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AN EXAMPLE OF MONITORING FOR A MULTIDISCIPLINARY NUCLEAR LABORATORY

Jacob Sedlet and N. W. Golchert

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**ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS**

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Jacob Sedlet<sup>1</sup> and N. W. Golchert<sup>1</sup>

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**ABSTRACT:** The environmental monitoring program conducted by Argonne National Laboratory for radionuclides in effluent and surface water is described and the results for the past six years are summarized. Small amounts of several radionuclides have been present in Argonne waste water, and are consequently detectable in the stream that receives this water. The most abundant of these is hydrogen-3, whose average concentration in the stream during this period was about 3000 pCi/l, equivalent to 0.1% of the drinking water standard. The distribution of plutonium and neptunium between stream water and particulate matter was studied. Plutonium tends to be relatively insoluble and become associated with the sediment, while most of the neptunium is in solution. This difference in behavior should be taken into account in designing environmental sampling and analytical programs and in dosimetric evaluation of effluent releases.

**KEY WORDS:** environmental monitoring, water, radionuclides, plutonium, neptunium.

Argonne National Laboratory (ANL) conducts a research and development program, both nuclear and non-nuclear, in a number of scientific disciplines. Much of the research is concerned with energy technology and its effect on man and his environment. The nuclear facilities and research efforts that may produce aqueous radioactive waste are a 5 MW heavy-water cooled and moderated research reactor fueled with enriched uranium, several other reactors or critical assemblies of lower power that use uranium or plutonium fuel; a 12.5 GeV proton accelerator; a 60-in. cyclotron; and laboratories and hot cells designed for work with radioactive materials, including irradiated fuel elements and multicurie quantities of the actinide elements.

#### Surface and Waste Water Systems

Most laboratory buildings at Argonne have two water supplies - one for laboratory use and one for all other purposes (e.g., drinking, sanitary). The laboratory waste water is collected in 261,000 liter (69,000 gallon) retention tanks in each building and monitored for radioactivity by a rapid, total activity measurement. Retention tank water that contains radioactivity above the discharge limits is evaporated or otherwise treated and disposed of as radioactive waste. If not, the water is released to the sewage treatment

<sup>1</sup>Occupational Health and Safety Division, Argonne National Laboratory, Argonne, IL 60439

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plant, where it is combined with the sanitary waste water, treated, and discharged into Sawmill Creek, a small stream that runs in a southerly direction through the ANL site. This stream collects most of the surface water runoff from the site, and flows into the Des Plaines River about 500 m downstream of the Argonne waste-water outfall. The Des Plaines River then flows into the Illinois River about 48 km southwest of Argonne.

Sawmill Creek also receives water from a municipal sewage treatment plant a few kilometers north and upstream from Argonne at the rate of 12.3 megaliters (3.25 million gallons) per day. The water flow in the Creek just above the outfall averages 24 megaliters (6.4 million gallons) per day; ANL waste-water effluent contributes another 3 megaliters (0.8 million gallons) per day. Thus, about 10% of the water in the Creek below the ANL waste-water outfall is due to Argonne, and about 45% is from the municipal plant.

The treated Argonne waste water, which consists of about equal amounts of laboratory and sanitary water, is also sampled during discharge and counted for radioactivity. Although it is possible that radionuclides can enter the Creek without first being detected in the retention tanks, e.g., by accidental discharge into building drains not connected to retention tanks or by accidental spillage on the grounds outside of a building, and subsequent drainage by the storm water runoff system, this has occurred rarely, if at all. The concentrations of radionuclides found in Creek water are less than expected based on the limits for retention tank discharge, and are not detectable by the rapid analysis required by the treatment plant operations. They are measurable by high sensitivity analyses, which require large samples and long counting times.

#### Sampling

Sawmill Creek is sampled upstream from the Argonne site and downstream from the waste-water outfall to determine if radionuclides are added to the stream by Argonne waste water or from surface drainage. The Des Plaines River is sampled upstream and downstream from the mouth of Sawmill Creek to evaluate the effect of Creek water on the radioactivity in the River, and the Illinois River is sampled to detect any effect on it from the Des Plaines River. The frequency of sampling decreases with increasing distance from ANL. Creek sampling downstream from the outfall is now continuous. Before 1977, daily grab samples were collected. Elsewhere, individual samples are collected at intervals from weekly to semiannually. Bottom sediment from streams is also collected, and other bodies of water in the area are sampled for comparison purposes.

#### Measurements

Samples were made 0.1N in nitric acid, after aliquots were removed for radiiodine and hydrogen-3 analyses, and filtered through Whatman No. 2 paper promptly after collection. Most hydrogen-3 analyses were performed by distilling the water and counting 10 ml in a scintillation counter; some samples were enriched in hydrogen-3 by electrolysis prior to counting. Strontium-89, strontium-90, barium-140, and iodine-131 analyses were performed by the usual methods for these radionuclides at low levels - addition of carrier, appropriate chemical separation, and beta counting in a low-background counter. Uranium

was analyzed fluorometrically, and the concentration units converted from mass to activity with the assumption that the isotopic composition of the uranium was normal. Plutonium, neptunium, and the transplutonium elements were separated from 10 to 50 l samples by coprecipitation with calcium fluoride. After dissolution of the precipitate in aluminum nitrate-nitric acid solution, neptunium and plutonium were absorbed on a Dowex-1 resin column. Plutonium was eluted with ammonium iodide solution and neptunium with hydrochloric-hydrofluoric acid solution. The column effluent was evaporated, adjusted to pH 2, and the trivalent actinides extracted with a solution of Aliquat-336 (an alkyl quaternary ammonium compound) dissolved in xylene, and re-extracted into dilute acid. The separated fractions were electrodeposited on platinum or silver from chloride solution and counted in an alpha spectrometer. Isotopic tracers were used to monitor the chemical recoveries: plutonium-242 for plutonium, neptunium-239 for neptunium, and americium-243 for the trivalent actinides (americium, curium, and californium). Additional details are given in annual reports of the ANL environmental monitoring program [1].

### Results and Discussion

Radionuclide concentrations in Sawmill Creek water for the past six years are summarized in Table 1. The error given for an average is its standard deviation. It is not the usual error or uncertainty in replicate analyses of the same sample, but is a measure of the range or spread of individual results that were used to calculate the average. For several nuclides, results for some of the samples were less than the detection limit. Averages that included a large fraction of such samples were calculated with the assumption that the concentration in those samples was at the detection limit, and the resulting average is preceded by a less-than (<) symbol to indicate this. It should be emphasized that this method of averaging gives a value that is biased on the high side, and such averages should be evaluated with this in mind.

A general examination of the data shows that 1) the concentrations are a very small fraction of the standard (the Concentration Guide given in Chapter 0524 of the *Department of Energy Manual*), 2) the nuclides that were added to the Creek in Argonne waste water were hydrogen-3, neptunium-237, plutonium-238, plutonium-239, americium-241, and the californium and curium nuclides, and 3) the average and range alone cannot be used to decide on the source of the activity if the concentrations and the upstream-downstream differences are very small. On the latter question, there is little uncertainty in the case of hydrogen-3 that the concentrations below the outfall resulted from tritium in Argonne waste water. For strontium-90 and iodine-131 the situation is less clear, and it is necessary to examine individual results for samples collected at about the same time, and correlate them with fallout monitoring results, principally radioactivity in air and precipitation. From these types of comparisons, we have concluded that about 25% of the individual samples contained some strontium-90 from Argonne waste water, while none contained iodine-131 attributable to Argonne. When increases in fallout were noted, particularly shortly after a nuclear test, and a fission product was found in approximately equal amounts at both sampling locations (or found below the outfall on days when no upstream sample was collected), it was reasonable to conclude that the activity is predominantly from fallout.

TABLE 1

## Radionuclides in Sawmill Creek Water, 1972-77

Nuclide	Location*	Concentration (pCi/l)		Percent of Standard (Avg.)
		Average	Range (Individual)	
Hydrogen-3	A	(<)240	< 200-470	(<)0.008
	B	3120 ± 4890	< 200-3.3 × 10 <sup>5</sup>	0.10
Strontium-89	A	< 2	< 2	< 0.07
	B	< 2	< 2-6.4	< 0.07
Strontium-90	A	(<)0.65 ± 0.15	< 0.5-1.6	(<)0.22
	B	(<)0.79 ± 0.27	< 0.5-1.1	(<)0.26
Iodine-131	A	(<)3.7 ± 0.8	< 3-24	(<)1.2
	B	(<)3.4 ± 0.5	< 3-14	(<)1.1
Barium-140	A	< 2	< 2	< 0.007
	B	< 2	< 2	< 0.007
Uranium (as natural)	A	1.9 ± 0.4	0.9-4.8	0.0048
	B	2.0 ± 0.4	0.7-5.9	0.0050
Neptunium-237	A	< 0.002	< 0.002	< 7 × 10 <sup>-4</sup>
	B	0.077 ± 0.08	< 0.002-1.9	0.0036
Plutonium-238	A	< 0.002	< 0.002	< 4 × 10 <sup>-5</sup>
	B	0.0035 ± 0.0014	< 0.002-0.089	7 × 10 <sup>-5</sup>
Plutonium-239, 240	A	< 0.0005	(< 5-9) × 10 <sup>-4</sup>	1 × 10 <sup>-5</sup>
	B	0.0088 ± 0.005	< 0.0005-0.25	1.8 × 10 <sup>-4</sup>
Americium-241	A	< 0.001	< 0.001	< 3 × 10 <sup>-5</sup>
	B	0.0053 ± 0.0007	< 0.001-0.092	7.3 × 10 <sup>-4</sup>
Curium-242/ Californium-252	A	< 0.001	< 0.001	< 1.4 × 10 <sup>-5</sup>
	B	(<)0.0041 ± 0.0019	< 0.001-0.010	(<)5.9 × 10 <sup>-5</sup>
Curium-244/ Californium-249	A	< 0.001	< 0.001	< 2.5 × 10 <sup>-5</sup>
	B	(<)0.0040 ± 0.0018	< 0.001-0.13	(<)1 × 10 <sup>-4</sup>
Total Alpha (nonvolatile)	A	2.1 ± 0.3	1.0-4.8	-
	B	1.6 ± 0.2	0.3-4.1	-
Total Beta (nonvolatile)	A	19 ± 4	7-33	-
	B	16 ± 2	7-44	-

\* Locations: A is upstream of the ANL site; B is below the waste-water outfall.

In some cases, iodine-131 could be attributed to fallout. In others, iodine-131 was detected at both locations, but the concentration was greater upstream, and no recent test occurred that could produce the observed concentration. A possible explanation for this finding is that the iodine-131 originated from a medical administration to a resident of the area served by the sewage treatment plant upstream from the Argonne site. The excretion of 10 to 100  $\mu\text{Ci}$  per day of iodine-131 would produce the observed Creek concentrations (10-20  $\text{pCi/l}$ ), and such excretion rates have been observed by us in individuals who received medical injections of this nuclide.

If a radionuclide were present in ANL effluent water in sufficient concentration, it is obvious that it could be detected in the Des Plaines and Illinois Rivers as well as in Sawmill Creek. Results for the two Rivers are summarized in Tables 2 and 3. All averages were essentially normal, and do not indicate the presence of radionuclides from ANL waste water. Except for hydrogen-3, the same is true for the individual samples. The upper end of the range at location B in the Des Plaines River indicates abnormal concentrations. These samples were collected in October, 1975, on the same days that the highest tritium concentrations were observed in Sawmill Creek (Table 1). At all other times, and for all other nuclides, the combination of low concentration and dilution reduced the concentrations in the Rivers sufficiently to make them indistinguishable from background or natural levels. In the Illinois River radioactivity from Argonne could not be detected in any sample.

Plutonium 239 was measurable in most Des Plaines and Illinois River samples at concentrations expected and attributable to fallout if sample sizes were sufficiently large (50 l). In Sawmill Creek above the site, the plutonium concentration was less than 0.5  $\text{fCi/l}$  in all samples, probably because a significant portion of the water originally came from wells, via the sewage treatment plant, rather than from precipitation. Below the outfall the effect of ANL effluent water on the plutonium concentration can be seen in Table 1. The neptunium-237 concentration below the outfall was nearly a factor of 10 larger than plutonium, but not necessarily because the amount released was greater. The difference is due, at least in part, to the relative insolubility of the plutonium in water. From 50% to 80% of the plutonium in Sawmill Creek water samples can be removed by filtration with ordinary filter paper, while less than 30% of the neptunium is usually removed by this procedure. This might be expected from the known solubility properties of the most stable oxidation states of these two elements. Laboratory studies of the absorption of these two elements from solution onto soil clay and filtration experiments on White Oak Lake water at Oak Ridge National Laboratory gave similar results [2].

Table 4 shows the distribution between water and sediment in a group of samples collected from the Creek at the outfall and at several distances downstream. The suspended sediment was separated into fractions by filtration, coarse (particle sizes greater than 2.5  $\mu\text{m}$ ) and fine (particle sizes between 2.5 and 0.45  $\mu\text{m}$ ). In water the neptunium concentration was higher than the plutonium concentration, while in the sediment the reverse was generally the case. The loss of plutonium and neptunium from solution and from sediment as a function of distance can occur by several processes. The concentrations in

TABLE 2

## Radionuclides in Des Plaines River Water, 1972-77

Nuclide	Location *	Concentration (pCi/l)	
		Average	Range (Individual)
Hydrogen-3	A	(<)220 ± 30	< 200 - 490
	B	(<)250 ± 70	< 200 - 4700
Strontium-89	A	< 2	< 2 - 5.9
	B	< 2	< 2 - 6.1
Strontium-90	A	0.74 ± 0.22	< 0.5 - 1.6
	B	0.75 ± 0.25	< 0.5 - 2.0
Iodine-131	A	< 3	< 3 - 6.3
	B	< 3	< 3 - 6.7
Barium-140	A	< 2	< 2 - 5.1
	B	< 2	< 2 - 4.8
Uranium (natural)	A	1.6 ± 0.3	0.7 - 3.4
	B	1.7 ± 0.4	0.4 - 4.1
Neptunium-237	A	< 0.002	< 0.002
	B	< 0.002	< 0.002 - 0.0072
Plutonium-239,240	A	(<)0.0006 ± 0.0003	< 0.0005 - 0.0021
	B	(<)0.0008 ± 0.0006	< 0.0005 - 0.0090
Total Alpha (nonvolatile)	A	1.7 ± 0.3	0.7 - 4.3
	B	1.6 ± 0.4	0.2 - 4.1
Total Beta (nonvolatile)	A	13 ± 4	5 - 43
	B	13 ± 4	5 - 33

\* Locations: A is 8 km above and B is 4 km below the mouth of Sawmill Creek.

TABLE 3

## Radionuclides in Illinois River Water, 1972-77

Nuclide	Concentration (pCi/l)	
	Average	Range
Hydrogen-3	( $<$ ) $220 \pm 40$	$< 200 - 390$
Uranium (natural)	$1.0 \pm 0.1$	$0.5 - 1.3$
Neptunium-237	$< 0.0005$	-
Plutonium-239,240	$0.00035 \pm 0.00004$	$0.00017 - 0.00090$
Total Alpha (nonvolatile)	$1.1 \pm 0.3$	$0.1 - 2.2$
Total Beta (nonvolatile)	$8.8 \pm 1.0$	$4.3 - 14$



TABLE 4

Distribution of  $^{239,240}\text{Pu}$  and  $^{237}\text{Np}$   
Between Water and Suspended Sediment

Date Collected	Location	Fraction*	Concentration, pCi/l (%)		Sediment mg/l
			$^{239,240}\text{Pu}$	$^{237}\text{Np}$	
October 10, 1977	Outfall	Water	4.5 (19%)	44.7 (90%)	-
		Fine Sediment	2.9 (12%)	< 1 -	0.12
		Coarse Sediment	<u>16.6 (69%)</u>	<u>4.2 (10%)</u>	5.1
			24.0	48.9	
October 10, 1977	200 m Below Outfall	Water	4.0 (24%)	22.8 (72%)	-
		Fine Sediment	1.8 (11%)	< 1 -	0.42
		Coarse Sediment	<u>10.9 (65%)</u>	<u>8.2 (28%)</u>	7.5
			16.7	31.0	
November 23, 1977	Outfall	Water	57.8 (32%)	82.6 (68%)	-
		Fine Sediment	15.5 (9%)	4.7 (4%)	0.003
		Coarse Sediment	<u>107.2 (59%)</u>	<u>33.6 (28%)</u>	3.1
			180.5	120.9	
November 23, 1977	30 m Below Outfall	Water & Fines	35.2 (35%)	62.4 (68%)	-
		Coarse Sediment	<u>66.4 (65%)</u>	<u>28.7 (32%)</u>	9.7
			101.6	91.1	
November 23, 1977	200 m Below Outfall	Water & Fines	7.1 (31%)	9.3 (48%)	-
		Coarse Sediment	<u>15.7 (69%)</u>	<u>10.2 (52%)</u>	9.8
			22.8	19.5	
November 23, 1977	500 m Below Outfall	Water	3.3 (20%)	17.7 (68%)	-
		Fine Sediment	9.8 (60%)	6.2 (24%)	0.055
		Coarse Sediment	<u>3.3 (20%)</u>	<u>2.0 (8%)</u>	7.5
			16.4	25.9	

\* Suspended sediment results are given in terms of the volume of water filtered.

water can decrease with distance by dilution and by increased association with sediment. Dilution probably predominated, since the decrease in solution content was not accompanied by a corresponding increase in sediment content. The sediment content can decrease with distance by sedimentation or by dissolution. Since the concentration in the sediment (per liter of water) decreased substantially while the sediment content per liter of water and the concentrations did not, loss of plutonium and neptunium probably occurred to a large extent by sedimentation, and resuspension of new sediment took place as the water moved downstream. It appears that loss by sedimentation (or at least from the sediment) was greater for plutonium than for neptunium close to the outfall. If the decrease with distance were simply due to mechanical settling of sediment particles, the rate of loss should be the same for both elements. However, the observed difference may be an artifact that resulted from the unusually high plutonium content of the sediment at the outfall. At large distances downstream the concentrations in the sediments and the rates of loss became similar for both elements, the sedimentation loss was greater for the larger particles (as expected), and the fines contained more neptunium and plutonium than the coarse sediment.

The results imply that much of the plutonium actually released into waste water may be removed in treatment, and that the total plutonium release cannot be judged on the basis of concentration in water alone. It is possible that neptunium, at about the same release level, may be more important dosimetrically than plutonium because of its apparent greater solubility.

The distribution of plutonium and uranium between stream bottom sediment and the overlying water are compared in Table 5. The uranium concentrations are in their natural ranges. Plutonium is evidently easier to detect in the stream bed than in the water. Since the bed can accumulate plutonium over a period of time, it is a very sensitive indicator of aquatic contamination, and can be useful in covering time periods during which no water samples were collected.

TABLE 5

Uranium and Plutonium in Water (fCi/l) and Bottom Sediment (fCi/g)						
Location	U (nat)		<sup>239,240</sup> Pu		<sup>238</sup> Pu	
	Water	Sediment	Water	Sediment	Water	Sediment
Sawmill Creek	1700	1400	2	10-30	< 2	1-3
Des Plaines River	1400	1500	0.6	5-30	< 2	2
Illinois River	1100	3500	0.3	1.0	< 2	< 0.1

A few algae and fish samples from Sawmill Creek have been analyzed. Concentrations were approximately 2 to 5 fCi/g for both elements, and corresponded to concentration factors of about 500 for plutonium and 200 for neptunium. The number of samples and the concentrations were too small to be conclusive.

Additional studies of the distributions between water and sediments, as well as studies of the physico-chemical behavior of the heavy elements in natural water systems are needed, but these are difficult and time-consuming in Sawmill Creek because of the low concentrations.

The results of regular monitoring of the same streams for a number of years show that the chemical and physical behavior of radioelements under environmental conditions need to be known or studied to design a proper monitoring and analytical program. Removal mechanisms, such as found for plutonium, may operate to modify the hazard expected on the basis of amount released.

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