, UNITED KINGDOM.

Two 7.6-cm-diam subcores were removed from five Reineck box core samples obtained at the northeast Atlantic disposal site. The cores were obtained for radionuclide analysis from the Cirolana research cruise to the dumpsite in October 1982. They were frozen in the vertical position and returned to the Lawrence Livermore National Laboratory (LLNL) for processing. We sectioned 2-cm-thick intervals to a depth of 10 cm and 5-cm-thick intervals below 10 cm from each of the frozen cores. A circular disk measuring 26.4 cm^2 was removed from the central portion of each section and the outer 1-cm-thick annulus was discarded so that any mixed sediment near the core barrel wall was not included in the final sample. The sediment was dried, homogenized, and transferred to sample containers for analysis by gamma spectrometry. Subsequently, the samples were processed to radiochemically separate plutonium radionuclides and ^{241}Am . The x rays of the cores were made on board the Cirolana and other subcores were removed from the box cores by Dr. Kershaw for analysis of natural radionuclides. We have not yet collated our results with those from Lowestoft.

COOPERATIVE STUDY WITH M. VAN DER LOEFF, NETHERLANDS INSTITUTE FOR SEA
RESEARCH, NETHERLANDS AND J. SMITH AND M. BEWERS, BEDFORD INSTITUTE OF
OCEANOGRAPHY, CANADA

Two 7.6-cm-diam subcores were removed from eight 0.25-m² Mark III box core samples obtained in and around the northeast Atlantic disposal site. These cores were obtained during the Tyro expedition to the region in August and September 1982. These samples were frozen and shipped to Dr. Smith at the Bedford Institute of Oceanography where each core was x rayed and sectioned into 1-cm increments. The sediment samples were weighed and freeze-dried. One gram of sediment was removed from each sample for ^{210}Pb determinations and the remainder was sent to LLNL for analysis. Each sample was transferred to suitable containers for analysis by gamma spectrometry. Subsequently, the samples were processed to radiochemically separate plutonium radionuclides and ^{241}Am . Dr. van der Loeff obtained additional sediment and pore water

samples from the box cores to provide information on additional biological, geochemical, and chemical parameters. The x-ray photographs of box core samples revealed traces of burrowing activity in the upper 8 to 10 cm of sediment. We have not yet collated our results with those of Dr. van der Loeff, but intend to do so within the year.

Locations of the sediment cores collected from both Tyro and Cirolana cruises are shown in Fig. 1 along with the boundaries of the northeast Atlantic site currently used for the disposal of low-level radioactive wastes. To date, only one of each duplicate pair of cores from each box core has been analyzed for man-made radionuclides.

INTERCALIBRATION

Over the years we have been involved in a number of interlaboratory analytical comparison exercises organized by national and international agencies. Most recently we participated in an intercalibration exercise organized by the International Atomic Energy Agency (IAEA) Monaco Laboratory for the analysis of plutonium and americium in a marine sediment sample. This intercalibration effort is part of the NEA program plan for assessments of radionuclides at the northeast Atlantic site. Results from our determinations of these radionuclides in IAEA sediment sample SD-N-1 are shown in Table 1. These samples were processed by several different methods and the mean values are in excellent agreement with values determined at the Monaco Laboratory and by other participating organizations (Fukai, 1982).

CONTROL SITE SAMPLES

Sediment samples were collected east of the dumpsite in the Bay of Biscay in 1981 to determine the fallout background levels of plutonium, americium, and other radionuclides in sediments from depths of 4000 to 5000 m in the north Atlantic between 40° and 50° N. latitude. The fallout concentrations have been reported previously (Noshkin, 1983) and are abstracted here for comparative purposes.

Figure 1. Location of Tyro and Cirolana sampling stations in and around the northeast Atlantic dumpsite used for the disposal of low-level radioactive wastes.

Table 1. Plutonium and americium concentrations in sediments SD-N-1 provided by the International Atomic Energy Agency and analyzed at Lawrence Livermore National Laboratory.

Bottle number	Aliquot	Dissolution method ^b	Concentration (fCi/g) (σ%) ^a		
			²³⁸ Pu	²³⁹ + ²⁴⁰ Pu	²⁴¹ Pu
24	1	A	4.7 (7)	14.8 (5)	--
24	2	A	<u>5.5 (10)</u>	<u>14.8 (4)</u>	--
24 average ± σ			5.1 ± 0.6	14.8 ± 0	--
325	1	A	5.8 (8)	15.3 (5)	--
325	2	A	<u>5.1 (8)</u>	<u>14.9 (4)</u>	--
325 average ± σ			5.5 ± 0.5	15.1 ± 0.3	--
76	1	A	5.2 (8)	15.3 (4)	12.2 (4)
76	2	B	5.6 (8)	15.7 (5)	11.3 (8)
76	3	B	5.2 (10)	15.3 (5)	12.0 (8)
76	4	C	3.7 (18)	16.0 (8)	15.9 (5)
76	5	C	<u>4.9 (8)</u>	<u>15.9 (5)</u>	<u>12.2 (9)</u>
76 average ± σ			4.9 ± 0.7	15.6 ± 0.3	12.7 ± 1.8
135	1	A	5.9 (10)	13.3 (6)	--
135	2	B	5.7 (9)	15.4 (5)	--
135	3	B	4.6 (8)	15.3 (4)	--
135	4	C	5.0 (12)	13.5 (6)	--
135	5	C	4.4 (15)	16.9 (7)	--
135	6	D	<u>5.6 (10)</u>	<u>13.0 (6)</u>	--
135 average ± σ			5.2 ± 0.6	14.6 ± 1.5	--
353	1	A	4.7 (12)	14.3 (6)	13.0 (11)
353	2	B	6.2 (7)	16.7 (5)	12.0 (11)
353	3	B	4.0 (9)	15.2 (4)	14.1 (6)
353	4	C	4.7 (8)	14.3 (5)	12.9 (8)

Table 1. (Continued)

Bottle number	Aliquot	Dissolution method ^b	Concentration (fCi/g) (σ%) ^a		
			²³⁸ Pu	²³⁹⁺²⁴⁰ Pu	²⁴¹ Pu
353	5	C	5.5 (7)	15.7 (5)	13.2 (10)
353	6	D	6.6 (10)	18.0 (6)	15.7 (9)
353 average ± σ			5.3 ± 1.0	15.7 ± 1.4	13.5 ± 1.3
Overall average ± σ			5.2 ± 0.7	15.2 ± 1.2	13.1 ± 1.5

^a Values in parentheses are the one standard deviation of the counting error given as percent of the activity. The ± values are the one standard deviation of the mean for replicate analysis of each bottle. Other systematic uncertainties estimated to be less than 3% are not included.

^b Dissolution method A = 5 to 20 g of sample digested in 8N HNO₃ for approximately 4 to 6 h with periodic addition of 30% H₂O₂; B = digested in concentrated HNO₃ and HCl (5:1) and 30% H₂O₂; C = digested in concentrated HNO₃ only; and D = dissolution in HNO₃, HF, and HClO₄.

RESULTS AND DISCUSSION

GAMMA SPECTROMETRY

Ge (Li) gamma-ray spectrometers were used to determine the presence and concentration of gamma-emitting radionuclides in the Cirolana and Tyro sediment samples. Dry weights of the 0- to 1- and 0- to 2-cm sections of sediment ranged from 13 to 30 g. Examples of our detection limits for several gamma-emitting fission and activation products, based on a counting time of 1000 min, are shown in Table 2. Therefore, with the size of the sample available for analysis, we were unable to detect for example, the presence of ¹³⁷Cs in the sediment if the concentration was less than 0.07 pCi/g. The minimum detectable activity, normalized to a unit weight, can be determined for the other radionuclides listed in Table 2 using the same weight. Except for ⁴⁰K (mean concentration detected in core sections is 4.4 ± 1.3 pCi/g

Table 2. Detection limits for several radionuclides as determined by gamma spectrometry.

Radionuclide	pCi/sample
^{137}Cs	2.0 ± 0.2
^{60}Co	2.2 ± 0.2
^{241}Am	5 ± 1
^{155}Eu	4 ± 1
^{125}Sb	4 ± 2

dry) and daughter products of the ^{238}U and ^{232}Th decay chains (all naturally occurring radionuclides), no other gamma-emitting radionuclides were present in concentrations above our minimum detection limits in any section of sediment sampled within or outside the disposal site.

PLUTONIUM CONCENTRATIONS

Our radiological separation methods have been published previously. They are essentially those used to generate the results in Table 1 for the intercalibration exercise. Concentrations of $^{239+240}\text{Pu}$ determined so far in the sections of Cirolana and Tyro sediment samples are shown in Tables 3 and 4. Table 5 is a summary of $^{239+240}\text{Pu}$ concentrations in sections of sediment obtained at 4100 m from the Bay of Biscay in 1981. Inventories of $^{239+240}\text{Pu}$ in the sediment columns and other supplemental information is provided in Table 6. The ^{238}Pu was above detection limits (by alpha spectrometry) in 29 sections analyzed to date. The mean ratio of ^{238}Pu to $^{239+240}\text{Pu}$ determined in these sections is 0.068 ± 0.035 . This value is identical to the mean fallout ratio of 0.05 ± 0.03 measured in the sediment from the Bay of Biscay (Noshkin, 1983). Although the plutonium results are incomplete, there are several features in the available data that are noteworthy.

In every core, a subsurface maximum in the concentration of $^{239+240}\text{Pu}$ is evident and appears at different depths in the sediment column (see Table 6). In the Tyro cores, these maxima are coincident with the maxima in

Table 3. Concentrations of $^{239+240}\text{Pu}$ in sections of cores (fCi/g dry weight) from Cirolana stations.

	Station number				
	120	122	119	124	125
<u>Depth increment (cm)</u>					
0-2	8.9 (9) ^a	--	--	9.1 (6)	8.2 (8)
2-4	4.4 (13)	--	--	2.7 (22)	6.4 (8)
4-6	6.0 (8)	--	--	0.6 (54)	3.2 (8)
6-8	1.9 (22)	--	--	1.0 (38)	7.1 (12)
8-10	0.7 (24)	--	--	0.1 (70)	2.5 (16)
10-15	0.1 (40)	--	--	0.15 (23)	0.21 (21)
15-20	0.1 (40)	--	--	<.06	0.04 (60)
20-24	<0.06	--	--	<.06	<.06
Overlying water					
depth (m)	4673	4515	4522	4515	4758
Collection date	10/20/82	10/20/82	10/19/82	10/20/82	10/20/82
Coordinates	46°00.03' N. 46°00.20' N.	46°00.03' N. 46°00.20' N.	45°59.84' N. 17°14.79' W.	16°54.95' N. 16°44.77' W.	16°54.95' N. 16°45.38' W.

^a Values in parentheses are the one standard deviation of the counting error expressed as the percent of the value listed.

^{210}Pb concentrations (Smith, 1983). This is true even when subtle maxima are seen such as in the Tyro core 1 between 4 and 5 cm, where it could be argued that with the analytical uncertainty in the results, a different interpretation of the profile could be suggested.

It would appear that translocation of ^{210}Pb and $^{239+240}\text{Pu}$ to certain depths in the sediment column occur by the same process. These maxima appear in horizons of the sediment column where lateral and vertical burrowing activity is evident from the x-ray radiographs made at the Bedford Laboratory. An example of this is seen in Fig. 2 for the Tyro station 2 core. A subsurface maximum in $^{239+240}\text{Pu}$ is evident in the sediment column

Table 4. Concentrations of ^{137}Cs in 10 sections of cores (fCi/gm dry weight) from Tyro stations.

depth Increment (cm)	Station number							
	1	2	4	5	6	11	13	15
1-1	8.9 (9) ^A	17.1 (10)	7.7 (6)	10.7 (14)	8.2 (11)	10.7 (12)	7.1 (10)	--
1-2	4.2 (9)	10.0 (10)	2.4 (15)	2.5 (20)	2.7 (16)	3.0 (21)	--	--
2-3	2.3 (16)	5.0 (11)	2.1 (26)	2.3 (21)	4.4 (11)	4.0 (15)	--	--
3-4	1.8 (16)	2.5 (12)	2.1 (11)	2.6 (19)	6.7 (9)	7.7 (8)	--	--
4-5	2.4 (24)	2.5 (12)	2.6 (18)	4.0 (16)	4.2 (12)	1.2 (20)	--	--
5-6	1.8 (18)	14.4 (5)	2.3 (26)	3.0 (15)	1.3 (20)	0.9 (26)	--	--
6-7	--	1.9 (19)	--	--	--	--	--	--
7-8	--	0.8 (34)	--	--	1.1 (20)	1.6 (37)	--	--
8-9	--	0.5 (46)	--	--	0.8 (25)	--	--	--
9-10	<0.06	1.3 (23)	<0.02	0.7 (30)	0.4 (32)	0.4 (48)	--	--
10-11	--	--	--	--	0.9 (22)	--	--	--
11-12	--	--	--	--	--	0.1 (50)	--	--
12-13	--	--	--	--	0.8 (23)	--	--	--
13-14	--	<0.06	--	--	--	<0.35	--	--
14-15	--	--	--	--	1.2 (18)	--	--	--
15-16	--	--	--	--	0.4 (20)	<0.05	--	--
16-17	--	--	--	--	--	--	--	--
17-18	--	--	--	--	--	<0.05	--	--
Water depth (m)	4800	4300	4300	4325	4579	4725	4700	4800
Collection date	8/25/82	8/26/82	1/2/82	9/3/82	9/4/82	9/6/82	9/8/82	9/8/82
Coordinates	47°1.0' N, 14°56.6' W.	46°3.3' N, 16°3.2' W.	45°51.8' N, 16°3.4' W.	45°3.3' N, 16°45.3' W.	45°53.6' N, 16°52.0' W.	46°01.1' N, 17°08.9' W.	46°04.2' N, 15°42.3' W.	45°56.1' N, 16°30.1' W.

^A Values in parentheses are the one standard deviation of the counting error expressed as the percent of activity listed.

Table 5. Concentrations of $^{239+240}\text{Pu}$ in sections of cores (fCi/g dry weight) collected in 1981 from the Bay of Biscay in the northeast Atlantic (47°35' N., 9°41' W.) at 4100 m.

Depth increment (cm)	Station number			
	212-1	212-2	221-3	221-4
0-2	3.2 (9) ^a	6.1 (7)	8.0 (6)	8.8 (5)
2-4	9.6 (6)	6.6 (6)	3.9 (7)	5.6 (8)
4-6	6.1 (7)	5.2 (6)	6.4 (5)	2.4 (10)
6-8	1.0 (15)	1.4 (13)	3.2 (6)	2.8 (9)
8-10	0.2 (50)	1.0 (16)	1.3 (17)	3.9 (8)
10-12	<0.2	0.5 (20)	0.3 (33)	1.1 (12)
12-16	<0.05	0.07 (70)	0.1 (53)	0.04 (45)
16-20	<0.06	<0.04	--	0.06 (50)
20-25	--	<0.08	<0.08	<0.03
25-30	--	--	--	<0.04

^a Values in parentheses are the one standard deviation of the counting error expressed as the percent of activity listed.

between 5 and 6 cm. The x ray of this sample shows lateral intrusions, possibly recent burrows, exactly at this depth. The x ray of the duplicate core (not shown) from the same box core shows this feature but at a different depth in the sediment column, suggesting there may be differences in concentrations between cores over small spatial scales. This is supported by the plutonium data from the set of duplicate cores, 221-3 and 221-4, taken from the same box core at the control site. The $^{239+240}\text{Pu}$ subsurface maximum occurs at different depths in the sediment column. A full and complete discussion of these features and interpretation of the mixing processes awaits the comparison of all ^{210}Pb and $^{239+240}\text{Pu}$ analyses and x rays and biological data for these samples.

Overall penetration depths of $^{239+240}\text{Pu}$ in the cores are quite different. On the average, $79 \pm 9\%$ of the total plutonium is found in the upper 6 cm of sediment over the regions sampled. The remaining 21% is

Table 6. The $^{239+240}\text{Pu}$ sediment inventory (mCi/km^2) at the northeast Atlantic disposal site.

Depth increment (cm)	1	2	5	4	6	11
<u>Tyro stations</u>						
0-6	0.13	0.29	0.17	0.13	0.16	0.18
0-10	--	0.32	--	--	0.19	0.21
0-16	--	--	--	--	0.21	--
0-20	--	--	--	--	--	0.21
Below detection						
depth increment (cm)	9-10	13-14	--	9-10	--	13-14
Depth of subsurface						
maximum (cm)	4-5	5-6	4-6	3-4	3-4	3-4
<u>Cirolana stations</u>						
	120	124	125			
0-6	0.18	0.16	0.17			
0-10	0.21	0.17	0.28			
0-20	0.22	0.18	0.28			
Below detection						
depth increment (cm)	20-24	15-20	20-23			
Depth of subsurface						
maximum (cm)	6-8	6-8	4-6			
<u>Northeast Atlantic cores</u>						
	212-1	212-2	221-3	221-4		
0-6	0.27	0.21	0.21	0.24		
0-20	0.29	0.26	0.28	0.34		
Below detection						
depth increment (cm)	10-12	16-20	20-24	20-24		
Depth of subsurface						
maximum (cm)	2-4	2-4	4-6	8-10		

Depth (cm)	$^{239,240}\text{Pu}$ (fCi/g dry)
0	
	17.3 (5)
1	
	10.0 (10)
2	
	5.0 (11)
3	
	2.5 (12)
4	
	2.5 (12)
5	
	14.4 (5)
6	
	1.9 (19)
7	
	0.8 (34)
8	
	0.5 (35)
9	
	1.3 (23)
10	
11	
12	
13	
	<0.06
14	
15

Figure 2. The $^{239+240}\text{Pu}$ concentrations in depth increments from Tyro core collected August 26, 1982, at station 2 (4200 m) and x-ray photograph of original core before sectioning.

distributed to depths exceeding 15 cm in some cores, and in others, is not detected below 10 cm. There is little question that the penetration depth of $^{239+240}\text{Pu}$ exceeds depths of sediment accumulation over the last 30 y. Therefore, this must result from geochemical or biological processes and interpretation awaits the compilation and comparison of ancillary results currently being generated by others.

Comparison of the available concentrations and inventories of $^{239+240}\text{Pu}$ in the sediments collected from within the disposal site with those outside the site, known to be contaminated only by global fallout, shows no evidence of plutonium contamination from any source other than global fallout. The ^{238}Pu results also show no other source for this radionuclide except global fallout. Disposal of packaged radioactive wastes has not led to area-wide contamination of the sedimentary environment within the dumpsite with waste-related plutonium or gamma-emitting radionuclides.

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REFERENCES

- Fukai, R. (1982), International Atomic Energy Agency, Monaco Laboratory, Principality of Monaco, private communication.
- Smith, J. (1983), Bedford Institute of Oceanography, Canada, private communication.
- Noshkin, V. (1983), "Fallout Concentrations in Sediments and Some Biota from Regions of the Northeast Atlantic" in Interim Oceanographic Description of the North-East Atlantic Site for the Disposal of Low-Level Radioactive Waste, Nuclear Energy Agency, Organization for Economic Cooperation and Development, Paris, France.