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PROCEEDINGS OF AN ACTINIDE-SEDIMENT REACTIONS WORKING MEETING AT SEATTLE, WASHINGTON ON FEBRUARY 10-11, 1976

Edited by
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DISTRIBUTION

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PRESENTATIONS

too short - outline
+ diagrams + discussion
only

U.S. GEOLOGIC STORAGE PROGRAM

H. C. Burkholder

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U.S. GEOLOGIC STORAGE PROGRAM

H. C. Burkholder

Objective: To fully qualify at least three nuclear waste repositories for final storage operations by 1997.

Seven Phase Program

1. Generic site reconnaissance--

   Identify at least 30 specific sites in the contiguous U.S. worthy of further study

2. Detailed site reconnaissance--

   Choose from those 30 sites the six best sites for pilot plants

3. Engineering design--

   Design the waste management systems for each pilot plant

4. Design performance evaluation--

   Evaluate each pilot plant system to determine its efficiency in keeping the waste isolated from man

5. Construction--

   Construct each pilot plant

6. Operation--

   Operate each pilot plant and monitor operation

7. Conversion to disposal--

   Seal each storage facility and mark the site

Design Performance Evaluation

A. Radionuclide source

   Initial inventory

   Decay dynamics

B. Waste form

   Initial form

   Degradation phenomena

      Initiation

      Mechanisms

      Rates

C. Engineered containment

   Initial containment

   Degradation phenomena

      Initiation

      Mechanisms

      Rates

   Recovery/repair

D. Geologic retention

   Geosphere transport models

   Nuclide-media interaction data

E. Biologic accumulation/dispersion

   Biosphere transport models

   Nuclide-biota interaction data

F. Publicly acceptable release consequences

   Attitude survey

   Education

G. Post-emplacement system dynamics

Waste container position stability

  Forces

  Consequences of loss

Cavern stability

  Forces

  Consequences of loss

Retrieval

  Signals for need

  Methods

Illustration: Chart showing geologic disposal → media → dissolution → biosphere pathways

Illustration: Waste management control surface for incremental background dose with no partitioning

Nuclide-Media Interaction Data

Questions to be answered:

1. What nuclides?

2. What measurements?

3. What techniques?

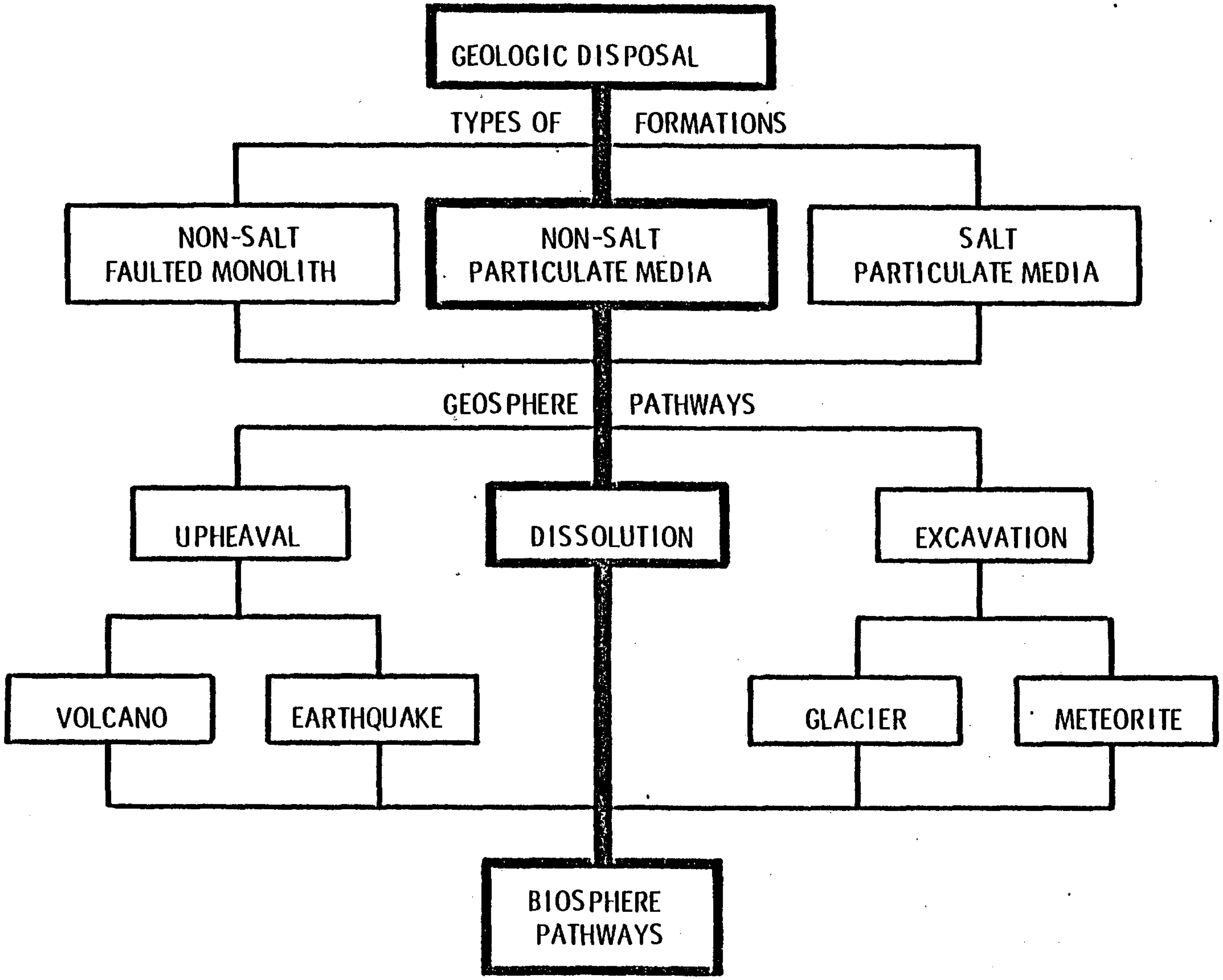
4. Level of sophistication needed?

5. Level of sophistication achievable?

6. How should media be sampled?

7. Where should samples be taken and how many?

8. Laboratory or in-situ experiments?


GEOLOGIC DISPOSAL
TYPES OF FORMATIONS
NON-SALT FAULTED MONOLITH
NON-SALT PARTICULATE MEDIA
SALT PARTICULATE MEDIA
GEOSPHERE PATHWAYS
UPHEAVAL
DISSOLUTION
EXCAVATION
VOLCANO
EARTHQUAKE
GLACIER
METEORITE
BIOSPHERE PATHWAYS

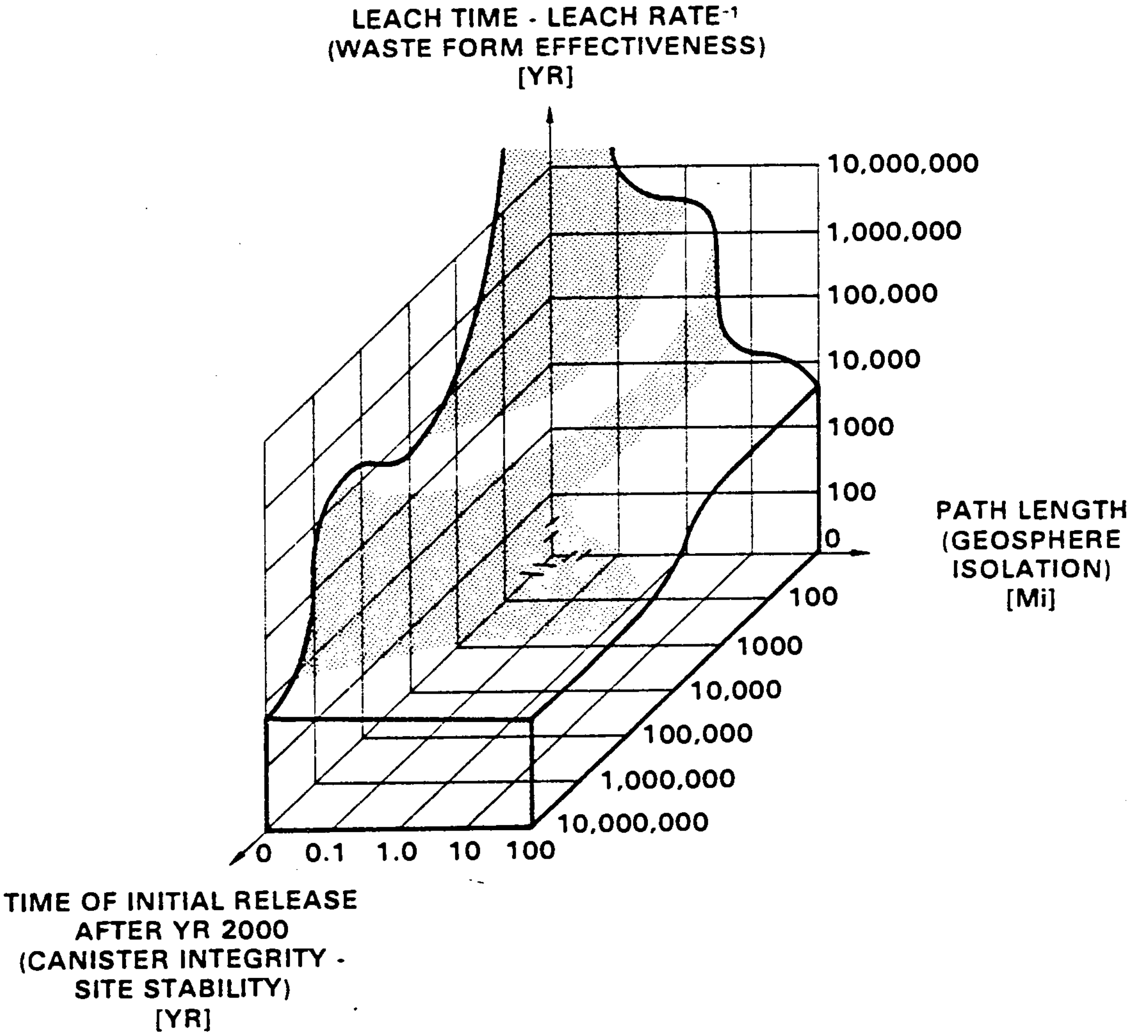


FIGURE 1. Waste Management Control Surface for Incremental Background Dose

FOLLOWING H. C. BURKHOLDER'S PRESENTATION

QUESTIONS AND ANSWERS

Mendel: Harry, you didn't give a time schedule for this; is there a schedule set up for this program as to when the pilot plants might come into operation?

Burkholder: We would like to have the six pilot plants in operation by 1985 at the latest. We are projecting that the design evaluations phase will cost in the neighborhood of $200 million.

Serne: Harry, I've got a question. You say that the generic choosing of the 30 sites is being done by Oak Ridge. Is there any documentation as to what the criteria are for choosing these sites? You say you'd like help from the expertise that's here; I don't know about the others, but we've had very low input to this point, and I think it would be important that geological transport people have input into the criteria from which these sites would be chosen.

Burkholder: This work is currently going on at Oak Ridge because they have been historically doing that kind of work. I do not think the program has been sufficiently fleshed out to say exactly who is going to have responsibility for what and how it is going to mesh together, but I think it's very certain that this problem will take a multi-laboratory approach.

Serne: Who is ultimately in charge? Some branch of ERDA, right?

Burkholder: The Division of Fuel Cycle Production is ultimately in charge. I do not believe the decisions have been made yet as to exactly who is going to manage the program or who is going to do the various parts of the work. I agree with you that we need to have some input into what the criteria are going to be. Certainly the generic site reconnaissance can go forward without the criteria because in that phase we are simply looking at what's available. However, before a selection of the 30 sites can be made, some criteria are going to have to be developed. Furthermore, some additional criteria must be developed in order to choose the six best sites from the original 30. Then when we start looking at those six sites in detail, we must have some very explicit criteria.

Holcomb: All the current main interplay is now between ERDA and Oak Ridge, is that right?

Burkholder: Yes.

DISPOSAL FORMS FOR THE ACTINIDE WASTES FROM THE NUCLEAR FUEL CYCLE

p. 11-36

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INTRODUCTION

This paper concerns the actinides associated with the generation of nuclear power, which are handled for the most part by private industry rather than in government-operated installations.

NUCLEAR FUEL CYCLE

The nuclear fuel cycle of a fully implemented light water reactor (LWR) nuclear economy utilizing plutonium recycle is shown in Figure 1. There will be 30 to 50 reactors for each reprocessing plant and probably 2 or more fuel fabrication plants. The actinides of interest are produced in the power reactors by neutron-induced transmutations in the mixed UO_2-PuO_2 fuel, which remains in the reactor approximately 3 years. Each reactor will discharge about 30 metric tons of spent fuel each year containing approximately 800 kg of plutonium, 4 kg of neptunium, 40 kg of americium and 20 kg of curium. After a storage period of at least 150 days in a water basin at the reactor, the fuel is shipped to the reprocessing plant.

At the reprocessing plant uranium and plutonium are recovered for reuse. The plutonium is sent to a mixed oxide fuel preparation plant for recycle; the uranium is sent to an enrichment plant and then to a fuel fabrication plant for recycle. The other actinides, neptunium, americium and curium

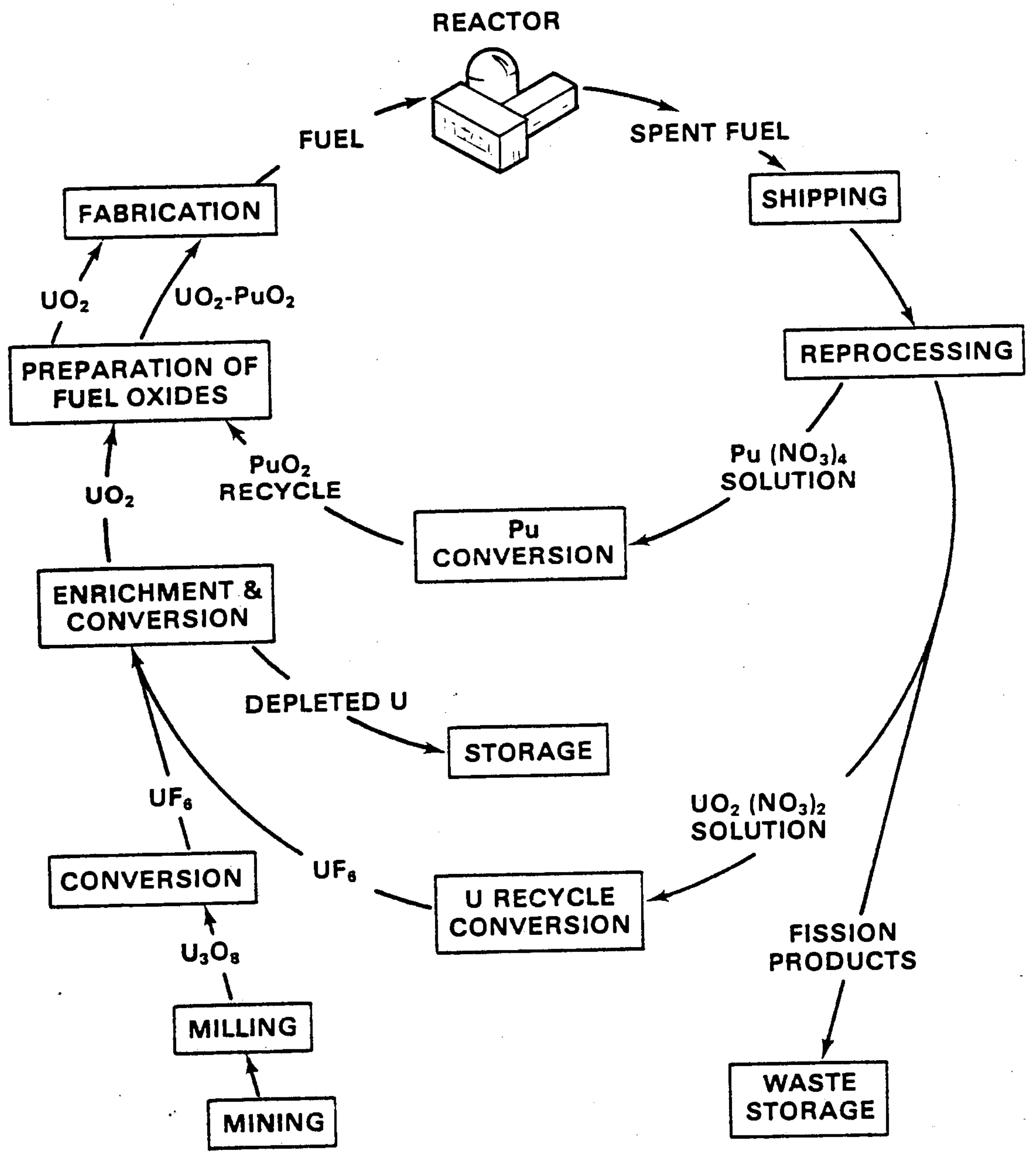

FIGURE 1. Nuclear Fuel Cycle with Plutonium Recycle

are collected with the fission products in the high-level waste (HLW) which is solidified and sent to a Federal repository for terminal storage. Because of processing losses the HLW will also contain perhaps 0.5% of the plutonium and uranium initially in the spent fuel.

The various wastes containing the actinides, and there are other actinide waste streams besides the HLW, may be stored on the commercial sites temporarily, but ultimately will go to a Federal repository for terminal disposal.(1) The Federal repository will be a carefully selected, stable, monolithic geologic formation. The first pilot plant repository will be located in bedded salt in New Mexico, but other potentially suitable geologic formations, such as shale beds, limestone, granite, basalt, etc., will be investigated.

DISTRIBUTION OF ACTINIDES IN THE NUCLEAR FUEL CYCLE

In an equilibrium fuel cycle most of the actinide inventory remains in the operating cycle at all times, either in fuel elements, or in a purified form being refabricated into fresh fuel elements for recycle, as shown in Table 1. There are significant waste losses, however, during reprocessing and fuel fabrication. The major actinide waste is the high-level waste from the reprocessing plant. The second most important waste from the standpoint of actinide activity is expected to be the combustible waste from the mixed oxide fuel fabrication plant.

However, it can be seen that there are also several other waste streams containing significant quantities of actinides all of which will be converted to some type of solidified form for disposal.

TABLE 1. Distribution of Actinides in the Nuclear Fuel Cycle (based on a 1500 MT/yr reprocessing Plant)(2)

Operation	Source of Activity	Actinides, MCi/yr
Spent Fuel Shipment	Fuel Elements in Cask	400
Reprocessing Waste Treatment	Solidified High Level Liquid Waste	4
	Noncombustible Solid Waste (Hulls, Filters, Etc.)	0.02
	Solidified Intermediate Level Liquid Waste	0.01
	Solidified Combustible Waste	0.002
Pu Shipment	Solidified in Shipping Container	400
Mixed Oxide Fuel Fab Waste Treatment	Noncombustible Solid Waste	0.002
	Solidified Liquid Waste	0.05
	Solidified Combustible Waste	0.2

CANDIDATE FORMS FOR ACTINIDE WASTES

It must be kept in mind that no significant quantity of commercial fuel cycle actinide wastes has been generated as yet so as I discuss actinide wastes and their long-term immobilization, I will just refer to candidate solid forms. The whole area is still evolving and, as I will discuss in a later section, the direction of that evolution will certainly be influenced by what is being learned about actinide-sediment interactions. Some of the candidate forms for actinide wastes are shown in Table 2.

TABLE 2. Candidate Solidified Waste Forms for Actinide Wastes(3)

Waste Category	Fraction of Total Actinide Wastes in Waste Category	Candidate Solidified Waste Forms
High-Level Liquid Waste	0.934	Melt-Formed Glass Sintered Glass Glass-Ceramic Oxide Calcine "Super Calcine" Coated or Matrixed Particles Titanates
Noncombustible Solid Waste	0.005	Uncompacted Compacted Matrixed Fined-Cost
Combustible Solid Waste	0.047	Incinerated Untreated Ash Concrete Asphalt Ceramic
Non High-Level Liquid Waste	0.014	Salt Cake Asphalt Concrete Ceramic

HIGH-LEVEL WASTE

U.S. policy since 1970 has been that commercial high-level waste must be converted by the reprocessor to a "dry solid" which is "chemically, thermally and radiolytically stable" and shipped to a Federal repository for terminal storage.(1) There are several candidate "dry solids" but it is anticipated that the probable choice will be either a melt-formed or sintered glass. Except for processing details there is not much difference between the two glass forms; therefore, I will limit my comments to melt-formed HLW glasses. In England, France and Germany plans are also quite well formulated for converting HLW to melt-formed glass.

NONCOMBUSTIBLE SOLID WASTES

These wastes include the spent fuel element cladding "hulls" from which the fuel has been dissolved, failed equipment pieces, and various filters and miscellaneous trash. Various techniques of compaction and consolidation are under investigation, but it is anticipated that for some time much of this kind of material simply will be placed in strong boxes or drums for terminal disposal.

COMBUSTIBLE SOLID WASTES

These wastes are composed of large volumes of paper, plastic, rubber, etc. and will be incinerated to effect a 10- to 100-fold volume reduction. The incinerator ashes can then be immobilized in concrete or other solid forms.

NON-HIGH LEVEL LIQUID WASTES

These wastes can simply be evaporated to dryness, as is planned for some reprocessing plant intermediate-level waste, which will be stored in the form of a $NaNO_3$ cake. The wastes in this category, which also include decontaminating solutions, resin beds, etc., can be immobilized in asphalt, concrete and other solid forms.

HIGH-LEVEL WASTE GLASSES

I will devote most attention to HLW glasses because that is the waste form that will contain the largest amount of waste actinides, and since it will also contain over 99.9% of the fission products, it must withstand by far the most severe thermal conditions and radiation doses of any of the waste forms. The compositions of some typical HLW glasses and their formation conditions are shown in Table 3.

TABLE 3. Composition of Typical HLW Glasses (5,6,7)

	English	French	German	Indian	U.S.
SiO_2	43	51.6	35.1	40.1	27.2
B_2O_3	22.1	14	9.5	16.4	11.1
Na_2O	9.9	8.6	19.1	7.3	4.1
K_2O					4.1
CaO			1.9	3	1.5
SrO					1.5
MgO					1.5
BaO					1.5
Fe_2O_3				13	
Al_2O_3			1.0		
ZnO					21.3
TiO_2			2.9		
Waste Oxides	25	25.8	30.5	20.2	26.2
Processing Temperature, °C	1050	1150	1150	1050	1050

Sometimes well-meaning experts say we are putting the wastes in Pyrex glass.(4) This is not true. The waste glasses are chemically much more complex than Pyrex and are melted at 1050 to 1150°C, about 500°C below the Pyrex manufacturing temperature. To obtain the low melting points (and the desired high waste loading) the silica content in the waste glass is reduced to about half that in Pyrex glass. Nevertheless the waste glasses, as made, compare favorably with commercial glasses, including Pyrex, in their water leachability. This is shown by some comparisons made for us by Corning Glass Works (Table 4).

TABLE 4. Comparison of Durability of Water Glass and Commercial Glasses

Chemical Resistance		Typical Zinc Borosilicate Waste Glass	Borosilicate Glass Code 7740	Soda-Lime Glass Code 0088
Plate Tests	NaOH(pH13)(Mg/Cm^2)	1.2	1.2	0.8
	Na_2CO_3(pH10)(Mg/Cm^2)	0.02	0.1	0.05
	HCl(pH0.1)(Mg/cm^2)	>500	0.01	0.01
Powder Tests	H_2O(pH7)(%Na_2O)	0.002	0.002	0.02
	H_2SO_4(pH2)(%Na_2O)	0.8	0.005	0.02

Around pH 7 and on the alkaline side the waste glasses compare favorably with the standard Corning glasses. As would be anticipated from the very low silica content of the waste glass its acid side resistance is very poor. We are developing waste glasses with better acid side resistance but at the cost of some loss in neutral and alkaline side resistance.

FACTORS POTENTIALLY AFFECTING LONG-TERM STABILITY

A fundamental problem in evaluating HLW glasses is to determine that once a satisfactory glass formulation has been produced, it can retain its desirable characteristics during subsequent handling procedures and ultimately long into terminal storage. Some of the factors that must be considered are shown in Table 5. Each will be described here briefly and then discussed in more detail further on.

TABLE 5. Factors Potentially Affecting Long-Term Stability of HLW Glasses

Thermodynamic Stability

- Glass is a metastable material
- Rate of devitrification as function of temperature

Radiation Effects

- Stored energy
- Helium behavior
- Density changes
- Metamorphic changes
- Physical strength

Environmental Interactions

- Temperature
- pH
- Flow rate of contacting water
- Composition of contacting water
- Pressure

THERMODYNAMIC STABILITY

Vitreous glass is metastable. The free energy of the system can be decreased by the crystallization of certain phases. This spontaneous formation of crystals in the glass is called devitrification, which it occurs to different degrees depending upon glass composition. The maximum rate of devitrification usually occurs 100 to 300°C above the softening point of the glass (defined as the temperature at which the glass viscosity is 10 poises) and is easy to determine because this devitrification proceeds in a matter of days. The lower temperature limit below which devitrification will not occur, even in thousands of years, is more difficult to determine. Our approach, therefore, is to assume that devitrification will take place, and to characterize its most severe effects.

RADIATION EFFECTS

Although HLW glasses will be subjected to a very high beta-gamma radiation dose (on the order of 5×10^{11} R) the actinide content will cause the preponderant radiation effects. This occurs as a result of the much greater radiation energy density associated with the alpha particles and, particularly, the alpha-recoil atoms. We are therefore using waste glasses spiked with curium-244 to accelerate alpha depositions in the glass, and measuring stored energy, helium behavior, and changes in density, strength and leach behavior as a function of time and curium content. Because the actinides are the major sources of radiation damage in glass it is important that they be distributed as uniformly as possible in the waste glass. Another part of our program, just beginning, is to determine actinide distribution in HLW waste glasses.

ENVIRONMENTAL INTERACTIONS

Finally, as was described earlier, many different geologic sites are being considered for terminal storage of radioactive wastes. The potential interactions with the waste form may vary markedly at the different sites. The pH of the ambient water is an example. Another is the life of the canister containing the HLW, which would be much different in salt than in limestone for instance. As work on geologic disposal progresses it may become obvious that certain geologic sites favor one waste form, and other geologic sites another.

EFFECTS OF DEVITRIFICATION

The major effect of devitrification of HLW glasses is an increase in the leach rate of the glass (Figure 2). In a series of experiments in which specimens of a typical HLW glass are being held at different temperatures for varying lengths of time, the maximum increase in leachability has occurred in specimens held at 700°C. The maximum increase in leachability has been about a factor of 10. It should be noted that the temperature of the outside of a canister of HLW will never be allowed to exceed about 425°C. Even in the hottest canisters a surface layer at least 2 to 3 inches thick is expected to remain unaffected by devitrification. Another effect of devitrification is an increase in porosity. The porosity appears to be associated

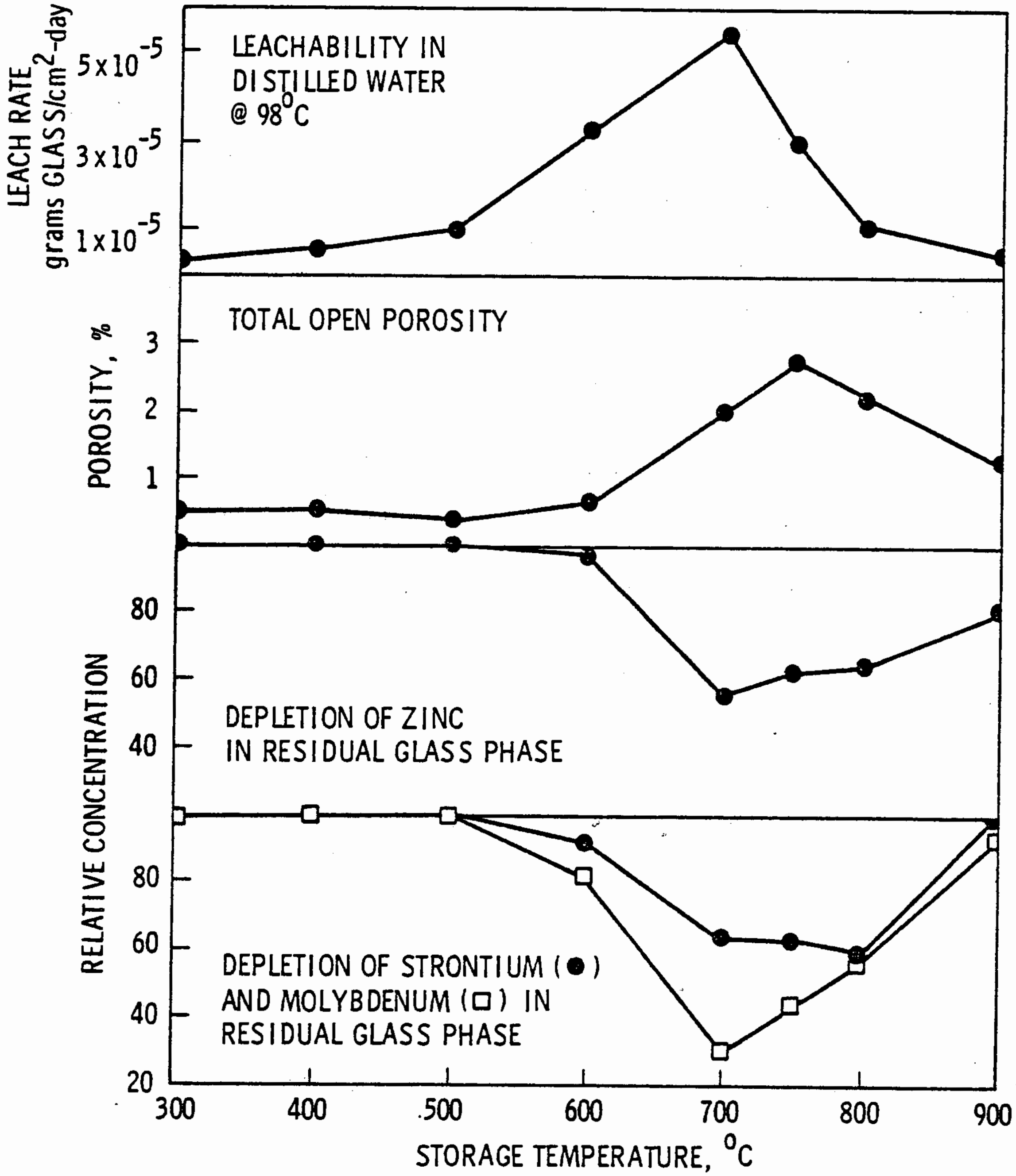

FIGURE 2. Effects of Devitrification

with microcracking caused by density increases and differences in the thermal expansion coefficient between the crystallized phases and the bulk glass. In this glass composition, the major phases that crystallize are Zn_2SiO_4 and $SrMoO_4$, which results in a significant change in the composition of the residual glass phase.

EFFECTS OF ACCELERATED ALPHA DOSES

Waste glass specimens have been prepared containing approximately 1 wt% curium-244. Based on the density of alpha events within the glass the oldest of these specimens, which are now over 2 years old, have simulated 2000 years storage of typical HLW glass from a UO_2 fuel cycle or 80 years for a plutonium recycle fuel cycle.

STORED ENERGY AND DENSITY CHANGES

The buildup in stored energy and density change in the curium-doped glass specimens as a function of alpha dose is shown in Figure 3. Stored energy, or Wigner energy, results from the displacement of atoms from their lattice positions. The energy is stored in the sense that it is released as heat when the specimen is heated.

In the HLW glasses the stored energy starts to release when the specimens are heated about 100°C above their storage

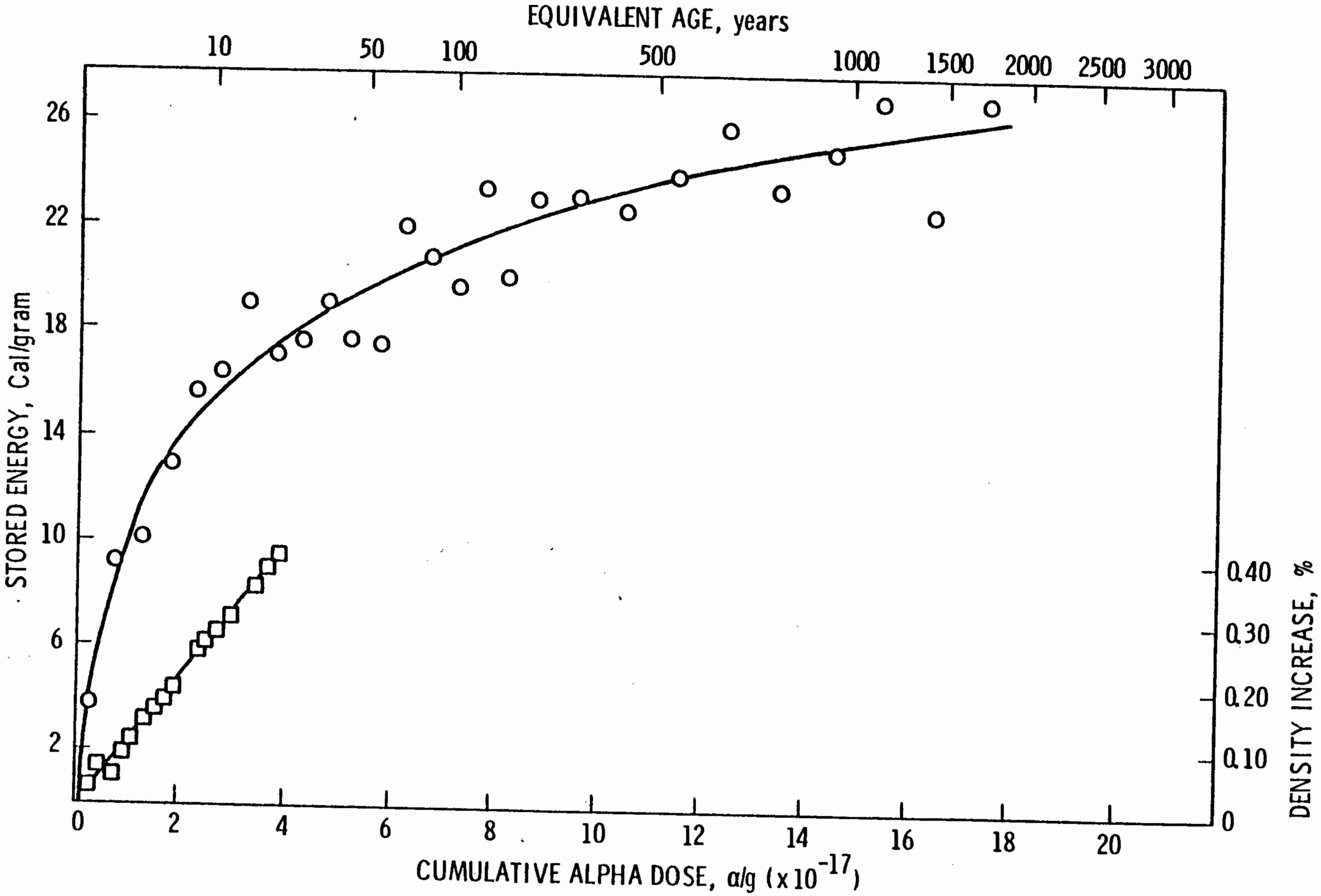

FIGURE 3. Stored Energy and Density Changes Due to Alpha Radiation in Glass

temperature and is released in a relatively uniform manner until all has been released at the softening point of the glass, about 540°C. The stored energy in the HLW glass is approaching saturation at a safe level. A radiation-induced change in density is also occuring which is quite small.

METAMICTIZATION

The term, metamict, is used by geologists to describe minerals that have been altered by the radiation effects of the contained uranium and thorium. This term has also been used to describe neutron-irradiated silica (Figure 4). Although initially differing markedly in density, if crystalline quartz and vitreous silica are irradiated sufficiently, radiation effects cause one to shrink and the other to swell until both reach the identical equilibrium metamict state.

It may be assumed that waste forms containing sufficient quantities of actinides will also reach a metamict state which may be somewhat independent of the original form. Thus, from the standpoint of geologic storage, the thermodynamically more stable crystalline waste forms may be indistinguishable from glass forms.

The metamict minerals are X-ray amorphous and of lower density than their crystalline progenitors. Since the metamict minerals have survived in varied environments for geologic

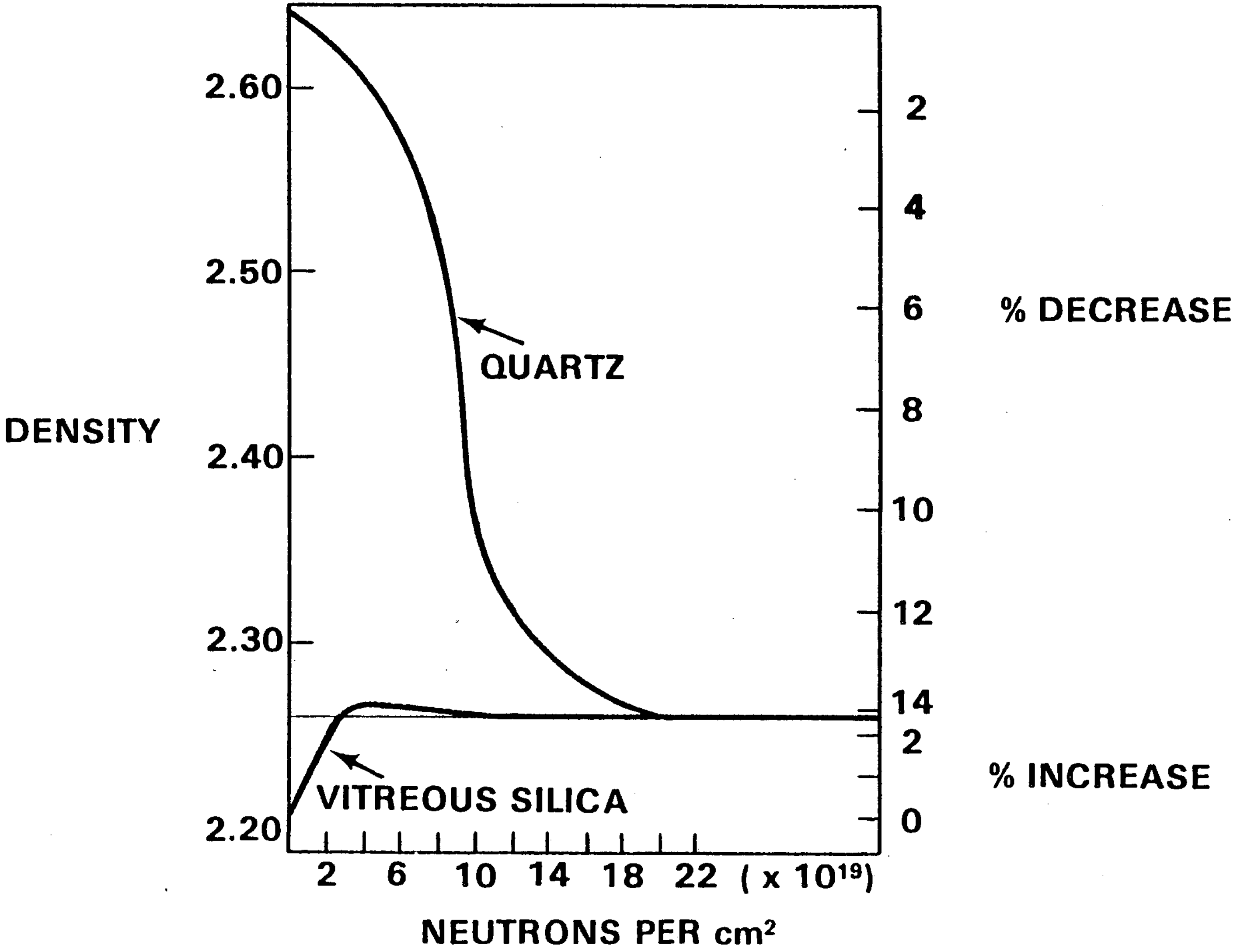

FIGURE 4. Density Changes in Neutron-Irradiated Silica(9)

times, it may be inferred that their resistance to weathering has not suffered greatly from the radiation-induced changes.

EXTRAPOLATION OF LEACH RATES TO LONG TIMES

Thinking about the behavior of minerals in nature leads to what is perhaps the most important consideration of all, namely, what is the long-term behavior of waste glass in a geologic environment. Most of the work to date has made use of data obtained over a period of a few weeks or months, and by fitting to a model, attempting to extrapolate to a larger time frame.

There are few guidelines, even for obtaining the leach rate data. Most industrial glass durability data are obtained using accelerated tests at elevated temperature similar to the measurements Corning made. Yet it is well established that the leaching mechanism for glasses changes as a function of temperature, being significantly different at 95°C than at 25°C. The latter temperature is of most interest for waste forms in long-term contact with the environment. Recognizing the lack of a standard 25°C leach test the IAEA has proposed a standard test to compare waste forms at ambient temperature.(8) An example of leach data obtained for vitreous and devitrified waste glass by a modified version of the IAEA-suggested test is shown in Figure 5. Note that the leach rate changes with

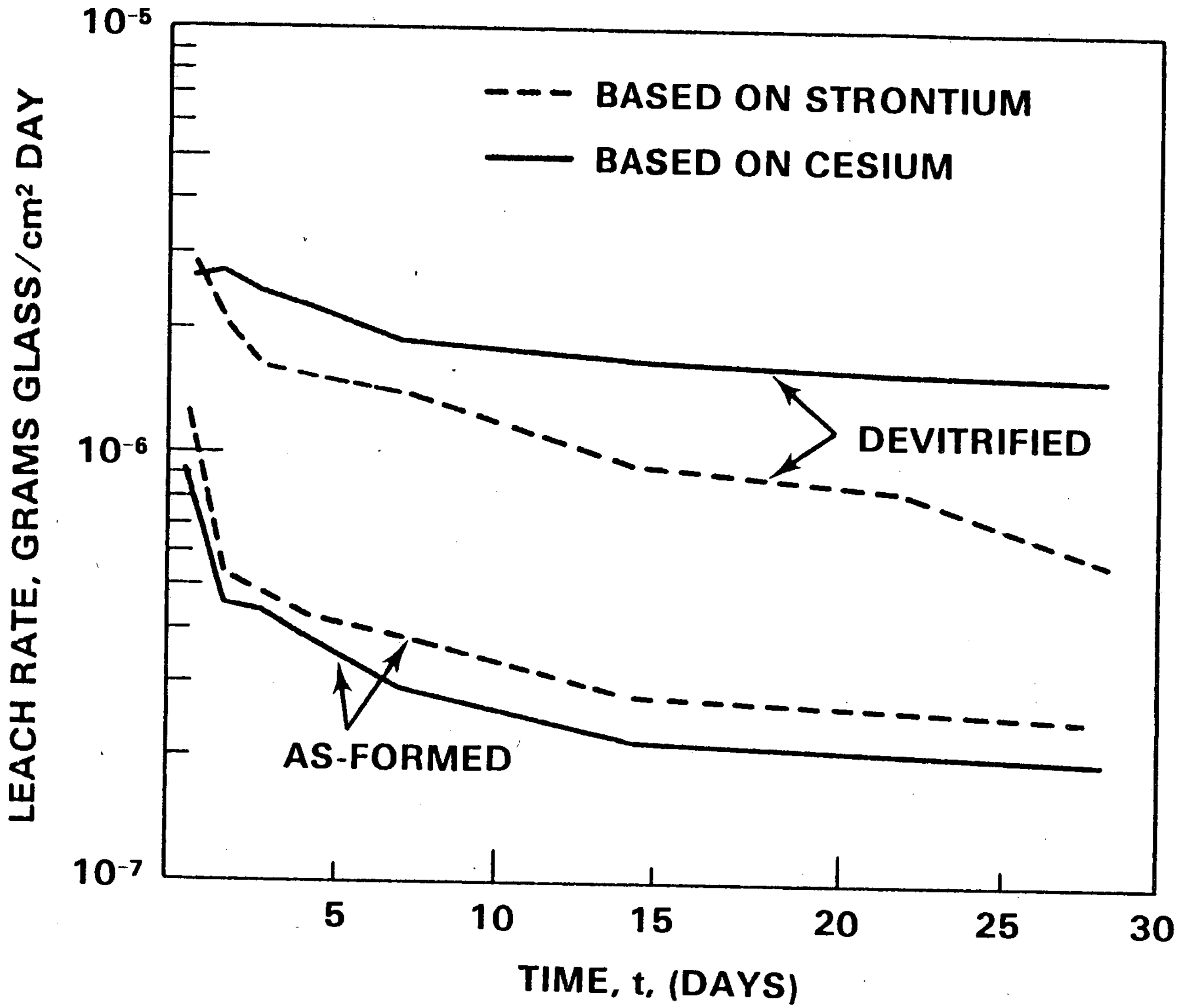

FIGURE 5. Leachability of HLW Glass

time and is different depending on which element is being used as the basis for calculation. The leach rate is calculated as follows:

$$R_n = \frac{a_i}{A_o} \cdot \frac{W}{ST_n} = \text{grams of glass/cm}^2\text{-day.}$$

where

a_i = Amount of element leached during leachant renewal period.

A_o = Amount of element initially present in the specimen.

W = Weight of specimen in grams.

S = Exposed surface in cm^2.

T_n = Leachant renewal period in days.

Thus, although the amount being reported is grams of glass dissolved/cm^2-day, the reported rate will be much higher if based on an element which is preferentially leached than if based on an element which is firmly attached to the silicate lattice.

Several techniques for extrapolating leach data have been proposed. For instance, Godbee has extrapolated some of our earlier HLW glass leach data from the WSEP program using a technique which derives an apparent diffusion coefficient and another coefficient which represents surface corrosion.(10) For the expression used, the leaching time was sufficient to fully define the two coefficients. This was indicated by a good fit of the experimental data (Figure 6) and by the analysis (Table 6). The experimental data covered 196 days of leaching. The expression then can predict the release of activity from the waste as a function of time and thus serve as a source term for models of the migration of isotopes from entombed radioactive waste.

TABLE 6. Extrapolation of Leach Rate Data Using Mathematical Model

	$(\frac{\Sigma a\eta}{A_o})(\frac{V}{S})$, (Fraction Leached) (cm)		
Time (days)	Date	Predicted by Transport Equation	Approach to Asymptote (%)
1	2.6×10^{-5}	3.0×10^{-5}	18
7	7.4×10^{-5}	8.2×10^{-5}	47
14	1.19×10^{-4}	1.19×10^{-4}	68
21	1.56×10^{-4}	1.48×10^{-4}	81
28	1.91×10^{-4}	1.75×10^{-4}	90
56	2.64×10^{-4}	2.66×10^{-4}	93
84	3.30×10^{-4}	3.48×10^{-4}	92
112	4.21×10^{-4}	4.26×10^{-4}	97
140	5.09×10^{-4}	5.02×10^{-4}	101
168	5.82×10^{-4}	5.77×10^{-4}	100
196	6.50×10^{-4}	6.52×10^{-4}	100
	End of Data		
3,650		9.76×10^{-3}	
36,500		9.64×10^{-2}	
365,000		9.62×10^{-1}	

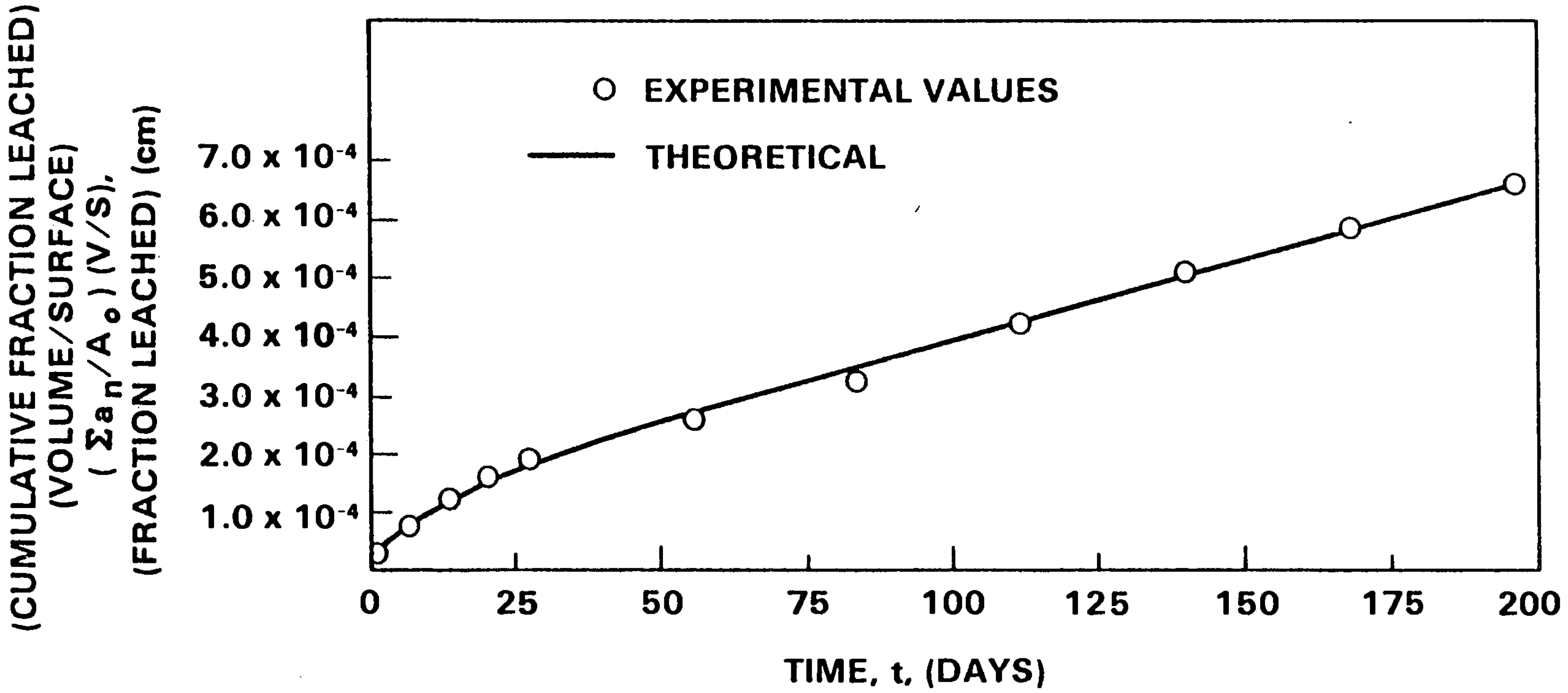

FIGURE 6. Cumulative Amounts Leached from HLW Glass

FUTURE WORK

There is, however, a problem with the approach just described. The flow rate of the leachant has not been considered a variable. The leachant in contact with the sample is replaced with fresh leachant on a set schedule and the effects of changing that schedule have not been determined. In particular the effect of greatly decreasing the renewal frequency to simulate an almost stagnant system, which would almost certainly be more likely in a terminal storage location, have not been studied. Another problem is that to date the leachant used has always been pure water. Water typical of environmental situations must be used also. These considerations are being factored into our future program.

REFERENCES

1. Federal Register, Vol. 35, No. 222, page 17533, 1970.

2. Estimates in Table 1 are based in part on information from a German report by K. Scheffler, V. Riege, W. Hild, and A. Q. Jakubick, Long Range Behavior of HLW Glasses: A Contribution to the Evaluation of Problems Related to the Disposal of α-Bearing Waste from Reprocessing and Fuel Element Fabrication. KFK 2170, July 1975.

3. Management of Radioactive Waste from Fuel Reprocessing, Proceedings of Symposium held in Paris, November 27 - December 1, 1972. Available from OECD Publication Center, Suite 1207, 1750 Pennsylvania Avenue N.W., Washington, DC 20006.

4. W. Clelland, "Is Clean Power Possible?" New Scientist, p. 788, September 26, 1974.

5. Glass Composition SON 60.30.14.013 from R. Bonniaud and C. Sombret. "Statement of Research in the Field of Solidification of High Level Radioactive Wastes in France", presented at the 77th Annual Meeting of the American Ceramic Society in Washington, DC May 3-8, 1975.

6. Glass Composition VG 98 from W. Guber, L. Kahl and J. Saidl. "Recent Experiments in Fixation of High Activity Waste in Karlsruhe", presented at the 77th Annual Meeting of the American Ceramic Society in Washington, DC May 3-8, 1975.

7. A. S. Sanyal and J. Makerji. "Fixation of High-Level Atomic Waste in Glass for Ultimate Disposal: Part II - Development of Vitreous Matrices for the Containment of CIRUS, Tarapur and Ranapratapsager Nuclear Fuel Reprocessing Wastes, Journal of Scientific and Industrial Research, 3(9):40, September 1974.

8. E. D. Hespe. "Leach Testing of Immobilized Radioactive Waste Solids - A Proposal for a Standard Method", Atomic Energy Review, 9:195-207.

9. E. Lell, N. J. Kreidl, and J. R. Hensler. "Radiation Effects in Quartz, Silica and Glasses", Progress in Ceramic Sciences, 4:6, 1966.

10. H. W. Godbee and D. S. Joy. Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory. ORNL-TM-4333. February 1974.

FOLLOWING J. E. MENDEL's PRESENTATION

QUESTIONS AND ANSWERS

Burkholder: [Talking about leach rates] Would that hold true if you waited a long time, say a million years? Would those two differ in leach rate?

Mendel: I don't think we have enough data to really say. There are expressions that would indicate, or models for what the leaching mechanism is, that would indicate that they should come together. But it's hard to find experimental verification that that's ever happened at the lower temperatures.

Rai: It seem to me that the different leach rates would be a function of the concentration of the element in the glass rather than just leaching solution composition. Does this hold true?

Mendel: The quantity of cesium that appears is proportional to the amount in the glass, true. The fraction leached remains constant over a range of concentrations. The bigger A_o, the amount in the glass, then the bigger a_i, the amount leached. Several techniques for extrapolating leach data have been proposed. For instance Herschel Godbee at Oak Ridge has extrapolated some of our earlier glass leach data using a model which derives an apparent diffusion coefficient and another coefficient which represents surface corrosion and is quite a complex model, but has obtained a good fit with the data. Here are plotted not leach rate, but the cumulative amount leached as a function of time. And you can see the good correlation between the theoretical curve using these coefficients and the experimental data. Then, using that expression, the last column shows the approach to the asymptote. One hundred and ninety six days of leaching appear to be enough data to illustrate that the model was really corresponding to the data and then using the model to extrapolate on out to much longer times. I think there are probably several problems with an approach of this type. Most of them are connected with the way the data are obtained. I think probably the biggest problem is that the flow rate of the leachant has not been considered as a variable in this kind of approach. The leachant in contact with the sample is replaced with fresh leachant on a set schedule, but the effects of changing that schedule have not been determined; in particular, the effect of greatly decreasing the renewal frequency. Simulation of an almost stagnant system, which would almost certainly be more likely in a terminal storage location, has not been done.

Serne: All these leaching data, if I'm not mistaken, don't have the alpha contribution in them. What is going to be the effect of the large amount of alpha radiation?

Mendel: That's another reason we are doing the work with curium. We're obtaining leach rates on those curium glasses, so we are looking at the effect of alpha damage on the glass and its effect on leach rate.

Serne: So far what have you found in terms of curium leaching vs. the previous leachings in which people haven't considered the alpha?

Mendel: There is a slight difference in the leach rate. The alpha-containing glass is leaching at a slightly higher rate than the glass without the alpha. I think it's significant, but again we haven't simulated the total alpha dose. It's going to take a long time to do that.

Nyhan: If a lot of the containers were buried, depending upon how far into the soil they were deposited, you would want to consider the effect of changing or diurnal variations in temperature vs. leachability, or wetting and drying situations rather than a constant leach at 25°C. Have you looked into this at all?

Mendel: No we haven't. Most of the leaching that is being done on these candidate waste forms to date has been in distilled water. There has been a little bit of looking at salt, but that's about it. This is mainly, I think, because the candidate geologic formations or the conditions at the sites haven't been defined well enough. Things like alternate wetting and drying, we know from tests that have been made on window glass and so forth, can be a more severe condition often than continual immersion in water, so that's a good point. It could be a serious problem.

Rai: Since the tests are done with distilled water, how realistically would these tests predict the behavior in the natural environment? In the natural environment, one can find water of many different compositions which would have differing effects on the glass dissolution.

Mendel: Up to date we have really been looking for a comparison test between the various waste forms and the various glass compositions and because there are so many possibilities for the water in geologic formations, we have been waiting until we got some guidance as to what particular waters we should be looking at. I have always felt that probably distilled water is a severe case, actually. More severe than most of the soil water, just because you don't have any ions in there to give any common ion effects.

Rai: In my opinion distilled water would be the mildest situation. If you have other cations and anions in water which can interact with the glass and form complexes in solution, that may increase the probability of enhancing dissolution of glass rather than lowering it.

Nyhan: How do you think saltwater would compare with distilled water?

Rai: It would depend upon the composition of the saltwater. For example, carbonate ions form strong complexes with plutonium and generally these complexes are negatively charged. Thus, the salt water high in carbonates would dissolve more plutonium than the distilled water. These negatively charged complexes would not enter into exchange reactions with negatively charged exchange complexes of soils, which would enhance their mobility in soils.

Mendel: We need more dialogue between us. Right now we are using distilled water. If there is something else we should be using, we need to know.

Burkholder: One thing that is very evident here is the interaction between all of the parameters, and it's difficult to isolate the various aspects of the probelm from each other in order to investigate them. Until we have made some definite decisions about, for example, where the repositories are going to be located, it's difficult to do the proper experiments. But then, on the other hand, we want to choose that location based on experiments we have already done. So it's difficult to make a match here.

ACTINIDE OCCURRENCES IN SEDIMENTS FOLLOWING GROUND DISPOSAL OF ACID WASTES AT 216-Z-9

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INTRODUCTION

Past waste disposal practices at Hanford have included the disposal of liquids containing low levels of actinides to the ground via structures collectively termed trenches. As part of the waste surveillance responsibilities of Atlantic Richfield Hanford Company, the current distribution and migration potential of these actinides is being examined under a program entitled Actinide Trench Characterization. Under this program, Battelle Northwest was requested to study the microdistribution of the actinides in samples acquired from the 216-Z-9 Trench. This research provided an unusual opportunity to examine the results of solution-sediment relationships and associated actinide removal mechanisms under acid conditions.

Between 1955 and 1962, the 216-Z-9 covered trench received acid wastes mainly from the plutonium recovery facility.(1) The waste solution composition is described in some detail in a following section. The trench is covered by a concrete slab flush with the surface and supported by pillars. The floor of the trench is about 200 m^2 and located 7 m below the top of the concrete slab. A generalized geologic cross section was given in an earlier report.(2) Core wells were drilled into the glaciofluviatile sediments in which the covered trench is situated. A core well also was drilled in the immediate vicinity to recover uncontaminated glaciofluviatile sediments for petrological study and comparison with contaminated sediments.

WASTE SOLUTION COMPOSITION

The 216-Z-9 enclosed trench received wastes from the Plutonium Finishing Plant, including plutonium-bearing wastes originating in the plutonium recovery facility, between July 1955 and June 1962. Several constituents in the wastes are listed in Table 1. As may be seen, Z-9 covered trench received, among other things, an estimated 38 kg of plutonium contained in about four million liters of solution.(1) The pH of the effluent was usually close to 2.5. An occasional malfunction of the neutralizing apparatus resulted in disposal of solutions at a lower pH than 2.5.

The solids, including refractory PuO_2 particles, carried by the influent formed a sludge on the trench floor during disposal operations. The sludge still persists on the top of the sediment column. The depth of the sludge varies over the bottom of the trench from zero to a few centimeters.

UNCONTAMINATED GLACIOFLUVIATILE SEDIMENTS

PETROLOGICAL EXAMINATIONS

Two samples of uncontaminated glaciofluviatile sediments were examined for mineral and rock fragment identification and quantitative estimation. One of the samples was a silty sand

TABLE 1. Estimated Inputs to 216-Z-9 Covered Trench(1,4)

Constituent	Form	Constituent Wt, Metric Tons if Unlabeled
Al	$Al(NO_3)_3$, $Al(OH)_3$, $AlF(OH)_2$; small amounts of Al_2O_3, $Al_2(SO_4)_3$, $AlCl_3$	100
Am	Am_2O_3, $Am(NO_3)_3$, $Am(OH)_3$	2.5 kg
Ca	$Ca(NO_3)_2$, $Ca(OH)_2$, CaF_2; small amounts of $CaSO_4$, $CaCO_3$	30
Cd	$Cd(NO_3)_2$, $Cd(OH)_2$	0.9
Cr, Pb, Sn, Zn	nitrates, hydrated oxides, or hydroxides	2
Fe	$Fe(NO_3)_3$, $Fe(OH)_3$, FeF_3; small amounts of $FeCO_3$, $Fe_2(SO_4)_3$	25
Mg	$Mg(NO_3)_2$, $Mg(OH)_2$; some $MgSO_4$, $MgCO_3$ and $MgCl_2$	35
Pu	PuO_2, $Pu(SO_4)_2$, $Pu(OH)_4$, $Pu(OH)_x$, PuF_4, $PuCl_4$, $Pu(CO_3)_2$, $Pu(NO_3)_4$	38.3 kg
Cl	CCl_4 deteriorating to HCl, CO and CO_2	100
F	AlF^{2+}	30
NO_3^-		1500
SO_4^{2-}	$CaSO_4$, $Al_2(SO_4)_3$, $Pu(SO_4)_2$	2
Organic	15-25% tributylphosphate in CCl_4, dibutylbutylphosphate and trace methylbutylphosphate	120
Organic	lard oil (50% CCl_4 + 50% lard oil)	60
H_2O		4.09×10^6 liters
Solids	SiO_2, Al_2O_3, $Fe_2(DBP)_3$, $CaSO_4$, $MgSiO_3$, carbonaceous material and other metallic DBP's such as with Cr	6

typical of the many finer lenses found in the glaciofluviatile sediments. The other was a typical sand. Particle size results and calcite contents for the two samples are given in Table 2. A further size fractionation was used to obtain major and minor constituents in the various fractions by X-ray diffraction. The X-ray diffraction results are given in Table 3. The particle size separations were partly accomplished on screens and partly by elutriation. A minus 200 mesh (<0.075 µm) size fraction was retained on the pan. The minus 200 mesh fraction was then mixed vigorously with water and allowed to settle for 40 seconds, at which time the unsettled fines were removed. The settled material was 50 to 75 µm in size and was saved for further examination. The unsettled fines from the same mixing produced a sample of <50 µm size. The sample was remixed and allowed to settle for 1 hour and for 7 hours, 45 minutes to produce size fraction samples of <5 µm and <2 µm, respectively. The X-ray diffraction tracings from the last two size fractions often yield the identity of clay size minerals that are not readily obtained in any other way.

The ≤5 µm size fraction of the sand contained only quartz and mica, while the same fraction of the silty sand also contained some chlorite. The smallest fraction of the sand contained a degraded, or hydromica in which part of the potash probably has been replaced with water. The smallest fraction of the silty sand contained a montmorillonite. Note that feldspar

TABLE 2. Sediment Sample Particle Size Range and Calcite Contents

	>2mm (Gravel)	2mm-0.063mm (Sand)	<0.063mm (Silt+Clay)	Wt % $CaCO_3$
Sand	0.0	96.5	3.5	0.1
Silty Sand	0.0	74.2	25.8	0.1

TABLE 3. X-ray Diffraction Results

Size Fraction	Major Constituents	Minor Constituents
	Sand	
0.42-2.0 mm	Feldspar, Quartz	--
0.075-0.42 mm	Feldspar, Quartz	--
<0.075 mm	Feldspar, Quartz	Mica
50-75 µm	Feldspar, Quartz	Mica
<50 µm	Quartz, Feldspar	Mica
<5 µm	Quartz	Mica
<2 µm	Hydromica	--
	Silty Sand	
0.42-2.0 mm	Feldspar, Quartz	--
0.075-0.42 mm	Quartz, Feldspar	Mica
<0.075 mm	Quartz, Feldspar	Mica
50-75 µm	Quartz, Feldspar	Mica
<50 µm	Quartz, Feldspar	Mica
<5 µm	Quartz	Chlorite, Mica
<2 µm	Montmorillonite	--

(including intermediate plagioclases, albite and microcline) and quartz are the most common sediment constituents. The last size fractions that showed the same approximate X-ray diffraction results as the whole sediment was the 50 to 75 μm size fraction. Consequently, this fraction was utilized to obtain a quantitative mineralogy of the sediment. This usable sediment size range must be determined for each sediment studied.

A technique for determining quantitative mineralogical makeup of a sediment sample based on elemental mapping with the electron microprobe was evolved. This technique used the 50 to 75 μm size range in a plastic mount in which the particles are very closely spaced, and takes advantage of the fact that the fragments in this size range are nearly monomineralic in composition. The close spacing of particles in the mount facilitates the use of the microprobe for elemental mapping of the particles in a given area because only a 300 μm^2 area can be viewed at a time. The greater the number of sediment fragments in this 300 μm^2 area, the more representative are the analytical results of the whole 50 to 75 μm size range sample.

Five different areas of the mount were examined and the quantitative results averaged to obtain a representative sampling. An area was examined by obtaining X-ray emission photos for sodium, potassium, calcium, phosphorus, iron, titanium, magnesium, aluminium and silicon along with the usual electron scattering photo. The above elements include those found in all of the major constituents and most of the minor minerals. The various minerals can be identified by determining the elements present in each fragment. Calcium, for example, would be higher in calcite and apatite than in a laboradorite or a pyroxene. Calcite can be distinguished from apatite by the absence of any other measured element in the calcite and the presence of phosphorus in the apatite. Garnet contains aluminum as well as iron and silicon. Quartz contains essentially only silicon.

The use of photos offers several advantages over point counting with a microscope. With point counting, the tedium level is high and the mistakes may be frequent. Also, there is no permanent record of a point count, as there is with photos. The photos were obtained on a given area and superimposed to obtain mineral identifications of sediment fragments. A tabulation of the fragments gave the number of each mineral fragment present plus another category called "other" or "glassy material" consisting of finely crystallized or glassy fragments. The results of the photo examinations are complied in Tables 4 and 5 for the sand and silty sand, respectively. Plagioclase includes the albites from the Belt Series rocks as well as the calcic plagioclases from local basalts. Small quantities of metamorphic minerals such as garnet and sphene were found. Quartz constitutes a fifth or more of each sediment sample. Microcline was the potash feldspar present in Belt Series rocks.

TABLE 4. Mineral Identification and Percentages Present in Five Areas of the Sand Sample, 50 to 75 µm Size Range

Mineral	% Area 1	2	3	4	5	Average
Plagioclase	30	38	34	32	30	33
Pyroxene	15	13	16	16	17	15
Quartz	17	23	22	27	19	22
Microcline	12	--	--	--	9	4
Metallics	--	6	--	--	3	2
Mica	9	6	6	5	6	6
Calcite	--	--	4	5	4	3
Garnet	--	--	--	3	--	<1
Apatite	--	--	4	--	--	<1
Olivine	--	--	--	--	3	<1
Sphene	--	--	4	--	--	<1
Other	17	14	10	12	9	12

TABLE 5. Mineral Identification and Percentages Present in Five Areas of the Silty Sand Sample, 50 to 75 µm Size Range

Mineral	% Area 1	2	3	4	5	Average
Plagioclase	19	25	19	22	20	21
Pyroxene	25	23	20	17	22	21
Quartz	19	23	26	19	15	20
Microcline	9	8	12	9	10	10
Metallics	5	3	3	7	2	4
Mica	5	3	5	3	7	5
Garnet	--	--	3	--	2	1
Apatite	--	3	--	--	--	<1
Calcite	--	--	--	7	--	1
Olivine	3	--	--	--	--	<1
Other	15	12	15	16	22	16

One of the main points of the mineral quantification is that although both samples were nearly the same in silica content, their mineralogical makeup was not the same. The sand sample contained the most plagioclase, while the silty sand contained the most pyroxene and microcline. A chemical analysis is of limited value in mineralogical quantification because it is the minerals or glasses that react and not the gross chemical composition.

In the 50 to 75 µm size range, most of the basalt fragments were glassy or very fine-grained. Most of the crystals in the basalt were larger than this size range. One could not expect to obtain a sample area in this size range that would reflect the amount of basalt in the whole sediment. The plagioclase content, chiefly associated with basaltic rock fragments, is 12% lower in the silty sand.

The basalt fragments tend to be larger in grain size than the remaining sediment rock fragments. It was necessary to use the whole sediment in determining basalt content. Each sediment fragment was identified in an optical photo as being basaltic or non-basaltic, and a planimeter used to determine the areas of each. Larger photos were used for this work, but it still takes considerable time to planimeter each fragment. However, there was no other way that an accurate quantification of the basaltic content can be obtained. The results based on planimeter areas are given in Table 6.

TABLE 6. Basalt Rock Fragment Content of the Glaciofluviatile Sediments

Sample	Area % Basalt	 % Non-Basalt
Sand	36.8	63.2
Sand	36.5	63.5
Sand	35.4	64.6
Sand Average	36.2	63.8
Silty Sand	25.9	74.1
Silty Sand	18.8	81.2
Silty Sand	20.1	79.9
Silty Sand Average	21.6	78.4

The basalt content of the glaciofluviatile sediments average very close to 30% by area or volume.(3) The sand contained 36% basalt indicating that the larger grain size sediments contained more of the basaltic rock fragments.

CONTAMINATED GLACIOFLUVIATILE SEDIMENTS

PREPARATION OF CORE SEDIMENT SAMPLES

The core samples from 216-Z-9 core wells, collected by ARHCO personnel and still in their original liners, were received in a glove box facility and over-dried at 80 to 90°C.(3) The dry, warm samples were placed in a vacuum and warmed epoxy resin applied several times to ensure good impregnation. Silty sediments are more difficult to impregnate than sands, but all sizes can eventually be satisfactorily impregnated in the above manner. The resin-impregnated sample was cured at 80°C for 16 hours. A diamond saw was used to cut a thin section from the core barrel segment containing the impregnated sediment. The section was trimmed to remove that portion of the sediment smeared by contact with the core barrel liner, remounted in a 3.2 cm mold in an epoxy resin and cured for 16 hours at 80°C. Location and orientation of samples taken from the cores were marked on each sample using a vibrating engraving tool.

The sectioned and mounted sediment sample was initially ground on a size 120 grit silicon carbide belt, followed by grinding on a 30 micrometer diamond wheel and 3/0 Emery paper. Polishing was accomplished with 0.3 micrometer alumina followed by use of a 1 micrometer diamond slurry, both on Syntron laboratory polishing tables for 16 hours.

The samples were cleaned ultrasonically with carbon tetrachloride to remove loose contamination resulting from grinding and polishing prior to sample removal from the glove box. Contaminated sediment column leaching studies showed that carbon tetrachloride removed a maximum of 3% of the plutonium, with removals of plutonium usually varying between 0.1 and 0.01%. Therefore, it was concluded that the carbon tetrachloride cleaning procedure removed very little plutonium from the sample except that contained in the loose grinding and polishing contamination. Subsequent examination of plastic-filled areas surrounding sediment particles in the autoradiographs showed that the sediment loose grinding contamination had been successfully removed, and that the actinides had not been smeared by the plastic during the impregnation process.

Few, if any, of the original clay size particles were present in the sediments that had received the acid waste influent. The minus 5 micrometer size fraction in the contaminated sediments was absent or consisted of relatively acid-resistant materials that had sloughed from altered rock fragments as a result of chemical attack.

TRANSURANIC CONTENTS

The particulate PuO_2 contained in the influent solution was removed very rapidly by filtration on the glaciofluviatile sediments. The filtration action results can be seen in Table 7. Note that the 5 to 15 cm depth sample contains many more milligrams of Pu/g of sediment than does the 46 to 61 cm depth sample, reflecting the fact that the bulk of the filtered PuO_2 particles are found in the top of the sediment column. Note also that a larger portion of the plutonium contained in the minus 0.063 mm size fractions is found in the 5 to 15 cm depth, again reflecting the presence of the 2 to 25 μm particulate PuO_2. An autoradiograph of the sludge overlying the glaciofluviatile sediments in 216-Z-9 covered trench was

TABLE 7. Plutonium and Americium Contents as a Function of Sediment Particle Size(5)

Depth, cm	Size Range - Millimeters >2	1-2	0.5-1	0.25-0.5	0.125-0.25	0.063-0.125	<0.063
				Wt% Soil in Fraction			
5-15	42	20	19	5.4	4.3	4.9	4.6
15-30	43	26	19	5.2	2.3	2.1	1.9
46-61	40	26	22	6.4	2.2	1.4	1.7
				Pu Content (mg Pu/g sediment)			
5-15	0.13	0.22	0.60	1.8	3.0	3.2	10.7
15-30	0.093	0.093	0.14	0.29	0.36	0.86	2.48
46-61	0.082	0.10	0.10	0.18	0.28	0.39	1.13
				Wt% Pu in Fraction			
5-15	5.1	4.1	10	9.0	12	14	45
15-30	22	14	15	8.4	4.6	10	26
46-61	26	21	18	9.4	4.9	4.4	16
				Am Content (g Am/g Pu)			
5-15	0.0025	0.0023	0.0021	0.0022	0.0021	0.0023	0.0021
15-30	0.0023	0.0021	0.0021	0.0018	0.0019	0.0020	0.0020
46-61	0.0022	0.0020	0.0017	0.0013	0.0017	0.0016	0.0014

given in a previous paper.(2) Exposure time for this autoradiograph was only 15 minutes. The sludge contained such a dense population of PuO_2 particles that the resulting positive print gave the appearance of a solid black gamma or beta autoradiograph.

The gAm/gPu ratio is very low, averaging 0.002. In terms of the amounts of americium and plutonium estimated to have been disposed to Z-9 trench, the ratio should be 0.065. This suggests that there has been a separation of americium and plutonium on the sediment column.

It also is of interest that the higher wt% plutonium shifts from the smaller sediment fraction at the top of the column, where the particulate PuO_2 is located, to the larger or basalt-rich fraction at the 46 to 61 cm depth. The cause of this shift can be found in the absence of particulate PuO_2 at 46 to 61 cm and in the enrichment in basalt of the larger size fractions. The solution-basalt reaction rates, and concomitant actinide removals, were increased by the presence of glass in the basaltic fragments.

Several pH values of the present sediments have been taken by adding a quantity of water to make a water-sediment paste and using a pH meter to obtain the apparent paste pH. The results are given in Table 8 along with wt% volatiles which included a small amount of organics as well as water. The

TABLE 8. Water Losses to 150°C and Sediment pH(1)

Depth, cm	% Water	pH
15	--	3.6
15	--	3.6
140	--	4.8
240	--	4.1
Normal Sediments	4-6	7.7-8.2
Sludge	31	--
0-15	12	--
30	4	--
60	6	--
90	4	--

results were reported as water losses to 150°C. The water content of the sludge was very high compared to sediment volatiles content.

AUTORADIOGRAPHY AND OPTICAL EXAMINATION

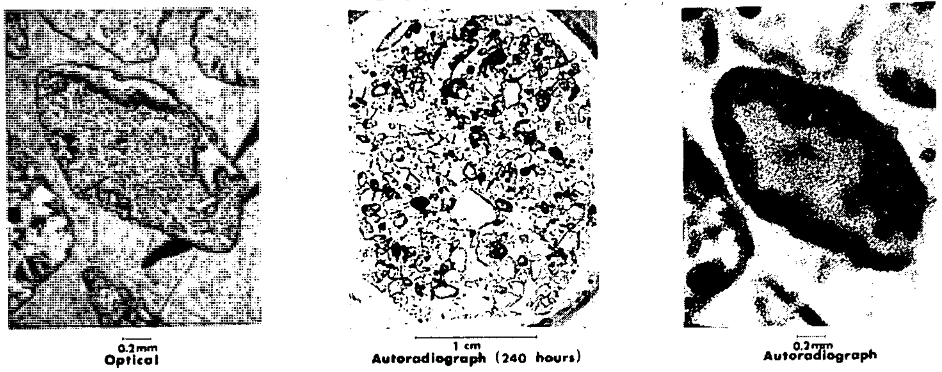
Autoradiographs of actinide-contaminated samples varied in exposure time from 15 minutes to 6 weeks as a function of actinide concentration levels. A minimum exposure time was sought to prevent buildup of film background. Contrast Process Ortho film was used and processed with D-76 film developer. A special cylindrical, solid metal holder was used to lower background and maintain good film-sample contact during autoradiography. Micrographs at a magnification of 50 were made of selected areas on the autoradiograph negative, and reflected light micrographs were made of the same sample areas using a Zeiss Ultraphot Metallograph.

In addition to the PuO_2 particles, the wastes also contained Am(III) and Pu(IV) in solution, at least partially as organo-complexes of plutonium and americium. These radioisotopes were removed, plutonium probably more than americium, during silicate hydrolysis reactions. Compared to the particulate plutonium, the plutonium associated with hydrolysis represents a low concentration in a very high volume of sediments.

Some of the autoradiographic and optical examination results for three well core samples are given in Figures 1 and 2. The sample at 2.23 meters depth shows a glaciofluviatile sand with the sediment fragments set in plastic and outlined by alpha radiation in the center photo. An optical photo of a single, magnified sediment fragment is shown on the left side and the matching autoradiograph of the same fragment is shown on the right side. Note that an apparently glassy material, higher in alpha activity, coats part of the outside surface of the fragment. The same material also occurs on other fragments in several photos. The composition of this altered material will be discussed in the next section. The actinide-containing coatings of the rock fragments represent, in addition to particulate PuO_2, plutonium associated with silicate hydrolysis. A closer examination by scanning

216-Z-9 CORE WELL SAMPLES

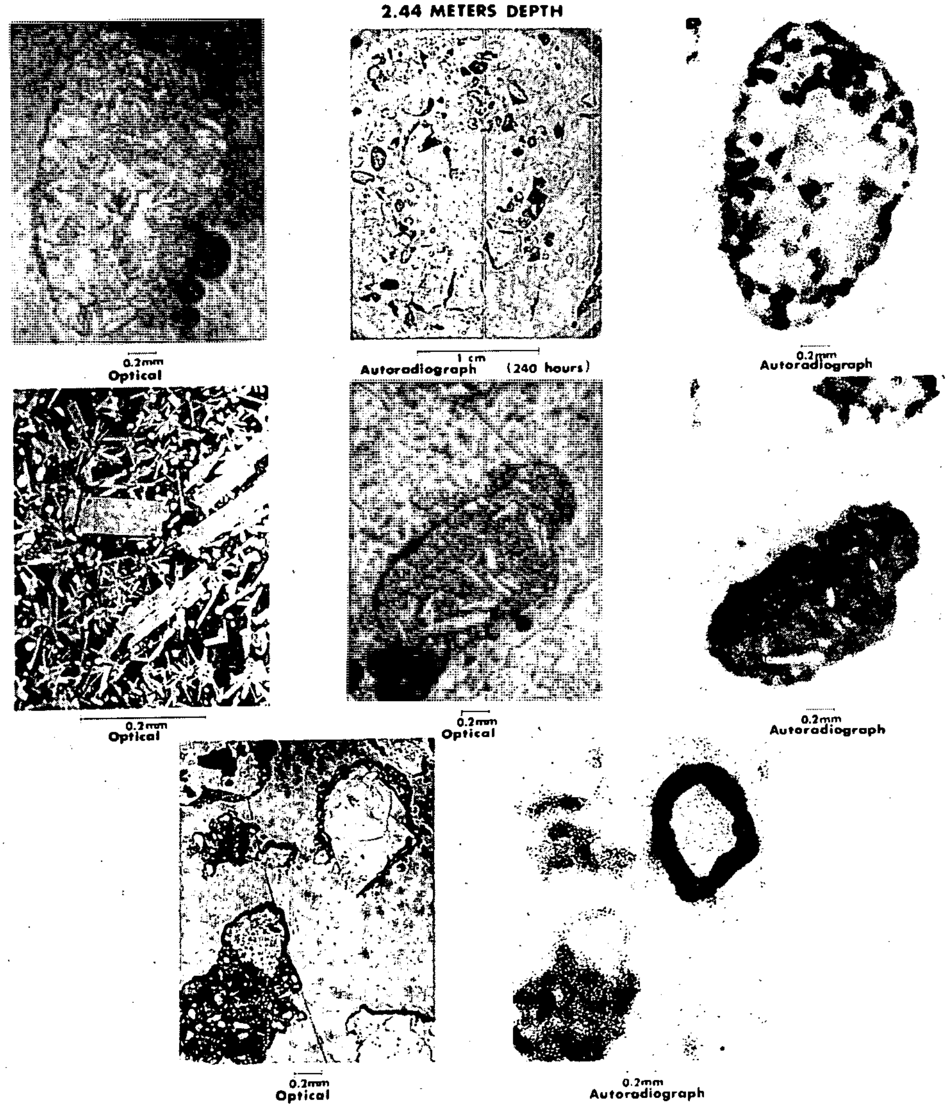
2.23 METERS DEPTH


0.2mm Optical

1 cm Autoradiograph (240 hours)

0.2mm Autoradiograph

2.44 METERS DEPTH


0.2mm Optical

1 cm Autoradiograph (240 hours)

0.2mm Autoradiograph

0.2mm Optical

0.2mm Optical

0.2mm Autoradiograph

0.2mm Optical

0.2mm Autoradiograph

FIGURE 1. Reflected Polarized Light (Optical) and Autoradiographic Photos of Rock Fragments From 2.23 and 2.44 Meters Depth in 216-Z-9 Covered Trench

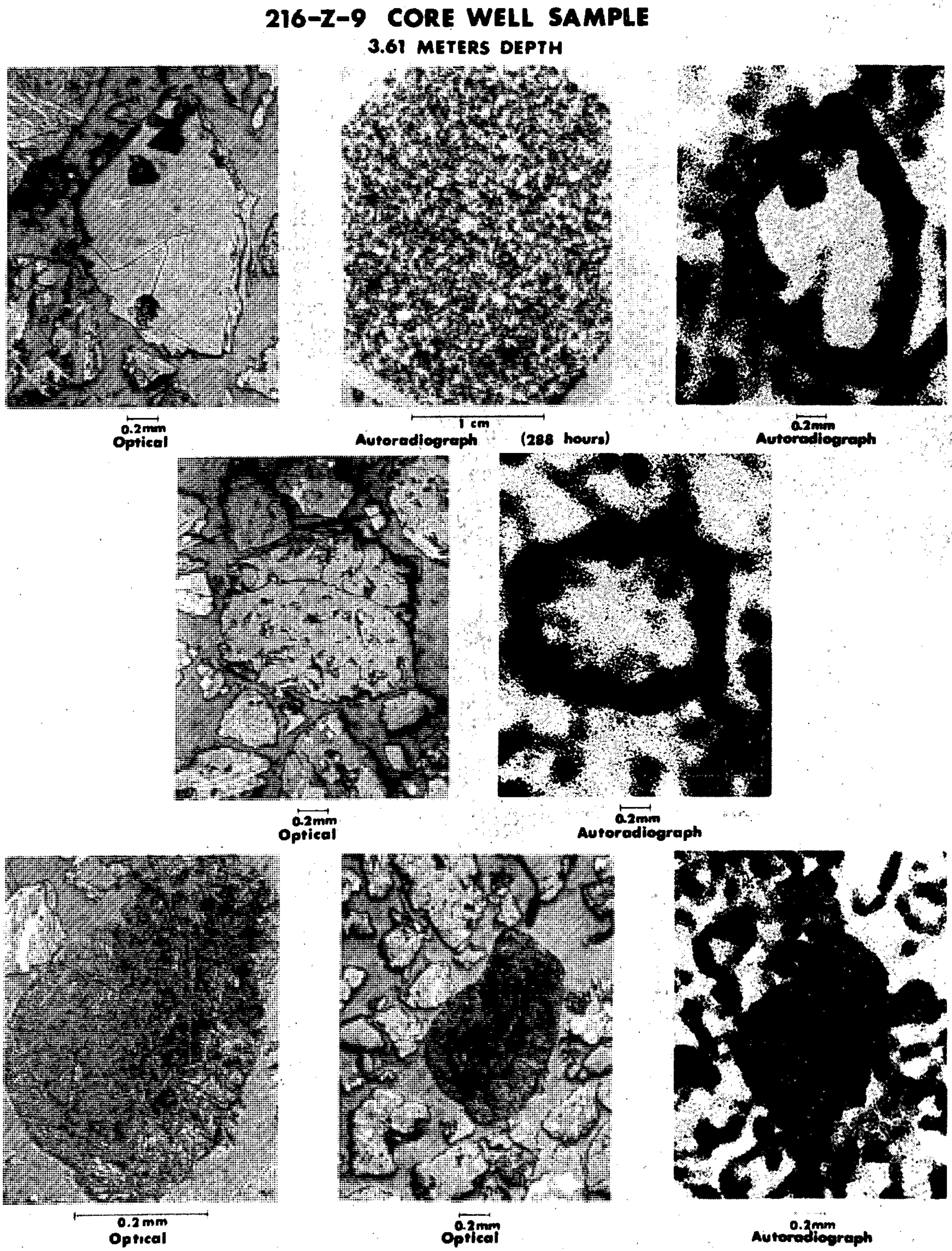


FIGURE 2. Reflected Polarized Light (Optical and Autoradiographic Photos of Rock Fragments from 3.61 Meters Depth in 216-Z-9 Covered Trench

electron microscope showed remnants of crystals and other artifacts that were contained originally in the unaltered rock fragment.

The sample at 2.44 meters depth shows a less well-defined sand in the autoradiograph. The optical photo to the left shows a typical, well-crystallized basalt fragment. The lightest colored crystals are titaniferous magnetites and ilmenites; the darker, irregular-shaped crystals are pyroxenes, predominately augites and the darker lath-shaped crystals are plagioclase feldspars, andesites to labradorites in composition. The groundmass material between the above crystals is microcrystalline to glassy, and is usually the first portion of the rock fragment to be chemically attacked by the acid waste. Small pieces of loose groundmass and crystals can be seen surrounding the fragment exterior. This fine, loose material results primarily from groundmass chemical attack. The three, round, black objects were gas bubbles in the impregnating plastic. Because the fragment was sectioned during sample preparation, the autoradiograph gives some indication as to how far into the fragment the acid waste containing actinides has penetrated.

The next rock fragment has had its groundmass completely altered. There are two generations of feldspar crystals present. The larger laths were probably contained in the original lava, while the smaller crystals formed later during cooling. There are some small, equidimensional magnetite crystals and a few pyroxene crystals in among the later generation of small feldspar crystals, as seen in the higher magnification optical photo. A probable cause of the almost complete alteration of this fragment is a high glass content in the groundmass. As can be seen here, the crystalline material is quite refractory to alteration as compared to the glassy groundmass.

The last rock fragment shown at 2.44 meters depth is almost completely glassy with some evidence of chemical attack. A thin altered zone containing relatively high concentrations of actinides can be seen in places, along with fine grain size debris, around the fragment exterior. This represents the hydrolysis mode of plutonium occurrence.

The well core sample from 3.61 meters depth is shown in Figure 2. This sample contains may more silt-size rock fragments than the above two core samples.

The first fragment examined was a glassy basaltic rock fragment. Essentially the whole fragment is glassy except for a few feldspar crystals. There has been little alteration of the fragment that is visible in the interior on the autoradiograph. There is, however, an altered exterior on the fragment that contains a relatively high actinide content, much like the fragment shown in the 2.23 meter core sample. The composition of this altered zone is given later.

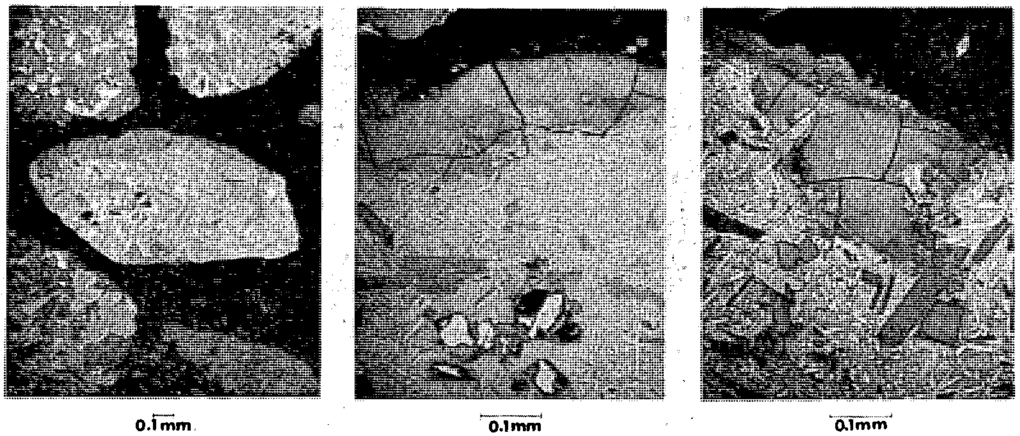
A similar rock fragment is shown next with the same combination of minor silicate hydrolysis and associated actinides and major actinide concentrations associated with the exterior alteration. There was very little evidence for the occurrence of PuO_2 particulates at these depths in the sediment column; PuO_2 particulates were very rare even at 0.5 meters depth.

The last fragment composed of many fine plagioclase feldspar crystals set in a glassy groundmass, completely lost its glassy groundmass to silicate hydrolysis. It is nearly uniformly radioactive with no indication of an exterior high actinide zone.

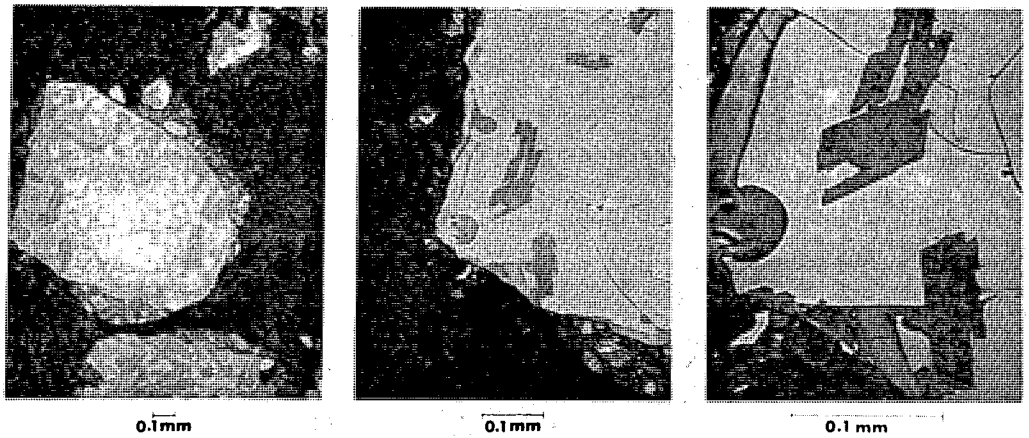
Scanning electron microscope (SEM) photos of selected rock fragments from Figures 1 and 2 are given in Figure 3. The first fragment from 2.23 meters depth clearly shows the claylike, porous alteration product on the exterior of the fragment. Even a large feldspar crystal has been partially altered. This example clearly goes beyond simple silicate hydrolysis in intensity of alteration. Remnants of small areas of crystals, and the absence of similar exterior materials on other rock fragments in the vicinity, strongly suggest an alteration of the original fragment rather than deposition of a rock fragment coating as an originating mechanism.

SEM PHOTOGRAPHS

2.23 METERS DEPTH



2.44 METERS DEPTH



3.61 METERS DEPTH

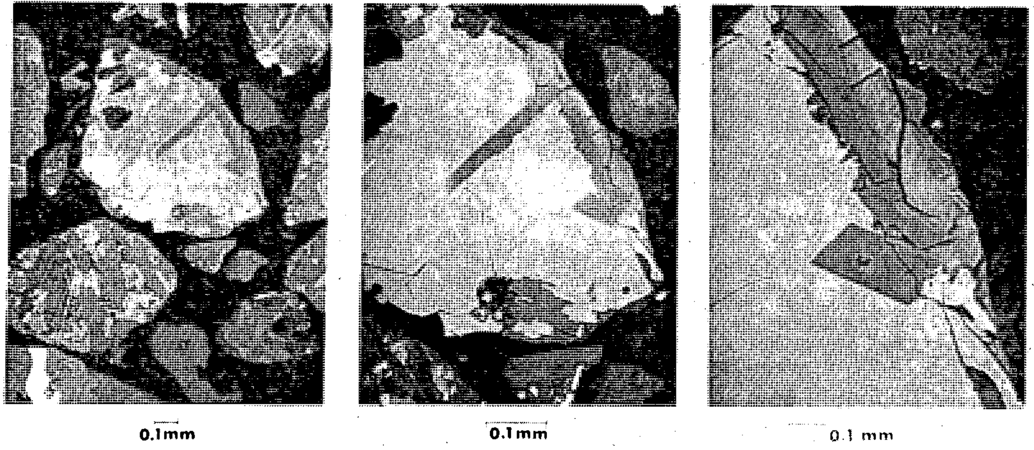


FIGURE 3. Scanning Electron Microscope (SEM) Photos of Selected Sediment Rock Fragments Also Seen in Figures 1 and 2.

The rock fragment shown from 2.44 meters depth has a largely glassy groundmass containing a few feldspar and pyroxene crystals. The cracks in the groundmass show evidence of having admitted altering solutions.

An area of altered material also is seen at the edge of the 3.61 meters depth rock fragment. Feldspar crystals can be seen in the higher magnifications to have survived fairly intact in the zone of alteration. There are several instances of altering solutions entering cracks in the glassy groundmass of this fragment as well.

ELECTRON MICROPROBE RESULTS

A Materials Analysis Company Model 400S electron microprobe was used for elemental mapping and chemical analyses of selected areas of the sediment samples after gold coating of the sample surface.

The results of electron microprobe chemical analyses of the altered and original rock fragment areas are given in Table 9. In the 2.23 meter depth rock fragment, the same as those seen in Figure 3 under their respective depths in meters, losses of potassium, calcium, titanium and aluminum are seen from the altered areas, along with some addition of iron. Silica and magnesia remained nearly the same during alteration. Changes in weight percent silica and magnesia were probably due as much

TABLE 9. Comparison of Original and Altered Area Analyses

Sample	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	BaO	Fe_2O_3	TiO_2	P_2O_5	PuO_2	Cl	Total
Original, 2.23 meters	54.6	14.1	<1.3	0.6	1.7	5.2	<0.1	16.8	4.0	1.7	<0.1	<0.1	98.7
Altered, 2.23 meters	59.7	5.6	–	0.3	2.2	<0.1	–	29.8	<0.1	0.7	–	–	98.3
	62.7	7.8	–	0.2	2.3	0.1	–	27.3	–	1.8	–	–	102.3
Original, 2.44 meters	56.2	11.9	–	1.3	3.3	6.4	–	15.1	4.1	1.3	–	–	101.2
Altered, 2.44 meters	40.3	2.2	–	<0.1	<0.3	0.7	(ZnO) 10.2	35.5	2.1	5.0	0.3	2.6	98.9
Original, 3.61 meters	56.8	12.4	–	1.3	3.8	6.9	–	16.7	4.2	0.6	–	–	102.7
Altered, 3.61 meters	45.6	11.2	–	0.8	0.8	0.1	(S) 0.8	34.0	1.1	7.1	–	0.2	101.7
	50.4	9.8	–	0.8	0.7	0.3	–	27.9	2.2	6.3	0.2	0.2	99.5

to the losses of other constituents as to the addition of silica and magnesia. The orginally porous altered materials have had their chemical analyses corrected for the presence of about 25% by volume of impregnating plastic.

The altered rock fragment at 2.44 meters depth was the only one examined that showed a measurable amount of plutonium as well as added zinc, phosphorus and chlorine. The added materials can be found in Table 1 under the waste constituents disposed to 216-Z-9 covered trench. The zinc probably was present in the waste influent just as the plutonium was. The marked loss of aluminum from the rock fragment glass indicates that the waste influent causing the alteration was originally quite acid in nature. The lesser amount of silica in the altered area probably reflects the addition of zinc and iron rather than the removal of silica. The presence of chlorine, coupled with increased phosphorus, indicates the presence of carbon tetrachloride and tributylphosphate degradation products.

The altered sample from 3.61 meters depth indicates that much the same process operated with the exception of aluminum removal. Alkalies and alkaline earth metal cations and titanium were removed, along with some silica. Iron was added once again along with a small amount of sulfur, probably from sulfates added to the waste influent. Chlorine and phosphorus also were added, as with the sample at 2.33 meters depth.

DISCUSSION

Silicates can be viewed as salts formed as the result of the reaction of weak acids and strong bases. Hydrolysis reaction products are therefore alkaline. Such a simplified reaction with the glassy portion of basalts would be as follows:

$$(Ca,K) - glass + 3H^+ \rightarrow (H_3) - glass + Ca^{2+} + K^+.$$

Hydrolysis, only a first step in the weathering or alteration of sediments and minerals, essentially leaves the silicate glass framework intact. More intense alteration is required to attack the alumino-silicate framework. In acid solutions such as the Z-9 trench wastes, the attack would take the form of aluminum solubilization with destruction of Al-Si bonds.

Three factors are of primary importance to the intensity or rate of hydrolysis reactions. These factors are temperature, leaching solution volume and hydrogen ion concentration. In the case of Z-9 trench influents, the outstanding factor in intensifying hydrolysis was leaching solution pH or hydrogen ion concentration. The iron loss from chemical attack of a glassy basalt fragment reported earlier(2) indicates that the nitric acid content of the influent was relatively high for some unknown time. The pH of a ferric nitrate solution has to be less than 2, or ferric iron does not remain in solution. The pH of the influent solution must have been less than 2 for a period of time. The pH of the bulk of Z-9 trench influents was adjusted to pH 2.5 before disposal. Even at pH 2.5, hydrolysis would proceed much more rapidly than at the normal sediment-groundwater pH of 7.7 to 8.2. The finer sediments hydrolyze more rapidly because of higher exposure of surface area/unit volume.

On a microscale, the hydrolysis and partial alteration of the glassy basalt fragments can be viewed as in Figure 4. Here part of a single glassy basalt fragment section is seen immersed in an acid influent solution containing Pu(IV). The pH gradient across the altered zone is shown along with the diffusion of plutonium and hydrogen ions into the reaction interface with the unaltered glassy groundmass of the basalt fragment, and the diffusion of an alkali and alkaline earth metal cations back out into the solution. The diffusion of materials into and out of the sediment fragment are the primary cause of the accompanying pH gradient and the precipitation or removal of plutonium from solution probably as the polymer. The kinetics of polymer conversion to a stable PuO_2 phase are largely unstudied. Little can be said, with certainty therefore, about the present state of the plutonium associated with silicate hydrolysis.

It is obvious from the chemical analyses of Table 9 that the silicate alteration process includes silicate hydrolysis, but also involves more than that. Aluminum has been removed

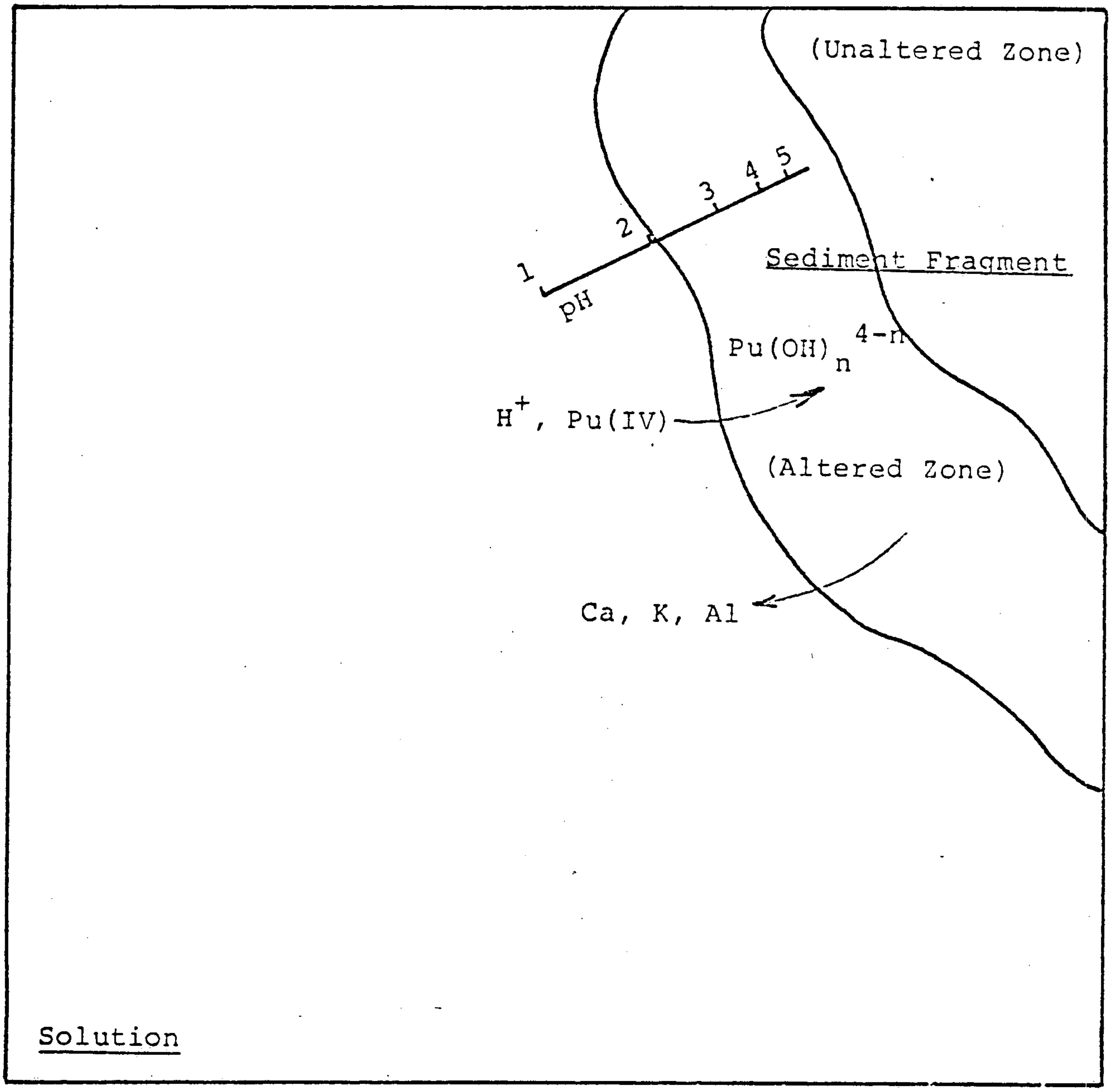


FIGURE 4. Reactions Involved in Formation of an Altered Zone Around a Glassy Basalt Fragment If Pu(IV) was the Plutonium Form in the Waste Solution

in all cases, indicating at least partial destruction and solubilization of the aluminosilicate framework of the glassy and microcrystalline, rock fragment groundmass. A considerable volume shrinkage at altered areas also was indicated by the SEM photos of Figure 3.

As there was a pH gradient across individual hydrolyzed glassy basalt or other rock fragments comprising the sediments, there must also have existed a pH gradient from the top to the base of the sediment column. At some point in the downward flow of the solution, the solution must have reached a pH between 4 and 8 at which silicate hydrolysis reactions proceeded very slowly and solution-sediment equilibrium was approached.

The form in which the plutonium associated with silicate hydrolysis occurs remains unknown, as does the form of the plutonium in the waste solution. With all of the solution constituents listed in Table 1 accompanying the plutonium and americium in the waste, they may easily have been transported as complexes. Disproportionation of Pu(IV) also may have occurred at pH 2.5 in the relatively dilute waste solution. Much work remains to adequately characterize the actinides associated with silicate hydrolysis.

REFERENCES

1. Nuclear Reactivity Evaluations of 216-Z-9 Enclosed Trench, A. E. Smith, ed., ARH-2915, Atlantic Richfield Hanford Company, Richland, WA, 1973.

2. S. M. Price and L. L. Ames. Characterization of Actinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford, ARH-SA-232, Atlantic Richfield Hanford Company, Richland, WA, 1975.

3. L. L. Ames. Characterization of Actinide Bearing Soils: Top Sixty Centimeters of 216-Z-9 Enclosed Trench, BNWL-1812, Battelle Pacific Northwest Laboratories, 1974.

4. Letter, April 10, 1973, L. E. Bruns to R. E. Isaacson, "Recuplex Inputs to Z-9 Crib." Atlantic Richfield Hanford Company.

5. J. L. Swanson. Nature of Actinide Species Retained by Sediments at Hanford: Interim Progress Report. BNWL-B-296, Battelle Pacific Northwest Laboratories, 1973.

FOLLOWING L. L. AMES' PRESENTATION

QUESTIONS AND ANSWERS

Burkholder: Lloyd, how much did that study cost?

Ames: Ask Sue; she's in charge of it. Sue, how much did it cost? Or don't you care to say?

Price: Counting the drilling?

Ames: The drilling cost a lot more than my part of it at that time.

Burkholder: I'm interested in what it costs to get that kind of information.

Price: The research costs were about $50,000 per year and Lloyd has been funded for about 3 years. Lloyd, you might know the cost per sample as far as your work is concerned.

Ames: It costs about $1400 a sample to run a sample all the way through from my end of it. I don't know what it costs to get the sample. When we get the sample in the glove box and make up the mounting in plastic, for a medium amount of micropobe work, electron microprobe work, SEM work, and petrographic work and autoradiographs, the costs are about $1400 per sample.

Burkholder: What about the drilling costs?

Ames: You had better ask Sue.

Price: Drilling probably cost per sample about that much because we use totally contained drilling and have to take into account operator costs. The equipment costs are very minimal compared to operator costs. We use four to five operators plus a radiation monitor when we drill for actinide samples.

Ames: Tomorrow I'll say something about other plans we have for the trench sediments. At 10:30 tomorrow, we'll have something to say about what we are doing now and what our future plans will be, including other types of waste that have gone into other sites. I want to emphasize that this is an acid site. It certainly isn't the usual thing. I doubt very much that you would see anything comparable in a neutral to basic system. It just wouldn't occur that way.

Garland: How deep in the sediment do you go before you run out of the acid?

Ames: We've examined down to about 30 feet and haven't gotten below its effects yet. There was still evidence of chemical alteration going on. There is less americium than plutonium associated with it.

Rhodes: Do you have any evidence that some of the very fine particles may have migrated great distances, as indicated by groundwater samples or other measurements?

Ames: No. The reason we haven't drilled any farther than about 33 feet is that Atlantic Richfield Hanford Company has some other plans for Z-9. What they are doing is mining the top foot or top 2 feet out of it, so we had to leave. We can't drill holes in it while they are scooping out the top. We didn't really get down into the lower part of it. We got down to where it took up to 4 weeks to 6 weeks for the autoradiographs. In other words, actinide concentrations are falling off at a rapid rate. It's a factor of 10^6 difference between the top of the column and where we were working at 33 feet. This poses all kinds of problems in itself.

Trying to bring samples into the same glove box is really not practical. It's very difficult to work with this contamination range because you should have six or eight hoods representing different contamination levels, to bring them into. We don't really have that kind of setup. There are a lot of problems associated with the soil. I'll go into some details tomorrow about the things we are trying to do to find out what state the plutonium is in. We have already X-rayed the one type, isolated the particles and X-rayed and positively identified PuO_2. The PuO_2 went in there in that form. The plutonium associated with the hydrolysis we know very little about except that it's low in concentration compared to the PuO_2 particles. It appears in a very large volume in the altered sediments.

MIGRATION OF PU AND AM

(Presented by
R. W. Atcher)

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A. Fried
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INTRODUCTION

The migration of actinide wastes, especially the long-lived isotopes of plutonium and americium, in rocks and soils, is of special interest since any major release of stored wastes from a depository will proceed by this path. It is therefore important to study the mechanisms involved in this migration. The following paper summarizes the results of FY 1974 in addition to the results of FY 1975.

The studies of FY 1974 led to several important conclusions. One of these was the experimental verification of the assumption that a dynamic process, such as the migration of plutonium in a solution flowing through a fissure or through pores, could be described in terms of a simple variable, the surface absorption coefficient. (The coefficient, k, is defined as the ratio of activity in a milliliter of solution to the activity absorbed per square centimeter of rock.) This coefficient was measured in a static system by equilibrating # solid samples of stone of known surface area with solutions of plutonium or americium in the appropriate chemical milieu. It was shown that these static coefficients and the physical constants of the system (pore size, flow, volume, etc.) were sufficient to predict the distance migrated. These coefficients were measured for various types of solutions, and it was demonstrated that they were sensitive to the concentration and types of other ions present. In general, desorption of actinide ions occurred if the aqueous phase contained high concentrations of other cations. It was evident that measurements for this year should be made both of the kinetics of the equilibrium process and of the values of k in aqueous solutions containing high concentrations of salts.

One other important result of this previous study was the identification of two chemical forms of Pu(IV). One of these forms, assumed to be ionic and highly charged, migrated at a rate tenfold less rapid than the second form, assumed to be a polymer. The investigation of the rapidly migrating form was felt to be one of our highest priorities in FY 1975 and FY 1976.

In addition, the success of our computer model in the prediction of flow through fissures made it feasible to consider preparing a laboratory-scale model of a migration experiment to test the predicted behavior of plutonium on rock samples taken from an existing waste depository.

These objectives have been achieved, and arrangements have been made with the Environmental Studies Group (H-8) at Los Alamos for a joint core-drilling program with ANL. This will be carried out at a former disposal site having a documented history. The objective will be to acquire core samples (containing actinides) at carefully determined coordinates from the point (or points) of deposition of the actinide wastes.

It is intended that the actinide concentrations be determined in such cores and the results tabulated so that the pattern of migration from a real depository can be discerned.

EXPERIMENTAL RESULTS

GENERAL STUDIES OF PLUTONIUM AND AMERICIUM MIGRATION

The absorption coefficients of Am(III) and Pu(IV) on solid cores of Los Alamos tuff and Idaho basalt* from aqueous solutions were measured at a pH ranging from 2 to 10. These were equilibrium studies, and it was found that after the first 24 hr k had a constant value.

The movement of Pu(IV) through Idaho basalt fissures was traced with two objectives in mind. The first objective was to determine if the presence of the more rapidly migrating chemical form of plutonium was affected by the kinetics of the experiment. For example, can the two forms of plutonium exchange by a slow equilibrium? If so, a very slow flow rate along the surface of a fissure may cause the plutonium to migrate as a single slowly moving band, since the equilibrium will be shifted towards the more strongly bound form. However, a rapid flow rate will not permit equilibrium to be established; the two forms will therefore become separated, giving either two peaks or a broad peak.

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*The basalt was taken from the EBR(II) waste-disposal site at the Idaho National Engineering Laboratory near Idaho Falls, ID.

The simulation of the fissure was accomplished by the apparatus shown in Figure 1. Tablets of basalt were cut with smooth surfaces. Five of the six surfaces of the tablet were rendered impervious to water by coating them with wax. The sixth surface was left untreated and was held in the apparatus to be exposed to and wetted by a solution containing plutonium. This "active" surface was held in the apparatus so that it faced an inert surface (Teflon) a short distance away (about 0.01 cm), as shown in Figure 1. The space between the basalt and Teflon surfaces then constituted the fissure through which the aqueous medium could flow. Since all other surfaces of the basalt were waxed, they were not used in the experiment, and all results on the distributions of plutonium on the surface of the basalt were unperturbed by effects that would have otherwise related to more complex geometries.

The plutonium was introduced at the top of the fissure in a very small volume (about 50 λ) by means of an infusion pump. The subsequent elution of the adsorbed plutonium from the surface of the basalt also made use of the infusion pump. Water was the elution medium, and since the infusion pump was constructed to deliver steady, slow, predetermined volumes, it was well suited for this kind of experiment.

After the requisite amount of water had been allowed to flow over the surface of the basalt, it was stopped and the basalt tablet was removed from its holder and dried. Scanning

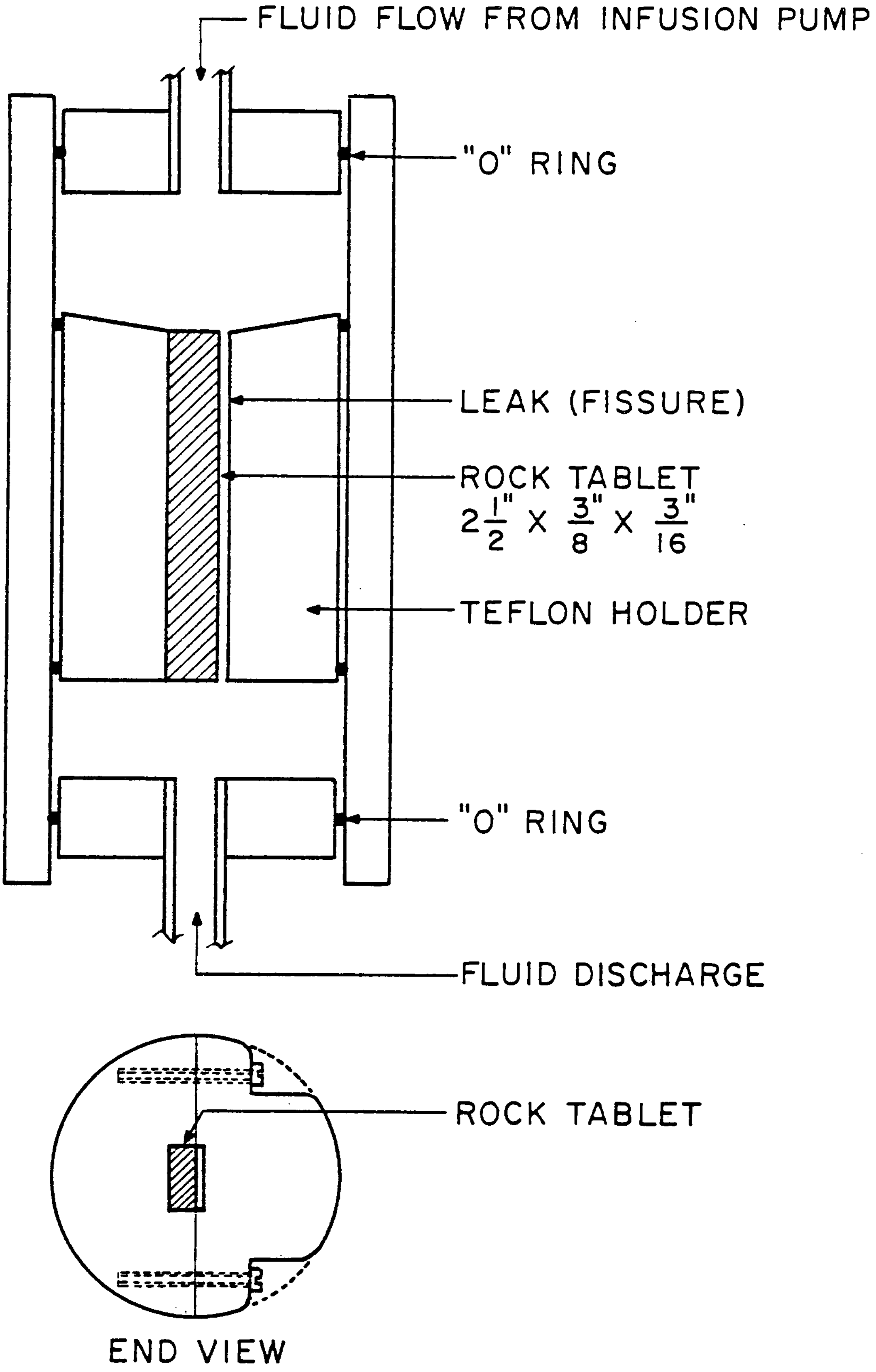

FIGURE 1. Artifical-Fissure Apparatus

the surface of the rock for alpha activity by means of a scanning alpha counter (SADSAC) delineated the distribution of the plutonium on the rock.

Varying the delivery rate of the infusion pump, as well as the total volume of water used, made it possible to examine the distribution of plutonium as a function of these parameters. For example, the apparatus was used in a series of survey experiments to determine the effects of flow velocities. The results indicate a nonequilibrium behavior. Figure 2 is a composite plot of the results of experiments on similar slabs of basalt. The curve marked Experiment 6 was taken using a flow velocity of 17.2 cm/hr; Experiment 9 used 51.7 cm/hr. As can be seen, at the slower velocity the peak is much sharper.

MODELING STUDIES - COMPUTER MODEL

A computer model, based on multiple reiteration of surface absorption and dissolution processes, was developed, representing the migration process through pores and along the surfaces of fissures. The model, which uses only the physical dimensions and surface absorption coefficients for the particular system, adequately describes the main features of the migration process. However, it does not take into account the second-order effects of nonsaturated flow and kinetic dispersion. The

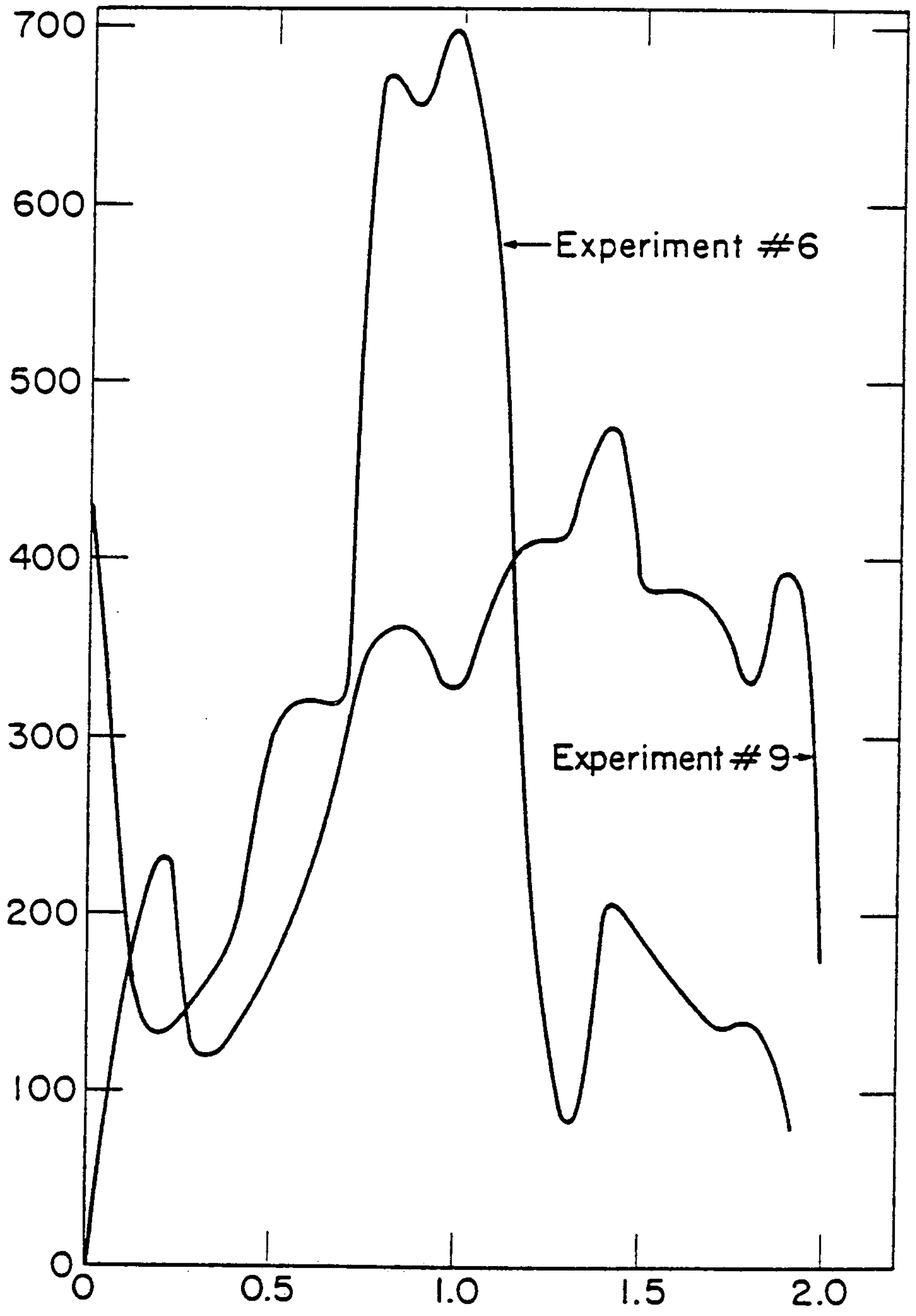

FIGURE 2. Counting Rate of Plutonium (counts/min-cm^2 as a Function of Distance Traveled Down Fissure

predictions of the model, along with the results of our laboratory modeling experiment, are discussed in the following section.

MODELING STUDIES - LABORATORY-SCALE MODEL

A laboratory-scale model of the migration of plutonium was studied using a block of tuff (25 x 30 x 23 cm) from the Los Alamos site. Figure 3 shows the experimental setup. Tracer ^{237}Pu was obtained for this experiment to facilitate counting. The plutonium was delivered to the center of a 1 x 2 x 0.5-cm indentation on the surface of the block. The delivery was made by means of the infusion pump at such a slow rate that the solution dried at the delivery point with little or no spreading. To simulate rainfall, the surface was alternately wet by means of a sprinkler and then allowed to dry. A total of 1270 ml of water was delivered in six 75-300-ml doses over a 7-day period, after which the rock was allowed to dry for 4 days. The rock was then cored as shown in Figure 4. A diagrammatic view of the coring apparatus is shown in Figure 5. The results of the distribution measurements are shown in Figure 6 for cores taken at various radial distances from the central deposit of plutonium. Figure 7 is a cross-sectional view of the distribution obtained. It is easily seen that there are two plutonium concentration peaks, presumably corresponding to the ionic and hydrolyzed forms.

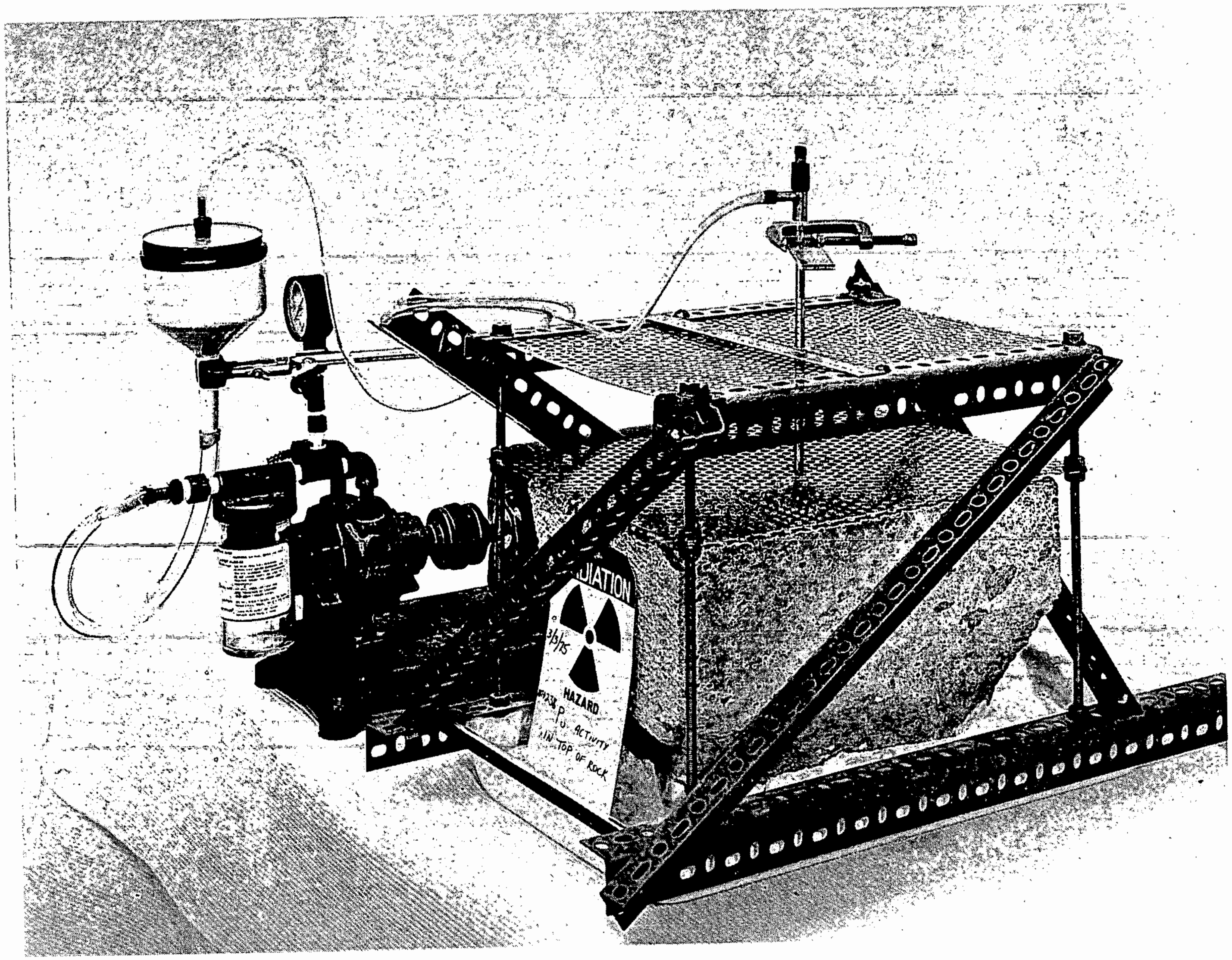

FIGURE 3. Experiment Arrangement for Coring Experiment

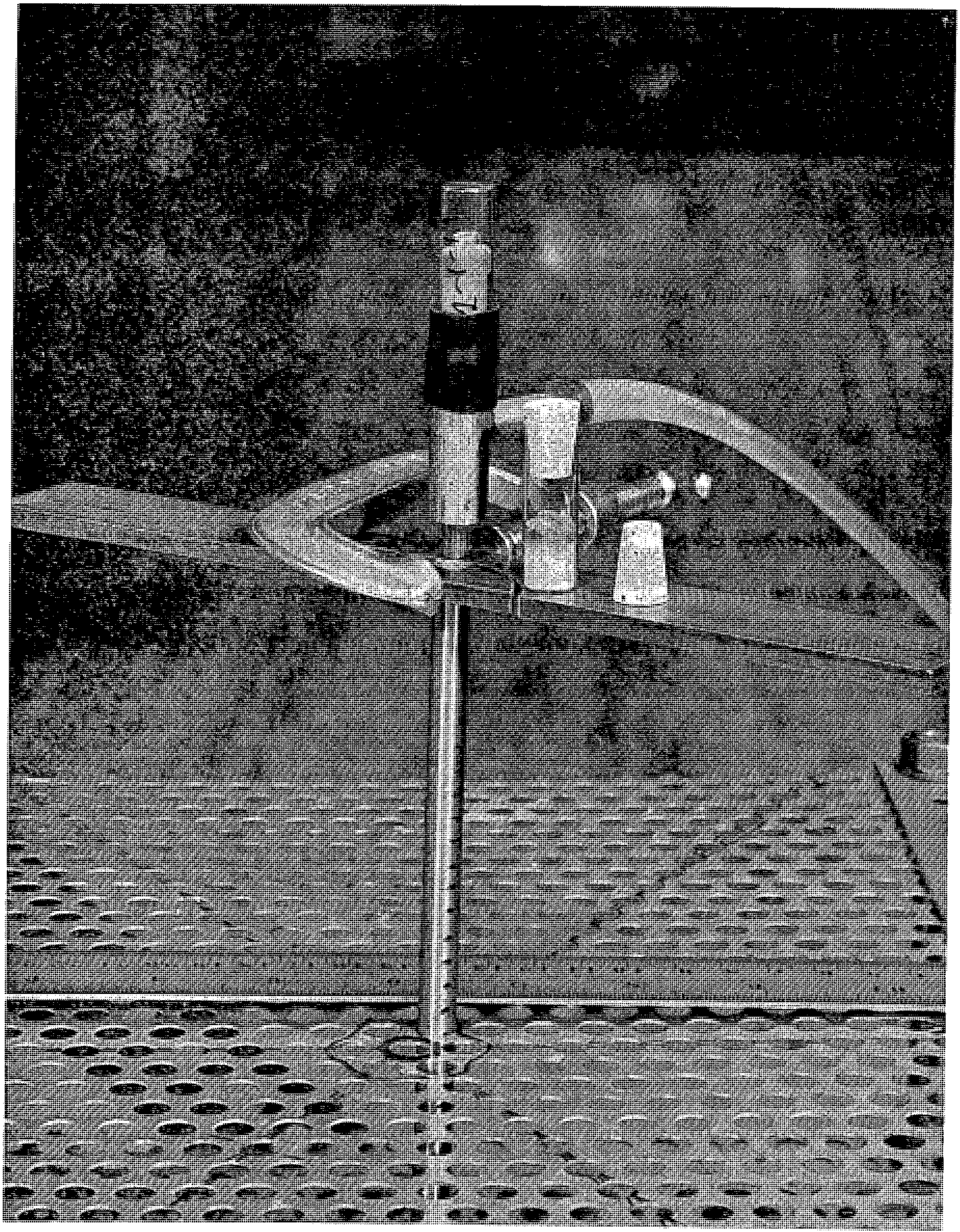

FIGURE 4. Sample-Coring Apparatus

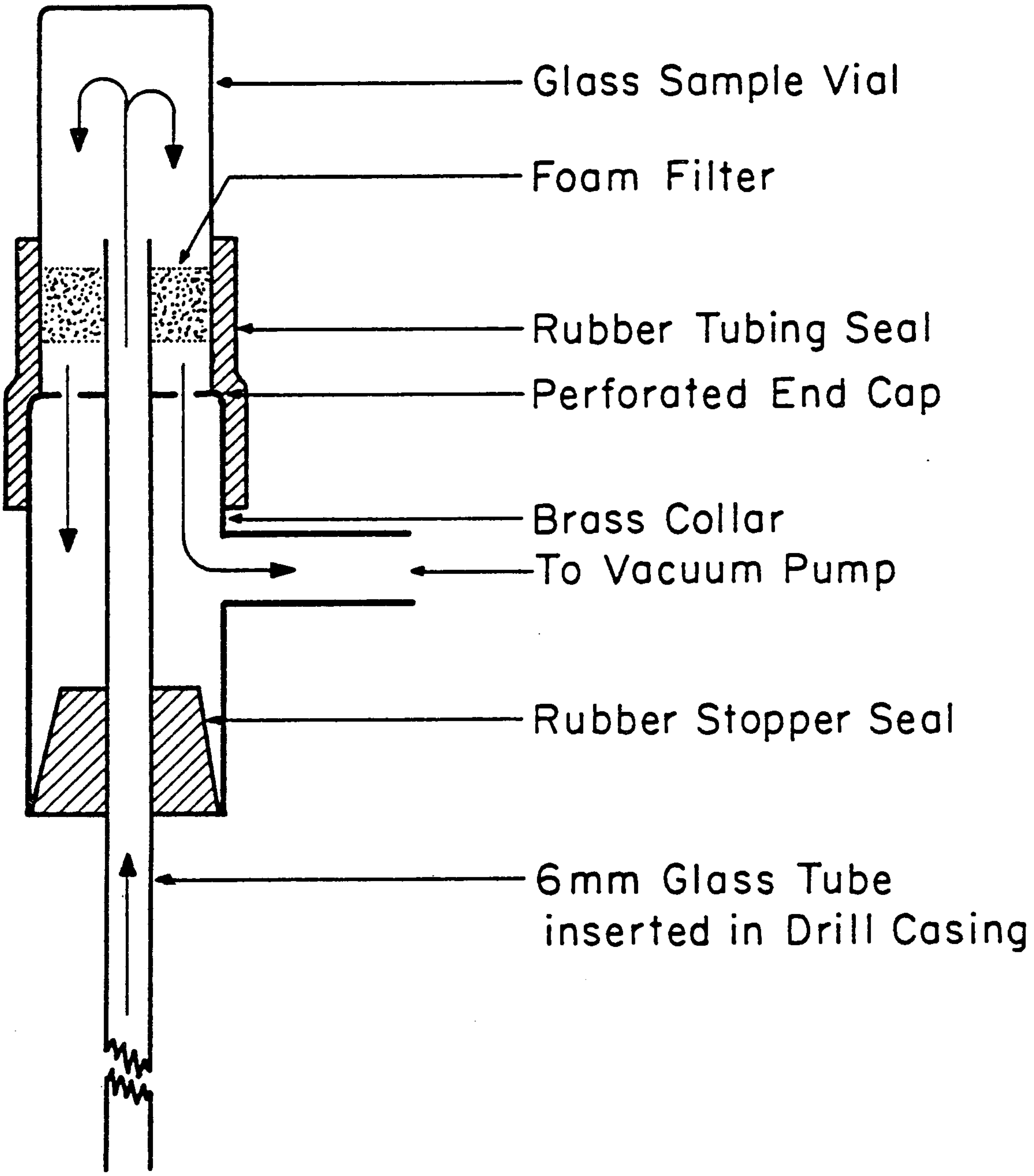

FIGURE 5. Results for Cores Taken at Various Radial Distances from Central Core

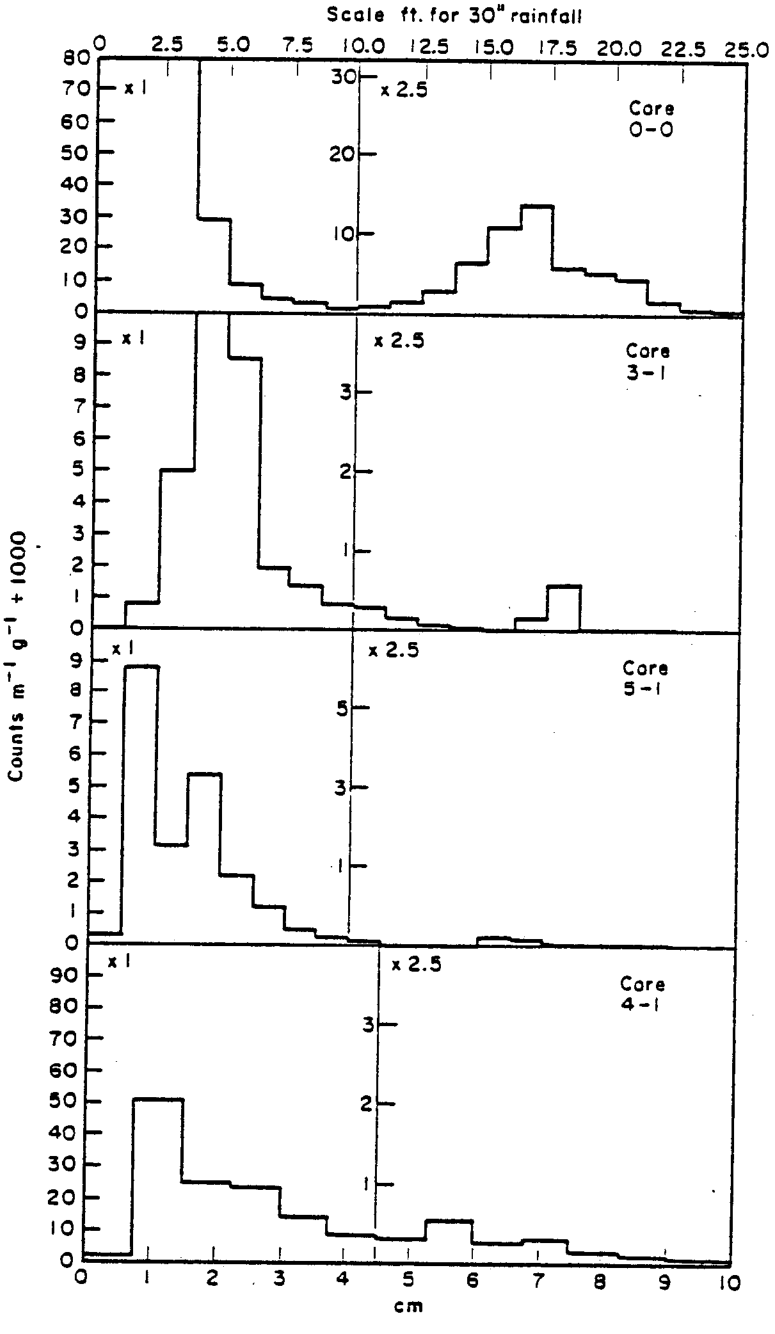

FIGURE 6. Cross-Sectional View of Activity Distribution

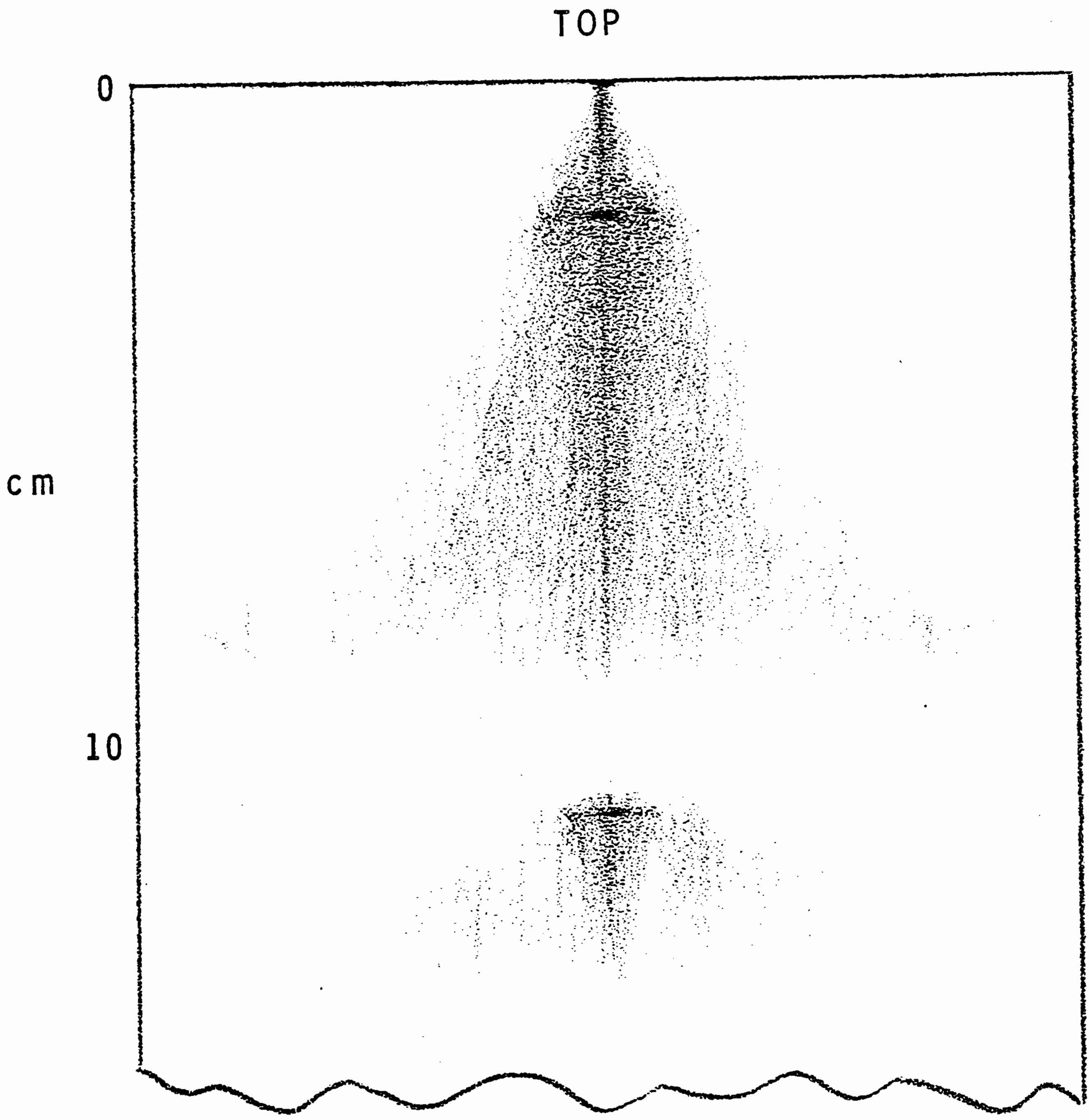

FIGURE 7. Activity Distribution in Central Core; Dotted Line is Result of Model Calculation

Figure 8 shows the distribution observed for the central core. The dotted lines show the computer-model results for the two plutonium peaks.

As can be seen, the model fails to predict the widths of the peaks and the exponential gradients. We are modifying the code in an attempt to correct these discrepancies.

SURFACE ABSORPTION COEFFICIENTS OF AMERICIUM

The surface absorption coefficients, k, of americium were measured for basalt. (See Introduction for definition of k.) The measurement was accomplished by sampling the supernatant solution from time to time after gentle agitation and determining the amount of americium remaining by radiochemical assay. When the concentration of americium in the solution remained constant for several successive determinations, equilibrium was presumed to have been attained. While equilibrium was generally reached within 24 hr, the sampling was continued for 5 days. This is in contrast to our results reported for plutonium, which required several days to attain equilibrium. This is probably indicative of the more complex situation in plutonium solutions where several species of ions are present and the exchange among them is slow. This is further confirmation of the kinetic effects noted above. The results obtained in solutions of $NaNO_3$, $SR(NO_3)_2$, and $La(NO_3)_3$ are listed in Table 1.

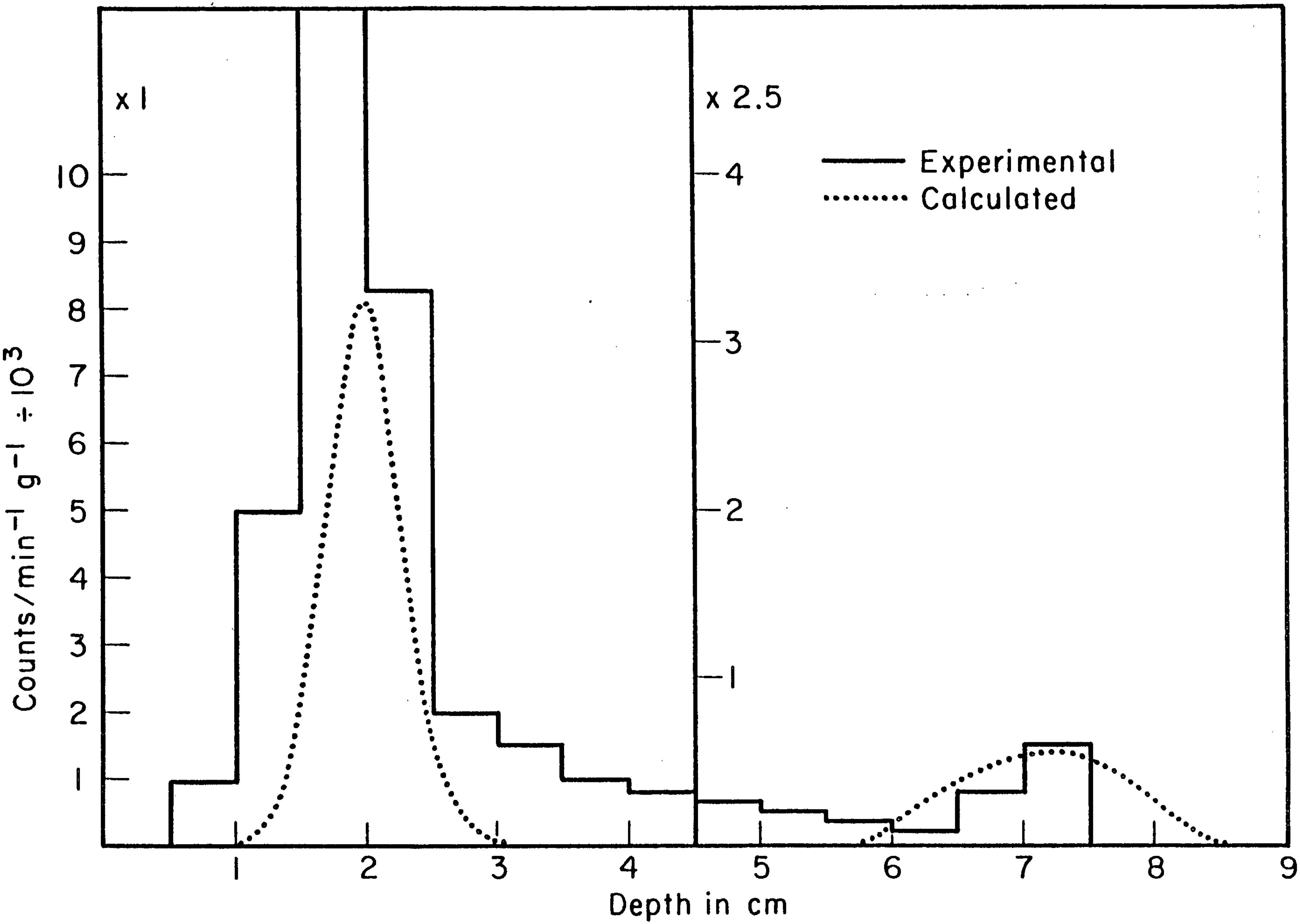

FIGURE 8. Activity Distribution in Central Core; Dotted Line is Result of Model Calculation

TABLE 1. Surface Absorption Coefficients for Americium on Tuff

Aqueous Solution	Concentration (M)	k
$LA(NO_3)_3$	0.01	9.44
	0.005	3.06
	0.001	1.93
	5×10^{-4}	0.60
	1×10^{-4}	0.06
	1×10^{-5}	0.02
	5×10^{-6}	0.05
$Sr(NO_3)_2$	0.5	0.196
	0.2	0.122
	0.1	0.025
	0.05	0.06
	0.01	0.02
	0.005	0.08
$NaNO_3$	1.0	0.45
	0.5	1.50
	0.1	0.013
	0.05	0.16

CHEMICAL IDENTIFICATION OF THE RAPIDLY MIGRATING FORM OF PLUTONIUM

Eluting plutonium solutions through columns made of plugs of tuff, as given in Figure 9, has been shown to separate the two forms of plutonium. This typical elution curve can be seen in Figure 10 as a solid curve. The rapid migrating plutonium is the peak at the left of the figure.

Two methods were used to remove hydrolyzed plutonium from solution. One was to evaporate the plutonium solution repeately with HNO_3. The other made use of a reversed-phase partition chromatography column using di-2-ethylhexyl

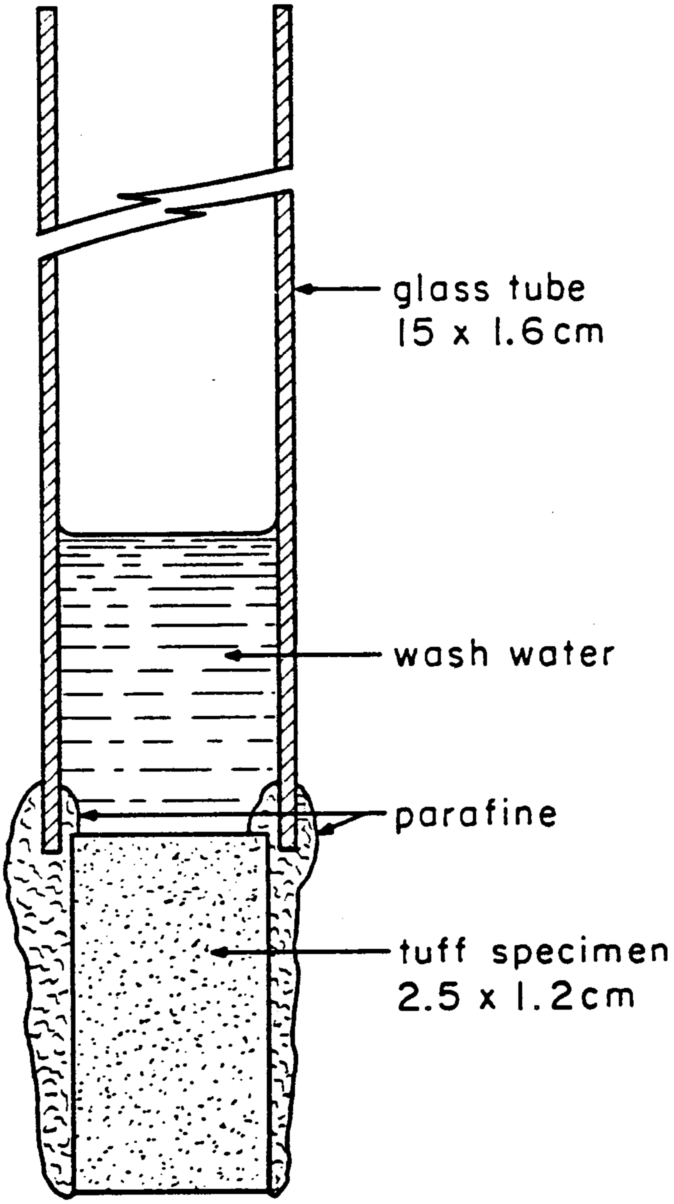

FIGURE 9. Schematic Diagram of Elution Column Made with a Plug of Tuff

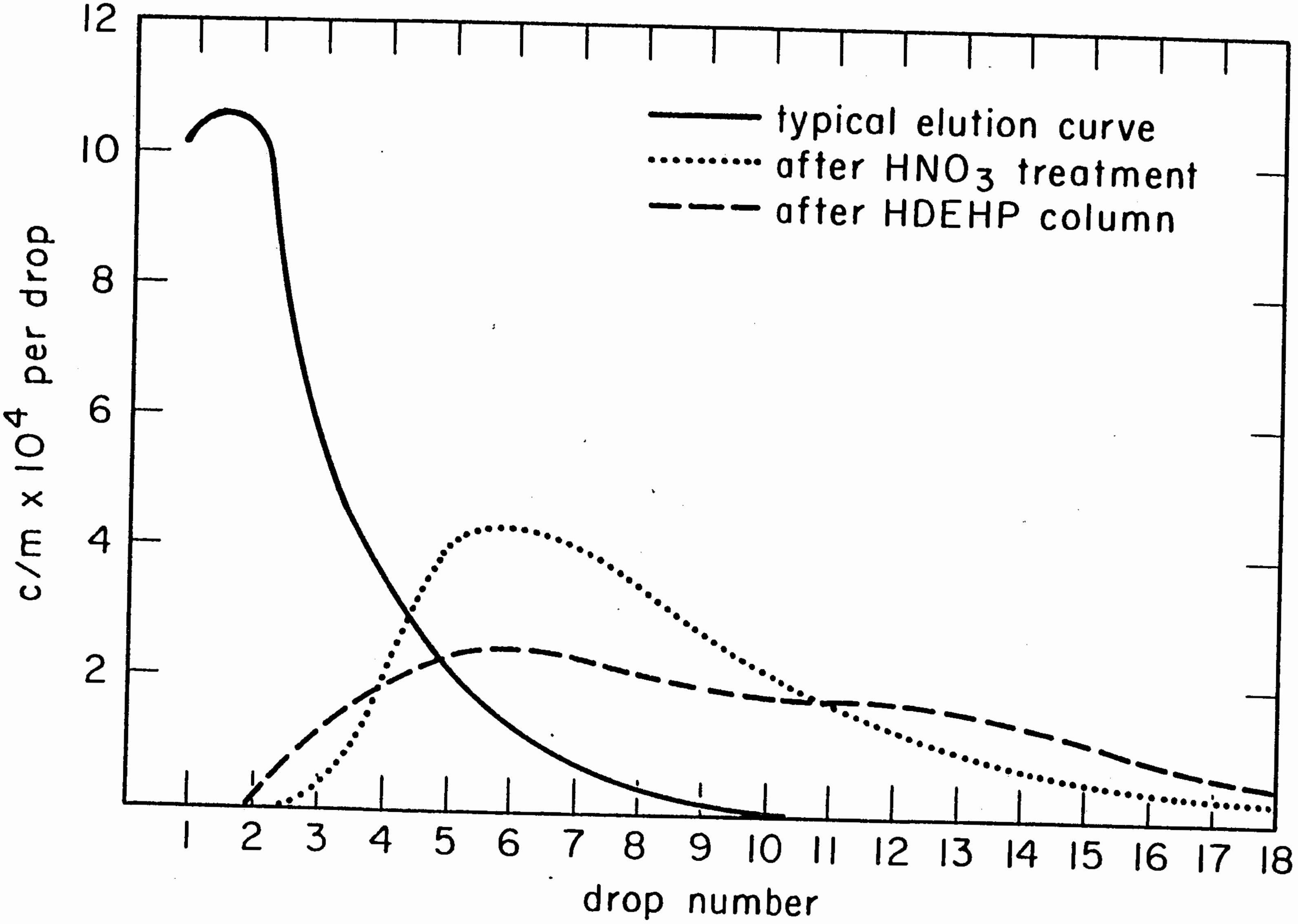

FIGURE 10. Elution Curves from Column

orthophosphoric acid (HDEHP). Since the plutonium-HDEHP system is well known (only the ionic species adsorbs), this column can be used to determine the relative amounts of ionic and polymeric (hydrolyzed) plutonium present.*

When plutonium from recently evaporated HNO_3 solutions was used, the rapidly migrating plutonium peak did not appear. The same result was obtained by removing the polymeric species with an HDEHP column and using only the adsorbed ionic material as feed.

Both of the above results are also shown in Figure 10.

FUTURE PRIORITIES

We feel that our program in the current year should be aimed at:

1. Testing our computer and laboratory models by comparison with results obtained at the plutonium waste site in Los Alamos. This onsite test under field conditions will provide a stringent evaluation of our method.

2. Extending our surface absorption measurements to include concentrated salt solutions. These results

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*Dr. E. P. Horwitz of this laboratory kindly supplied us with an HDEHP column.

will be needed to evaluate migration in case of water entrance into a bedded salt storage facility.

3. Studying the formation of the hydrolyzed form of plutonium and investigating ways of minimizing the fraction of plutonium that is in this form. This minimization is obviously pertinent to the operation of any plutonium storage facility.

FOLLOWING R. W. ATCHER'S PRESENTATION

QUESTIONS AND ANSWERS

Burkholder: Would that M ratio be a constant if we changed the concentration of the amount of uranium, plutonium and americium you put on top of the rock, for example, in the solution that is being forced through the rock? In other words, is the M a constant? Is the k a constant with concentration?

Atcher: That is something we have been debating a little. The question that I raised when I came in is: Are we seeing an effect of the trace amounts, i.e., are we in a semi-nonequilibrium type of a situation? We really can't use enough tracer to say that we've gone to the point where those are constants. But I believe that in the case of the M at least, it is a constant that would be essentially independent of the amount you deposited. With the k's, I'm not quite sure.

Serne: When you say the M would be a constant, you're basing this on the differences in mass or concentration vs deposition. How many times did you run this at varying amounts of deposition?

Atcher: I don't know. These experiments were done before I came on, so I really can't answer that. But I suspect that they were done enough times with varying concentrations that it's not a one-shot experiment.

Serne: You don't know the total range of concentrations or masses deposited vs how much leachwater--so you don't really know, say, over a large concentration range that, in fact, M would not change.

Atcher: That's true. That's the point. The question is, when you're using trace amounts and when you are using macro-amounts are you going to see a difference?

Serne: What is the definition of trace amounts?

Atcher: Most of these experiments are done with something of the order of 1-10 microcuries. We're dealing with fairly small amounts.

Serne: How much leachwater, volumewise?

Atcher: We're doing an experiment now on the tuffs, with a sample about 2 cm in diameter, and about 4 cm deep; we've run through about a liter and a half, and we haven't seen any significant amount of Pu come off yet. And similarly with these rainfall experiments, no significant movement of Pu is observed for differing amounts of rainfall. In some of these cases we put on 20 cm of rain, and we don't see really significant movement of that lower body of plutonium.

Holcomb: Would you just briefly describe what you did after you separated, either chromatographically or with your acid treatment, hydrolyzed, or so-called hydrolyzed forms of plutonium from the ionic forms. What did you do with the ionic forms once you got rid of your Pu polymer or whatever?

Atcher: I think they put them right onto that fissure overnight, and then started the wash experiments.

Holcomb: Was it in high acid form?

Atcher: I don't know because, as I said, that part of the experiment was in the report that I handed out, but that was before I came on, so I can't say for sure. What we suspect is that the equilibrium for the hydrolysis of the Pu is more than a day or so.

Rai: Once you removed the so-called hydrolyzed plutonium from the solution, did you ever check again whether the hydrolyzed species were present in the solutions from which you removed them?

Atcher: I'm pretty sure we did. It was just a matter of separating it out and assuming in both cases that we had virtually totally ionic species, and then run the experiment. But I can't say for sure. I suspect that they may have looked at one or two samples to see. The problem that we have is that, as far as I know, we haven't figured out a way to detect the hydrolyzed form. And if, in fact, what we're seeing deep in the tuff is the hydrolyzed form, it's only about one-tenth of one percent of the sample.

Rai: If hydrolyzed species are removed, then would more hydrolyzed species form in solution?

Atcher: Then you get into the question of kinetics. Is it going to take a week or a day? We think it's longer than a day. At least that seems to be our experience so far. If you let the solution sit for about a week. . .

Rogers: At what concentrations are you talking about?

Atcher: Somewhere in the neighborhood of 10^{-10}M.

Burkholder: Are these media being saturated by the plutonium and americium that is being transported through them? Are all the ion exchange sites available being taken up by americium or plutonium?

Atcher: At these low concentrations we have a site surplus.

Burkholder: When I envision what happens as water contacts the waste glass at a repository in a deep geologic formation, I see the nuclides being leached out at very, very slow rates. So I don't believe the geologic medium will be saturated. Thus I am interested in knowing whether the answer is the same for saturated and unsaturated experiments?

Atcher: We're going to attempt to find out whether there is, within the limits of the amount of tracer we have, a saturation. I asked that question as soon as I looked at the data. And they said they really hadn't determined it yet.

Nyhan: I think the answer to that is you're not even close to saturation. I did some work to show that the cation or anion exchange capacity of the tuff is much larger than the total amounts of plutonium absorbed by the tuff in the environment of the effluent-receiving areas at Los Alamos. However, we could take the tuff, and grind it up and add plutonium to it in the lab (maximize the contact of plutonium and tuff particles), and we could get a different answer.

Burkholder: Would you consider, then, that these values for M would be representative of what we would find if we did such an experiment in situ? Are these the migration rates we would find?

Atcher: The M values that I gave were for limestone and basalt, not for the tuff.

Burkholder: So we don't have any?

Atcher: No. One of the problems with the tuff is it's very porous and putting the fissure in it isn't going to change the characteristics very much.

Rai: I think it might change some, because tuff would have some dead-end pores, whereas a fissure wouldn't. If you have lots of dead-end pores in the tuff the percolating solution of plutonium would get trapped in them and thus retard plutonium movement. If it's a fissure the percolating solutions would probably go right through.

Rogers: When you calculated your M value of movement, what were your criteria for how far the plutonium had moved down? Were you talking about the peak of the plutonium or were you talking about the front? If you were taking about the front, how big a percentage of the Pu did you have to accumulate before you considered that it had moved?

Atcher: Based on peaks. It wasn't until we got into the fissure experiments really that we started seeing the movement of the two separate forms.

Serne: Those M values would have to have built into them some kind of a surface area. To go out into the real world, an M value for an experiment of one fissure is based on the characteristics of that fissure.

Atcher: The fissure size was involved in that computer model.

Serne: Yes. Okay.

Atcher: What we were trying to do, was just a "quick and dirty" analysis of parameters we could measure and then plug into a computer model. In this case we used fissure sizes and surface absorption coefficients. Now, can we go to a site and take a sample of the rock there and analyze it for just those two characteristics, signs of fissures and how many of them there are. Are the actinides going to just fly out or be absorbed fairly quickly? The secondary effect that we are seeing now is what is hanging us up a little bit. So what we are trying to do is get a computer model to get that secondary, deeper, movement of plutonium.

Burkholder: What does it cost to make one set of measurements tuff? Assume you already had the sample.

Atcher: I absolutely can't answer that. I can estimate material costs. . .

Burkholder: Suppose we leach some actual waste glass and give you a sample of the leachant and a sample of the geologic medium. What would it cost? Per sample.

Atcher: I have no idea.

Serne: He can't use ^{238}Pu or ^{239}Pu. You won't be able to gamma-count if you use the real case unless you put the 237 in the waste from the start, because that's not the natural isotopes you would be dealing with.

Burkholder: Are you suggesting that 238 and 237 are going to migrate at very different rates?

Serne: No. I'm just saying that using his facilities, you couldn't do it under the real case, because he is based on gamma counting, which is nice, and your costs would get a lot higher for the necessary alpha counting if you tried to make an estimate on actual contaminated material.

Atcher: We'd either go to alpha or something a little more esoteric.

Burkholder: Could we get it?

Atcher: They're claiming they can; in fact now I'm going into tomorrow's presentation. We're going to start looking at actual cores from the Los Alamos site and maybe a couple of other sites, and see whether we're in fact seeing this kind of a behavior in real life. In the meantime, we're going to examine the form of the deposited Pu. At the deposit site in Los Alamos, if I remember correctly, the majority went in as the citrate or fluoride so we'll probably be working along those lines in the next couple of months until we can get the cores and take a look ourselves.

Our group developed a scheme so that we won't have to go in and grind the rock up and try to separate out the plutonium, but they haven't let me in on it yet. But I have no idea in terms of your question. The other problem with ^{237}Pu is its 45-day half-life. So if you're talking about an experiment that's going to go over, say, 3 months, you're counting statistics start dropping off.

Ames: Could we make a glass as a reasonable waste form that has ^{237}Pu in it? How well would that simulate real life?

Burkholder: How are you modeling the nuclide transport?

Atcher: I don't think I have it with me, but I can show you basically what somebody threw together for us. It's basically just differential equations, of ion exchange, except we substitute counts for concentration and depths for volumes.

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SOIL PLUTONIUM IN THE LOS ALAMOS ENVIRONS AND AT THE TRINITY SITE

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INTRODUCTION

The first plutonium was sent to the Los Alamos Scientific Laboratory (LASL) in 1944 from the Oak Ridge and Hanford reactors for use in synthesizing the first atomic bomb, which was subsequently detonated at Trinity Site in New Mexico. During the last 32 years the LASL has developed an outstanding capability in many scientific fields required to support reresearch in weapons technology and in other uses of nuclear energy. The fabrication and experimental activities required for this effort have resulted in additions of plutonium in industrial effluents to Los Alamos soils, just as the Trinity soils received fallout plutonium after the 1945 Trinity detonation.

Formal radioecology-soils studies were initiated at the LASL in 1972 with the establishment of an ERDA-funded Ecology Section within the Environmental Studies Group. Our research relative to soil-actinide relationships has been mainly field-oriented and complements transuranic research dealing with the biota of several study areas. The objective of this paper is to summarize the current soil actinide research performed within three liquid effluent-receiving areas at Los Alamos and along the fallout pathway of Trinity, the first nuclear detonation.

SITE DESCRIPTIONS AND HISTORIES

In the process of treating the low level liquid wastes generated at the Los Alamos Scientific Laboratory, sodium carbonate, calcium hydroxide, and ferric sulfate are added to the wastes to concentrate plutonium activity in a ferric hydroxide floc at a relatively high pH. The resulting supernatant, containing low levels of plutonium, is then filtered and discharged to the intermittent streams in nearby canyons. Thus far, a limited amount of data indicate that about 60% of the plutonium in these liquid wastes is in a "particulate" form, in that it did not pass a 0.45 μm filter. In addition, the chemical composition of the effluents varies considerably as evidenced by highly variable chelate and hydrogen ion concentrations.

Effluent-Mortandad, DP-Los Alamos, and Acid-Pueblo Canyons (Figure 1) have been used as disposal areas for plutonium-containing liquid effluents for varying lengths of time at Los Alamos. Acid-Pueblo Canyon received untreated liquid wastes from 1944 to 1951, and treated waste products from 1951-1963 (2.1±1.8 [SD] millicuries [mCi] plutonium/year). Treated wastes have been discharged into DP-Los Alamos Canyon since 1953 (1.6±1.2 [SD] mCi plutonium/year) and into Effluent-Mortandad Canyon since 1963 (4.2±2.3 [SD] mCi plutonium/year).

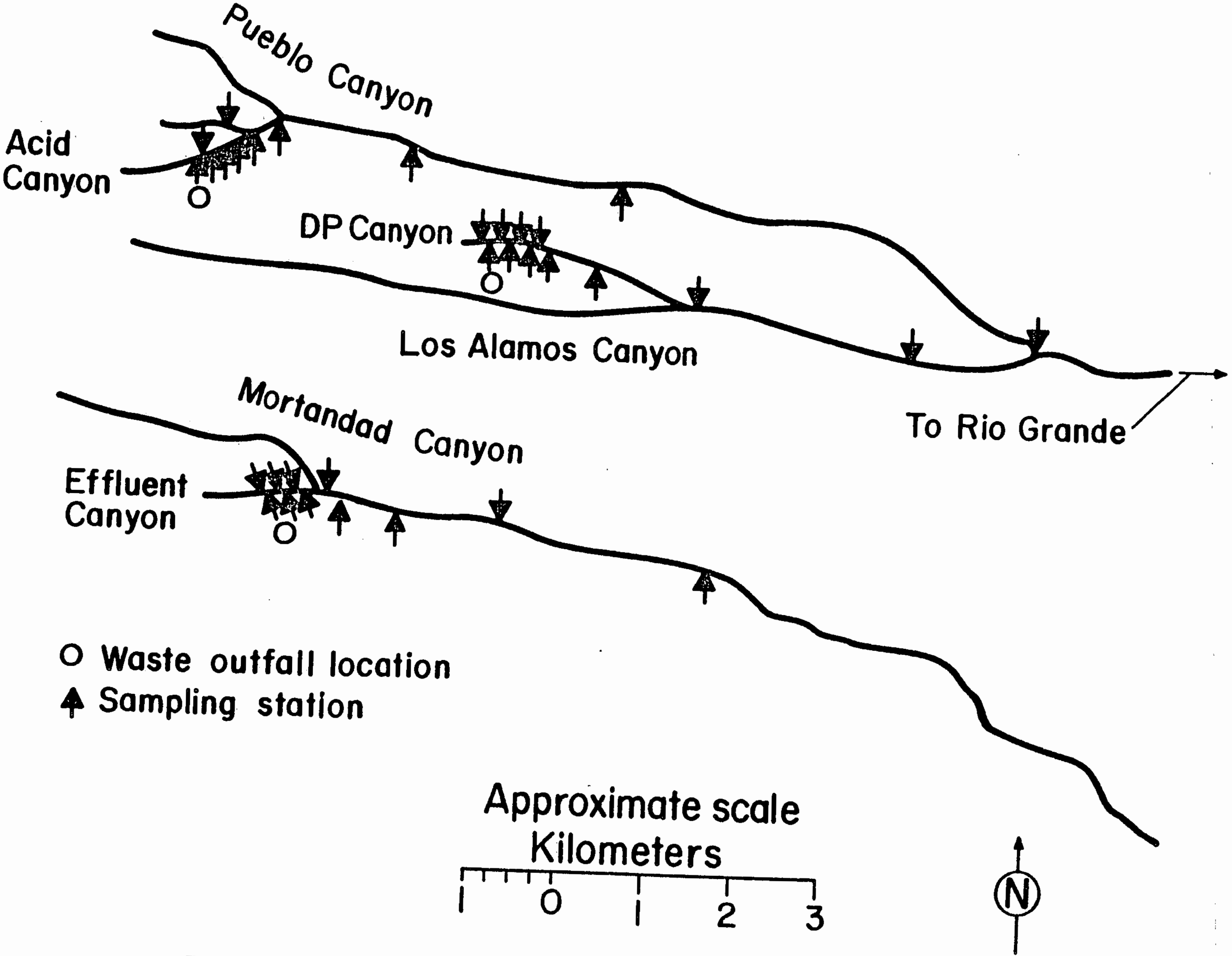

FIGURE 1. Location of Sampling Stations in Canyon Study Areas

The alluvium of the intermittent streams in Effluent-Mortandad, DP and Acid Canyons formed from the rhyolitic volcanic rocks of the Bandelier Tuff. The alluvial soils in Pueblo and Los Alamos Canyons were derived from the latite and quartz latite rocks of the Tschicoma Formation and from tuff particles from Acid and DP Canyons. The lower reaches of Pueblo Canyon also contain basaltic rocks in the stream channel matrix. Whereas the upper reaches of the canyons have stream channel widths of less than 1 m and alluvium depths of less than 0.15 m, stream channels in the lower canyon areas are about 3 m wide and 0.15-30 m deep at the sampling locations.

Trinity Site, a fenced area immediately around Ground Zero, is located in a semiarid region of central New Mexico on the White Sands Missile Range. Intensive study areas were established outside of and within the reported fallout pathway of the nuclear debris from the detonation (Figure 2), based on radiological survey data collected in 1948 (Bellamy et al., 1949), approximately 3 years after the first nuclear detonation.

The climate, physiography, geology and biota of the Trinity environs were previously reported (Bellamy et al., 1949; Blair, 1943; Hakonson and Johnson, 1974; Larson et al., 1951a, 1951b, and 1951c; Shields, 1956). Although a few soil profiles were described by Bellamy et al., in 1949, a comprehensive

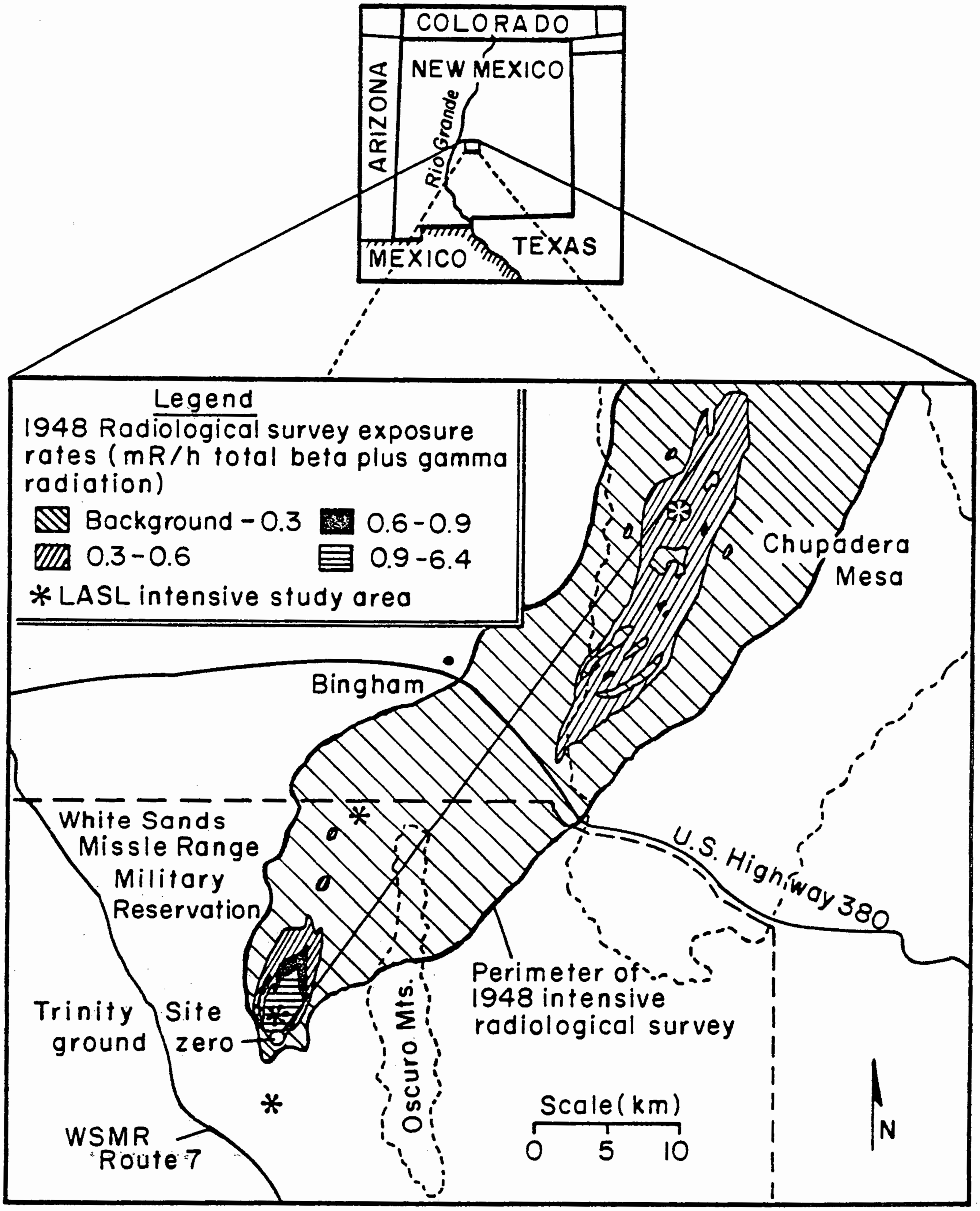

FIGURE 2. Location of Intensive Study Areas at Trinity Site Relative to Areas Involved in the 1948 Intensive Radiological Survey (Bellamy et al., 1949)

inventory of the soils of the entire White Sands Missile Range was only recently assembled using updated taxonomic procedures (Neher and Bailey, 1970).

SAMPLING AND ANALYTICAL METHODS

Soil samples were taken 100 m above each waste outfall at Los Alamos and at distances of 0, 20, 40, 80, 160, 320, 640, 1280, 2560, 5120 and 10,240 m below the outfall (Figure 1) and as far as 56 km from Ground Zero along the fallout pathway at Trinity Site (Figure 2). Soil core samples were collected with a polyvinyl chloride coring tube (2.4-cm i.d.) placed in a plastic bag, frozen, and cut up into segments corresponding to either 0-2.5, 2.5-7.5, 7.5-12.5, and 12.5-30 cm soil depths at Los Alamos or 0-2.5, 2.5-5.0, 5.0, 5.0-10, 10-15, 15-20, 20-25, 25-33, 33-40, and 40-50 cm soil depths at Trinity Site. A partial core section was obtained when the coring tube could not be completely driven into the soil, and its length also measured. At Trinity Site, surface samples of trinitite (large particles of soil and plutonium formed by the intense heat given off during the 1945 Trinity detonation) were collected at Ground Zero for plutonium analysis in 1972.

Soil samples were mechanically separated into six size fractions using a Model L3P sonic sifter (ATM Corporation, Milwaukee, WI): <53 μm, 53-100 μm, 100-500 μm, 500-1000 μm, 1-2 mm and 2-23 mm. Small soil particles were blown off of the larger soil separates with an air hose during the soil separations to minimize contamination of large soil particles with smaller particles. Soil samples were also analyzed for levels of calcium carbonate and organic carbon, as well as cation exchange capacity, pH, clay mineralogy and particle size distribution (U.S. Department of Agriculture, 1972). The surface area of the samples was calculated from the particle size distribution data.

The physical transport of plutonium was investigated at Los Alamos in a study of the runoff from a rainstorm occurring in Effluent-Mortandad Canyon. Data were gathered on the association of actinides with the suspended sediment and liquid fractions and the total activities transported by the event. A DH-48 stream flow sampler equipped with a 6 mm intake nozzle was used to collect duplicate water samples in the center of the stream about 6 cm below the surface of the flow and 6 cm above the stream bed. Samples were collected in 500 ml glass containers and prefiltered through Whatman Number 40 paper prior to filtration through a 0.45 μm Millipore membrane filter. The resulting filtrates were then acidified with 7.2 N HNO_3.

Fractionated and whole soil samples and filtered water samples were assayed for their ^{238}Pu and ^{239,240}Pu content (the term "total plutonium" used herein designates the sum of these three isotopes) as previously described (Hakonson et al., 1973). Liquid and particulate samples were dissolved in HNO_3 and HF, and the plutonium was isolated on an anion exchange column, electrodeposited on a stainless steel disc and determined by alpha-particle spectrometry. Absolute amounts of ^{238}Pu and $^{239,240}Pu$ were obtained by correcting the counting data for chemical recovery, which was determined from the level of ^{242}Pu initially added to the sample.

RESULTS AND DISCUSSION

DISTRIBUTION AND TRANSPORT OF SOIL PLUTONIUM IN LOS ALAMOS EFFLUENT-RECEIVING AREAS

Plutonium in Unfractionated Soils

Preliminary studies of the horizontal and vertical distribution of soil plutonium within the three effluent-receiving areas were performed from 1965 to 1971 (Purtymun et al., 1966; Purtymun, 1971) and 1972 (Hakonson et al., 1973; Hakonson et al., 1974; Hakonson and Bostick, 1976 and 1973 (Nyhan et al., 1976b and 1976c).

Maximum concentrations of plutonium generally occurred within 2.56 km of the liquid waste outfalls (Table 1). Elevated levels of plutonium were found in the alluvium 5.12 and 10 km

TABLE 1. Total Plutonium Concentration of Alluvial Soils of the Waste Disposal Areas in 1973

Distance from Waste Outfall	Total Plutonium Concentration (pCi/g)			
	0 - 2.5	2.5 - 7.5	7.5 - 12.5	Remainder[a]
Effluent-Mortandad Canyon				
-100 m[b]	2.69	.771	.117	
0	129	274	390	
20 m	158	189	70.9	
40 m	259	234	116	
80 m	61.6	33.3	16.9	
160 m	104	84.6	12.5	
320 m	70.8	59.0	27.4	6.68
640 m	32.7	31.4	31.3	
1.28 km	13.8	18.2	13.0	9.64
2.56 km	--[c]	9.04	6.97	2.26
5.12 km	.114	.079	.065	.105
DP-Los Alamos Canyon				
-100 m	.036	.036	.044	.051
0	957	1640		
20 m	24.8	16.4	2.63	
40 m	18.2	--	11.4	.488
80 m	--	10.4	1.87	.831
160 m	.332	2.25	.369	.328
320 m	.196	.252	.225	2.34
640 m	.344	.481	.445	
1.28 km	.864	.878	.644	1.78
2.56 km	.183	.0904	.114	
5.12 km	.599	.186		
Acid-Pueblo Canyon				
-100 m	.122	.137		
0	16.6	8.52		
20 m	16.8			
40 m	5.78	8.72	11.4	28.7
80 m	6.21	6.60	21.1	505
160 m	8.61	10.1	--	20.4
320 m	8.28	7.92	10.8	12.3
640 m	7.86	12.4	10.4	19.1
2.56 km	36.3	369	2250	
5.12 km	1.39	--	.617	1.65
10.2 km	.401	.518	.435	

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[a] The depth of the remainder section varied from 12.5-30 cm maximum.

[b] Negative distances represent background locations upstream from the waste outfalls.

[c] Missing data.

from the DP-Los Alamos and Acid-Pueblo outfalls, reflecting translocation of small amounts of laboratory wastes as far as 10 km away from their point of discharge. Since stream channel segments further than about 2 km from the outfalls are normally dry except during periods of storm runoff, the horizontal distribution of plutonium in these intermittent streams reflects periods of intense runoff from late summer rainstorms, which move soil and plutonium considerable distances downstream.

Levels of plutonium in Acid-Pueblo Canyon soils generally increased with depth at most sampling locations (Table 1), reflecting either dilution or loss of plutonium from the topsoil since liquid effluents were last added to this canyon in 1963. Soil plutonium concentrations did not exhibit a consistent relationship with soil depth at all of the sampling locations in Effluent-Mortandad and DP-Los Alamos Canyons (Table 1). In some cases, plutonium concentrations decreased steadily with depth and at other locations exhibited just the opposite pattern. Thus, this pattern reflects considerable vertical mixing of plutonium during runoff events from snowmelt and rainstorms in canyons currently receiving treated effluents.

Comparisons of the horizontal and vertical distributions of ^{238}Pu and ^{239,240}Pu were made to provide information on the rates of mixing of the individual isotopes as a function of canyon use history. Since the first appreciable amounts of ^{238}Pu appeared in laboratory liquid wastes in 1968, the horizontal-vertical distribution of the ^{239,240}Pu/^{238}Pu ratio is indicative of mixing-migration rates of ^{238}Pu in soils (Table 2). Relatively complete mixing of ^{238}Pu into the soils in less than 4 years was indicated by a ^{239,240}Pu/^{238}Pu activity ratio of 0.26±0.16 (SD) for Effluent-Mortandad (n = 27) and DP-Los Alamos (n = 29) samples collected as deep as 30 cm and as far as 2560 m from the outfalls. These ratios were not significantly different from the ratios in the treatment plant effluents in 1972 and 1973 (Schiager et al., 1974). It is also noteworthy that the soils 40-80 m from the DP waste outfall have plutonium ratios similar to the rest of the canyon, a distribution which took place in less than a year since the effluent discharge pathway was redirected to this previously uncontaminated segment in early 1972.

Soil physical and chemical properties were compared with the distribution of plutonium in the alluvium to elucidate soil-actinide interactions (Nyhan et al., 1976b). Since absorption and exchange reactions of radionuclides with soil colloids was previously shown to influence the distribution of radionuclides in soils (Carrigan et al., 1967; Kornegay et al., 1963; Pickering, 1969), the distribution of plutonium was compared with the soil cation exchange capacity (CEC) and levels of organic carbon in the canyon soils. The log of CEC was

TABLE 2. Ratios of ^{239,240}Pu^{238}Pu in Alluvial Soils of Waste Disposal Areas in 1973

	^{239,240}Pu-^{238}Pu			
	Soil Depth (cm)			
Distance from Waste Outfall	0 - 2.5	2.5 - 7.5	7.5 - 12.5	Remainder[a]
Effluent-Mortandad Canyon				
-100 m[b]	20	13	3.5	
0	.16	.16	.44	
20 m	.25	.36	.30	
40 m	.33	.84	.66	
80 m	.12	.13	.13	
160 m	.15	.17	.25	
320 m	.16	.20	.31	.25
640 m	.12	.16	.24	
1.28 km	.17	.18	.19	.33
2.56 km	--	.24	.28	.50
5.12 km	1.1	4.2	1.7	1.9
DP-Los Alamos Canyon				
-100 m	1.4	.93	.55	.49
0	15	14		
20 m	4.9	4.3	.41	
40 m	4.1	--	3.0	2.0
80 m	--	2.9	2.0	1.9
160 m	3.7	11	1.6	2.0
320 m	2.0	3.1	1.9	11
640 m	2.7	2.9	3.1	
1.28 km	3.4	3.2	3.0	8.5
2.56 km	17	11	4.5	
5.12 km	.39	11		
Acid-Pueblo Canyon				
-100 m	1.2	.56		
0	390	200		
20 m	83			
40 m	210	200	190	95
80 m	140	130	76	49
160 m	130	170	--	190
320 m	190	180	190	170
640 m	130	140	140	126
2.56 km	230	163	82	
5.12 km	120	--	18	43
10.2 km	81	100	62	

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[a] The depth of the remainder section varied from 12.5-30 cm maximum.

[b] Negative distances represent background locations upstream from the waste outfalls.

[c] Missing data.

significantly correlated with the log of plutonium concentrations in Effluent-Mortandad and DP-Los Alamos Canyons (Figure 3), whereas the plutonium levels of Acid-Pueblo soils were exponentially related to CEC (Table 3). The CEC of these alluvial soils was directly related to percentages of fine particles (less than 53-µm diameters) in the alluvium (Nyhan et al., 1976c). Plutonium concentrations were also exponentially related to levels of soil organic carbon in Effluent-Mortandad (Figure 4) and Acid-Pueblo (Table 3) Canyons and were correlated with organic carbon concentrations in DP-Los Alamos Canyon (Table 3). Thus, specific reactions may have occurred between plutonium and the organic constituents of the alluvial soils independent of CEC reactions. This observation could be partially explained by the fact that algae, a constituent of the soil organic carbon complex, have been shown to contain elevated levels of Pu in these ecosystems (Hakonson et al., 1974).

An attempt was also made to relate plutonium concentrations to the pH and levels of carbonates in the canyon soils. The average pH of the alluvium in the upper 1.28 km of Acid-Pueblo Canyon was 7.5 (range of 6.4 to 8.2), whereas the corresponding values for Effluent-Mortandad and DP-Los Alamos outfalls was 8.9 (range of 8.0 to 9.7), reflecting substantial additions of sodium and carbonates to the canyons in the liquid effluents (Schiager et al., 1974). No significant pH-radionuclide correlations were detected in any canyon because a large portion

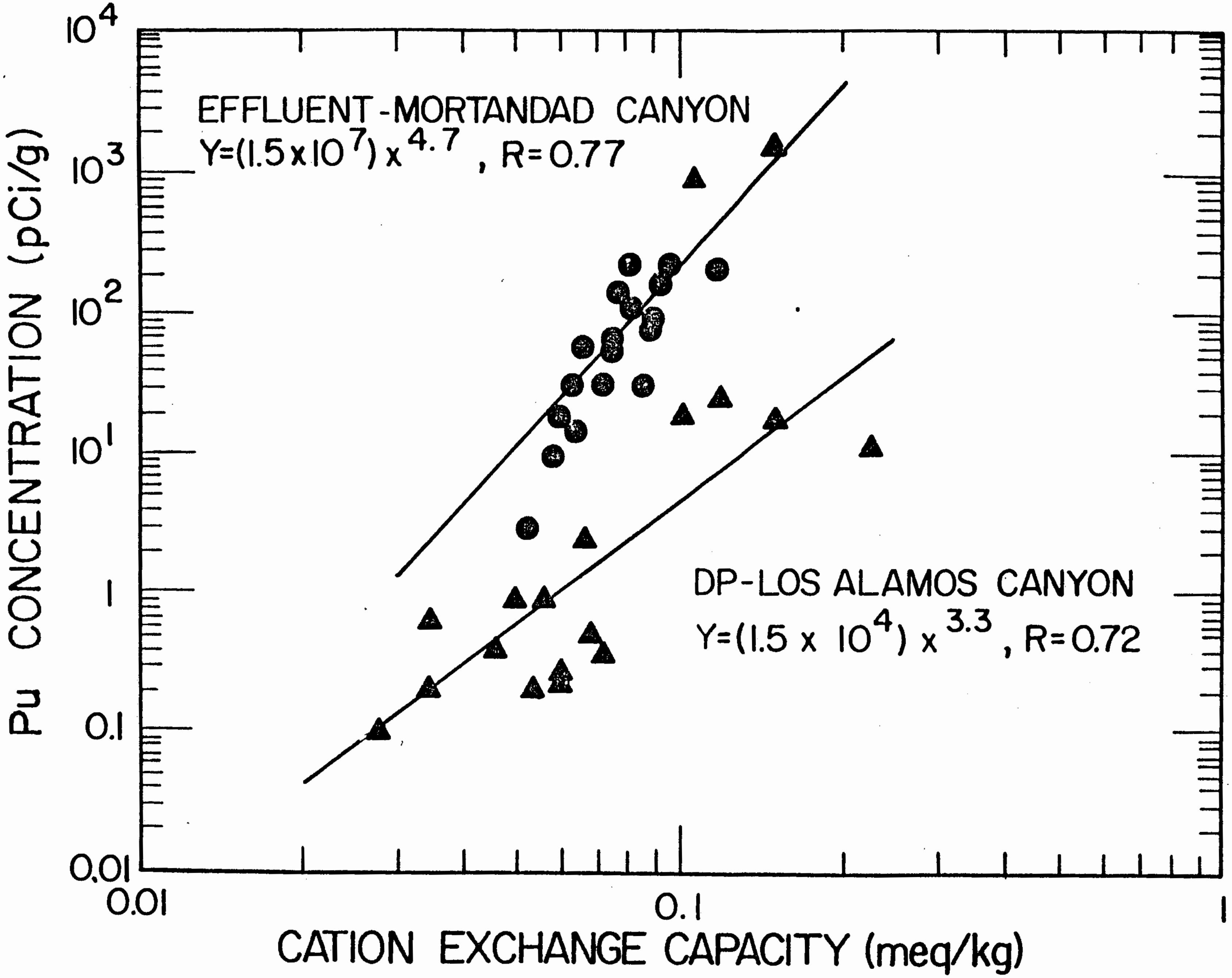

FIGURE 3. Relationship of Soil Cation Exchange Capacity to Levels of Plutonium in Alluvial Soils of Waste Discharge Areas

TABLE 3. Statistical Correlations of Soil Radionuclide Concentrations with Physical-Chemical Properties of the Soils of the Waste Discharge Areas in 1973

Dependent Variable: Radionuclide Concentration (pCi/g soil)	Independent Variable	Correlation Coefficient	Locations and Numbers of Samples Used in Comparison
DP-Los Alamos Canyon:			
Pu	Inverse of % Organic Carbon	0.75	0-5.12 km,[a] n = 31
Acid Pueblo Canyon:			
Log Pu	Cation Exchange	0.82	0-10.2 km, n = 31
Log Pu	% Organic	0.57	0-10.2 km, n = 31

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[a] Represents distance from waste outfall.

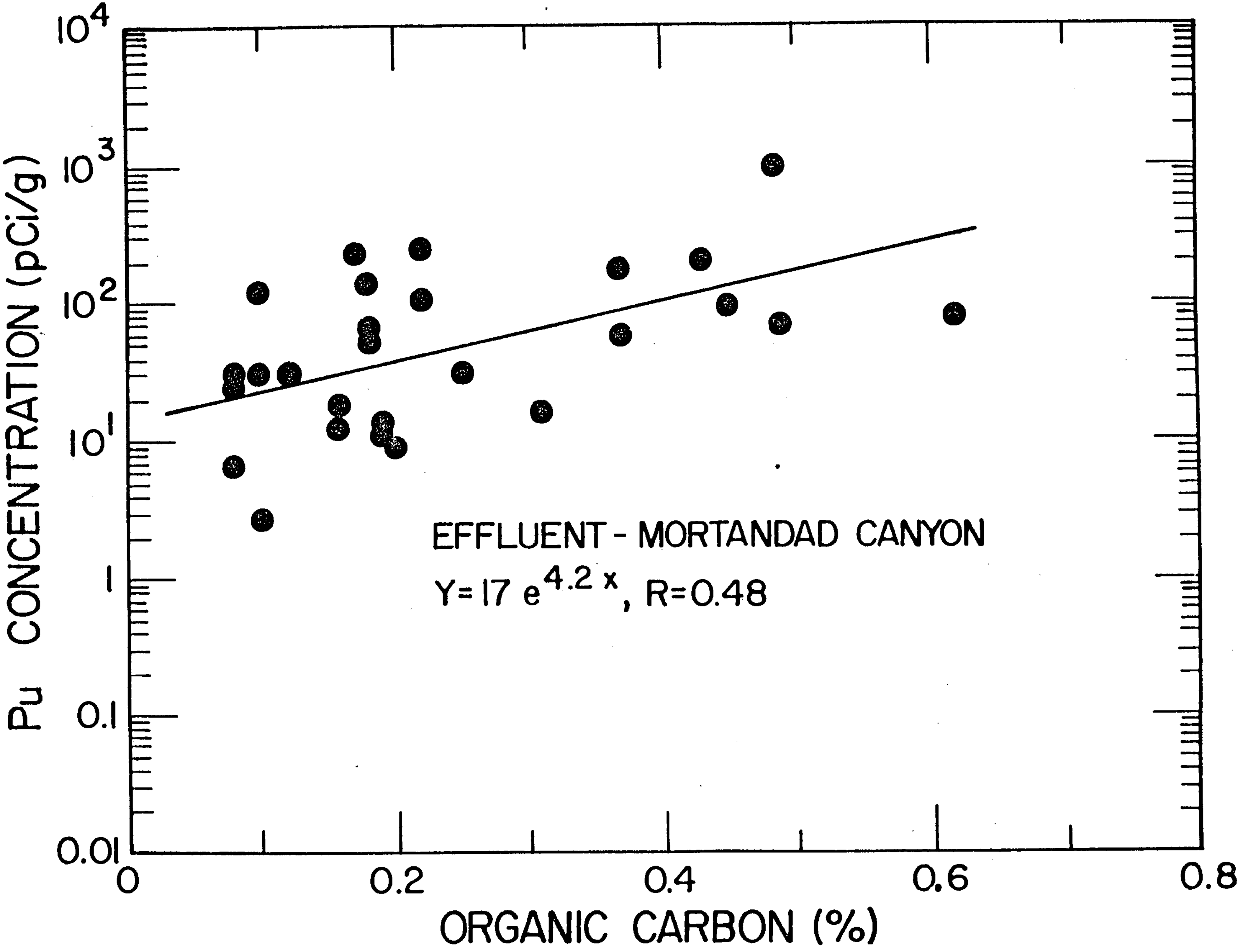

FIGURE 4. Relationship of Soil Organic Carbon Content to Levels of Plutonium Found in Alluvial Soils of Effluent-Mortandad Canyon

of the samples exhibited relatively high Pu concentrations and pH values. However, the log of the plutonium concentrations were significantly correlated with log of calcium carbonate levels in Effluent-Mortandad and DP-Los Alamos Canyons (Figure 5). Radionuclide concentrations were not significantly correlated with carbonate levels in Acid-Pueblo Canyon because most of the soil samples contained background levels of carbonates and plutonium, making a statistically-significant relationship nondetectable. However, the samples collected deep in the soil profiles in Acid Canyon did demonstrate high levels of carbonates where residual pockets of radionuclides were found.

Plutonium in Soil Size Fractions

Maximum total plutonium concentrations were generally associated with small soil particles in Effluent-Mortandad (Table 4), DP-Los Alamos (Table 5) and Acid-Pueblo Canyon (Table 6) soils (Nyhan et al., 1976c). The <53 μm soil size fractions, which were previously shown to contain <2 μm particles with amorphous clay mineralogy (Nyhan et al., 1976c), had an average of 10-fold higher total plutonium concentrations than the 2-23 mm particle sizes in the 0-2.56 km postoutfall segment of all the canyons.

Highest total plutonium concentrations were generally found in size fractions less than 105 μm; however, the largest

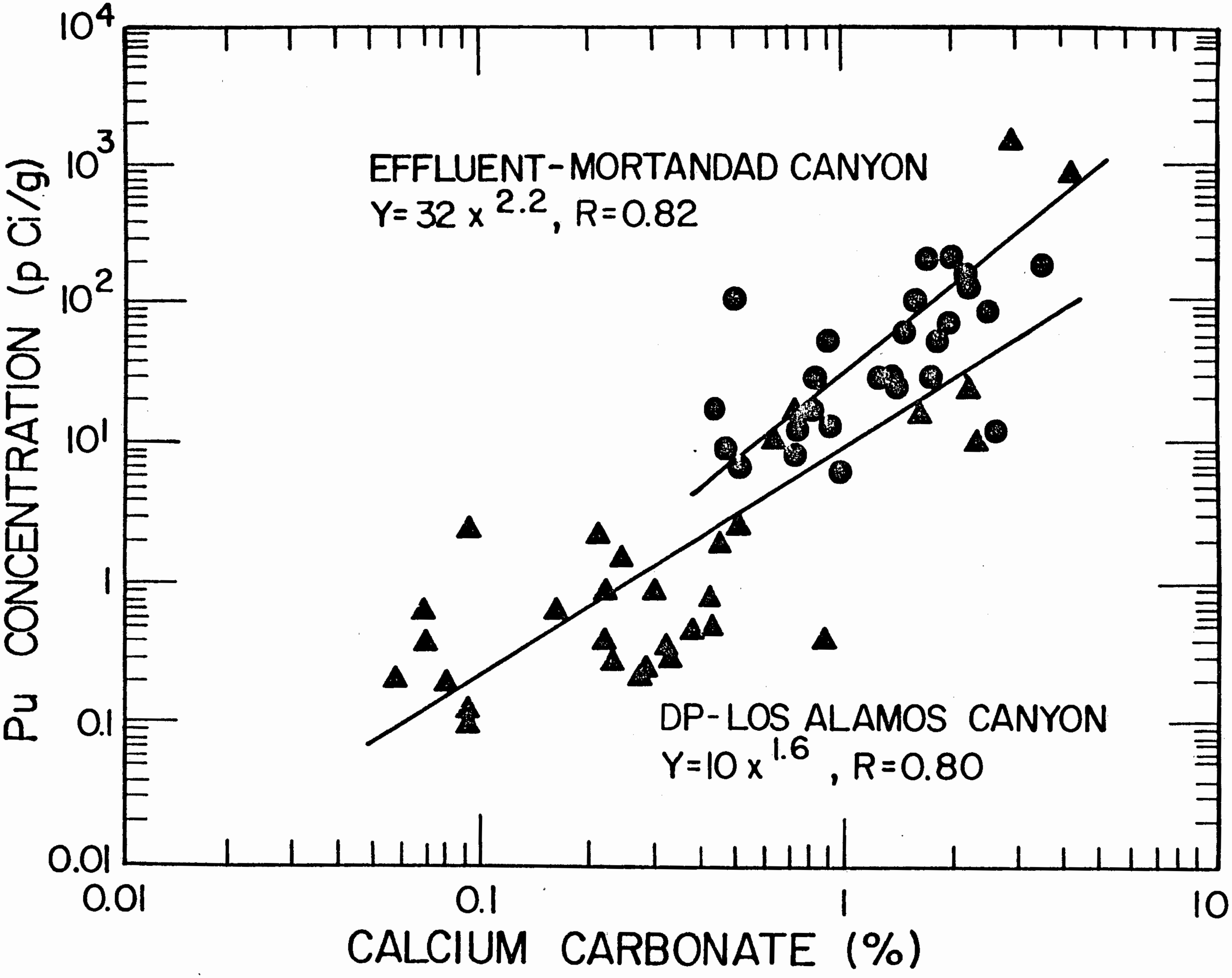

FIGURE 5. Relationship of Calcium Carbonate Content to Levels of Plutonium in Study Area Soils

TABLE 4. Total Plutonium Concentrations in Soil Separates from Effluent-Mortandad Canyon in 1973

Soil Depth (cm)	Total Plutonium Concentration in Size Fraction (pCi/g)[a]					
	<53 μm	53-105 μm	105-500 μm	500-1000 μm	1-2 mm	2-23 mm
100 m Pre-Outfall						
0 - 2.5	1.5	1.9	5.5	0.66	2.3	2.6
2.5 - 7.5	1.1	1.2	1.0	0.57	0.15	0.29
7.5 - 12.5	0.32	0.26	0.15	0.69	0.046	0.047
0-40 m From Outfall						
0 - 2.5	1500 (250)[a]	1300 (360)	610 (140)	310 (150)	87 (57)	69 (39)
2.5 - 7.5	1400 (610)	1200 (350)	540 (130)	230 (80)	230 (68)	91 (39)
7.5 - 12.5	1100 (720)	710 (430)	420 (360)	320 (360)	90 (87)	68 (65)
80-1280 m From Outfall						
0 - 2.5	380 (320)	390 (190)	140 (110)	62 (40)	45 (29)	27 (13)
2.5 - 7.5	240 (140)	140 (75)	76 (47)	43 (25)	27 (25)	29 (18)
7.5 - 12.5	120 (46)	94 (46)	39 (17)	20 (13)	12 (5.5)	11 (6.1)
12.5 - 22.1	39 (17)	31 (11)	16 (2.1)	7.4 (.85)	4.5 (.71)	3.6 (1.8)
2.56 km From Outfall						
0 - 2.5	24	16	7.6	2.4	1.5	---[c]
2.5 - 7.5	49	32	18	6.4	3.9	6.2
7.5 - 12.5	37	20	8.3	7.1	2.9	2.9
12.5 - 24	13	7.1	2.5	1.5	1.4	1.0
5.12 km From Outfall						
0 - 2.5	1.1	1.0	0.18	0.080	0.045	0.015
2.5 - 7.5	0.25	0.63	0.088	0.079	0.028	0.0063
7.5 - 12.5	0.30	0.38	0.11	0.062	0.034	0.0063
12.5 - 22.4	0.41	0.39	0.17	0.056	0.047	0.017

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[a] Each value represents the total plutonium concentration in a composite of five soil core segments.

[b] Numbers in parentheses represent the standard deviation of the mean total plutonium concentrations.

[c] Missing data.

TABLE 5. Total Plutonium Concentrations in Soil Separates from DP-LOS Alamos Canyon in 1973

Soil Depth (cm)	Total Plutonium Concentration in Size Fraction (pCi/g)[a] <53 µm	53-105 µm	105-500 µm	500-1000 µm	1-2 mm	2-23 mm
			100 m Pre-Outfall			
0 - 2.5	9.1	0.68	0.050	0.021	0.022	0.015
2.5 - 7.5	1.7	0.91	0.041	0.028	0.022	0.0091
7.5 - 12.5	0.23	0.16	0.055	0.028	0.038	0.0094
12.5 - 22.4	0.12	0.18	0.047	0.059	0.032	0.0068
			0 m From Outfall			
0 - 2.5	650	720	1000	1000	1000	930
2.5 - 7.5	2000	4300	2600	80	2000	1500
7.5 - 12.8	730	420	--[b]	1100	220	53
			20-80 m From Outfall			
0 - 2.5	38 (21)[c]	33 (15)	50 (6.4)	26 (13)	9.4 (4.7)	19 (6.8)
2.5 - 7.5	22 (11)	24 (10)	39 (23)	19 (19)	8.5 (5.7)	4.9 (6.5)
7.5 - 12.5	5.0 (5.2)	13 (13)	7.3 (9.3)	2.8 (3.3)	2.4 (2.8)	4.3 (6.7)
12.5 - 22.4	0.90 (0.86)	0.83 (0.24)	0.69 (0.20)	0.27 (0.07)	0.21 (0.13)	0.32 (0.26)
			160-1280 m From Outfall			
0 - 2.5	1.1 (0.45)	1.4 (0.77)	0.90 (0.43)	0.47 (0.34)	0.24 (0.20)	0.41 (0.40)
2.5 - 7.5	2.0 (0.80)	1.7 (0.30)	1.3 (0.59)	0.47 (0.25)	0.31 (0.16)	2.6 (4.0)
7.5 - 12.5	1.9 (0.29	1.8 (0.62)	1.1 (0.45)	0.50 (0.13)	0.24 (0.08)	0.36 (0.17)
12.5 - 22.6	3.6 (2.7)	3.4 (3.0)	2.1 (1.7)	2.2 (3.0)	0.67 (0.40)	0.43 (0.27)
			2.56 km From Outfall			
0 - 2.5	0.61	1.1	0.23	0.23	0.28	0.060
2.5 - 7.5	0.46	0.49	0.28	0.075	0.035	0.041
7.5 - 11.6	0.77	0.36	0.28	0.099	0.069	0.049
			5.12 km From Outfall			
0 - 2.5	0.05	0.45	0.76	0.058	0.052	0.83
2.5 - 7.5	0.94	0.71	0.46	0.14	0.13	0.084

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[a] Each value represents the total plutonium concentration in a composite of five soil core segments.

[b] Missing data.

[c] Numbers in parentheses represent the standard deviation of the mean total plutonium concentrations.

TABLE 6. Total Plutonium Concentrations in Soil Separates from Acid-Pueblo Canyon in 1973

Soil Depth (cm)	Total Plutonium Concentrations in Size Fraction (pCi/g)[a] <53 µm	53-105 µm	105-500 µm	500-1000 µm	1-2 mm	2-23 mm
			100 m Pre-Outfall			
0 - 2.5	2.7	2.2	0.50	0.18	0.099	0.035
2.5 - 7.5	1.7	2.1	0.58	0.23	0.16	0.024
			0-40 m From Outfall			
0 - 2.5	84 (74)[b]	60 (25)	25 (9.1)	8.8 (3.7)	7.9 (4.2)	25 (31)
2.5 - 7.5	90 (78)	45 (26)	41 (48)	13 (11)	14 (11)	19 (26)
7.5 - 12.5	33	39	21	8.7	6.1	5.6
12.5 - 21	110	70	39	21	16	5.8
			80 m From Outfall			
0 - 2.5	42	56	17	4.3	4.9	3.5
2.5 - 7.5	26	25	15	5.4	3.3	3.1
7.5 - 12.5	20	60	39	16	11	24
12.5 - 22	1700	1500	900	340	190	110
			160-640 m From Outfall			
0 - 2.5	50 (38)	53 (28)	10 (9.6)	8.2 (1.6)	6.7 (2.5)	5.5 (2.3)
2.5 - 7.5	46 (12)	46 (6.0)	20 (1.5)	9.5 (2.7)	6.1 (0.95)	8.9 (6.2)
7.5 - 12.5	42 (4.2)	67 (16)	25 (3.5)	7.9 (0.57)	6.6 (2.3)	12 (4.6)
12.5 - 21	57 (12)	58 (9.6)	35 (6.8)	13 (3.7)	10 (0.58)	12 (6.3)
			2.56 km From Outfall			
0 - 2.5	97	110	110	44	21	6.7
2.5 - 7.5	140	110	1000	160	350	195
7.5 - 12.5	2300	2000	2000	3100	3200	1600
			5.12 km From Outfall			
0 - 2.5	77	38	3.1	0.84	0.46	0.54
2.5 - 7.5	14	4.5	2.1	0.34	0.028	--[c]
7.5 - 12.5	4.8	3.6	1.3	0.14	0.49	0.50
12.5 - 22	3.5	3.5	1.8	0.48	0.35	3.7
			10.2 km From Outfall			
0 - 2.5	2.7	1.6	1.1	<0.0025	0.30	0.44
2.5 - 7.5	3.8	2.9	1.1	0.65	0.31	<0.0025
7.5 - 12.5	3.2	2.4	0.54	0.24	0.42	0.47
12.5 - 22	4.1	6.3	--	1.1	0.39	0.43

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[a] Each value represents the total plutonium concentration in a composite of five soil core segments.

[b] Numbers in parentheses represent the standard deviation of the mean total plutonium concentrations.

[c] Missing data.

percentage of the plutonium was usually found in coarser size fractions, which accounted for the largest amounts of soil mass in the alluvium (Table 7). Nearly 80% of the plutonium and 96% of the mass of Effluent-Mortandad Canyon soils was associated with soil particles >105 μm. The stream channel soils from Acid-Pueblo Canyon and from most of DP-Los Alamos Canyon followed this same pattern. An exception to this pattern was found for samples collected 40 and 80 m from the DP-Los Alamos outfall in that 45% of the alluvium consisted of <105 μm soil particles, which accounted for 50% of the plutonium inventory in these soils (Table 7).

The plutonium concentrations of the soil separates were compared with the surface area and CEC of the size fractions collected in each effluent disposal area, in order to identify factors important in the fractional distribution of plutonium. The calculated surface area of the size fractions ranged from 1.7 to 12.5 cm^2/g as the mean effective particle diameter varied from 12.5 mm (2-23 mm size fraction) to 26.5 μm (<53 μm size fraction). Plutonium levels were expressed as a percentage of plutonium concentrations in the 2-23 mm size fraction in these comparisons to minimize the effect of the horizontal and vertical plutonium concentration gradients on these comparisons. The log of these relative ^{238}Pu (Effluent-Mortandad Canyon) or $^{239,240}Pu$ (DP-Los Alamos and Acid-Pueblo Canyons) concentrations was significantly correlated ($P<0.05$)

TABLE 7. Particle Size Distribution Data and Total Plutonium Inventories of Soil Fractions (Average of Values from Each Soil Depth per Sampling Location) in 1973

Distance From Waste Outfall and Parameter Studied	Size Fraction					
	<53 µm	53-105 µm	105-500 µm	500-1000 µm	1-2 mm	2-23 mm
			Effluent-Mortandad Canyon			
100 m pre-outfall:						
Weight percent soil	23	9.3	24	17	17	9.7
% plutonium in fraction	28	12	39	8.8	7.4	4.8
0-2.56 km:						
Weight percent soil	2.2	1.8	14	21	26	35
% plutonium in fraction	14	6.0	27	21	16	16
5.12 km:						
Weight percent soil	2.9	1.0	23	35	33	5.1
% plutonium in fraction	16	7.4	34	28	14	.61
			DP-Los Alamos Canyon			
100 m pre-outfall:						
Weight percent soil	2.0	2.0	24	34	27	11
% plutonium in fraction	60	9.5	11	11	7.3	1.1
0-20 m and 160-5120 m:						
Weight percent soil	1.9	1.1	13	26	32	26
% plutonium fraction	5.7	7.3	24	22	20	21
40-80 m:						
Weight percent soil	30	15	26	12	12	5.0
% plutonium fraction	30	20	36	7.0	5.0	2.0
			Acid-Pueblo Canyon			
100 m pre-outfall:						
Weight percent soil	.72	0.85	8.4	18	26	46
% plutonium in fraction	7.0	6.0	26	22	27	12
0-5.12 km:						
Weight percent soil	3.0	3.0	16	26	28	24
% plutonium in fraction	7.0	7.0	31	19	17	19
10.2 km:						
Weight percent soil	0.60	1.4	16	31	26	25
% plutonium in fraction	4.4	5.6	35	19	22	14

with the log of the particle surface areas in Effluent-Mortandad (r = 0.82, n = 198), DP-Los Alamos (r = 0.46, n = 186), and portions of Acid-Pueblo Canyons (80-2560 m from the outfall; r = 0.57, n = 132).

The CEC of size fractions which were arbitrarily collected at sampling locations in Effluent-Mortandad (320 m and 2.56 km from the waste outfall) Canyons was also compared with the fractional distribution of plutonium and particle surface areas. The average cation exchange capacities of the 1-2 mm and <53 μm size fractions were 0.060 and 0.21 eq/kg, respectively. Thus, the smaller soil size fractions contained about 3-fold greater cation exchange capacities and 7-fold larger surface areas (Nyhan et al., 1976c) than the largest soil particles. Although the surface area and CEC of a particle size fraction are important in determining how plutonium reacts with a soil separate, the ratio of plutonium concentrations in small versus large size fractions was usually larger than the ratio of CEC's in small versus large soil separates. This may imply that surface area is more important than the CEC of the alluvium in determining the fractional distribution of plutonium.

The spatial distributions of ^{238}Pu and ^{239,240}Pu in the alluvium were compared with one another for the soil size fractions from each canyon. Statistically significant differences

($P<0.01$) in the distribution of $^{239,240}Pu$ and ^{238}Pu were found as functions of distance from the waste outfall, soil depth and soil size fractions. In Effluent-Mortandad Canyon, the $^{239,240}Pu/^{238}Pu$ ratios of size fractions collected 40 m from the waste outfall were higher than samples collected in the upper 2.56 km of this canyon (Figure 6) and higher $^{239,240}Pu/^{238}Pu$ ratios were also found in several size fractions with increasing depth (Figure 7). These observed spatial differences in the $^{239,240}Pu/^{238}Pu$ activity ratios in soil samples collected at various locations may be due to: (1) a change in the isotopic ratios or chemical forms of plutonium in liquid wastes added to the canyons since 1968, with subsequent re-location of plutonium-contaminated soil particles during runoff events in the canyons and/or (2) differential solubility, adsorption and physical mixing of plutonium isotopes in the soils of these intermittent streams. The latter possibility has been previously suggested and may account for the enhanced solubility and mobility of ^{238}Pu in soils compared to $^{239,240}Pu$ (Hanson, 1975).

Relatively high and statistically similar ($P<0.10$) $^{239,240}Pu/^{238}Pu$ ratios were found in the coarser size fractions (0.5-10 mm, 1-2 mm and 2-23 mm) of Effluent-Mortandad Canyon soils, with progressively lower, statistically different ($P<0.05$) plutonium ratios found in progressively smaller soil separates (Figure 6). Thus, a larger portion of the more

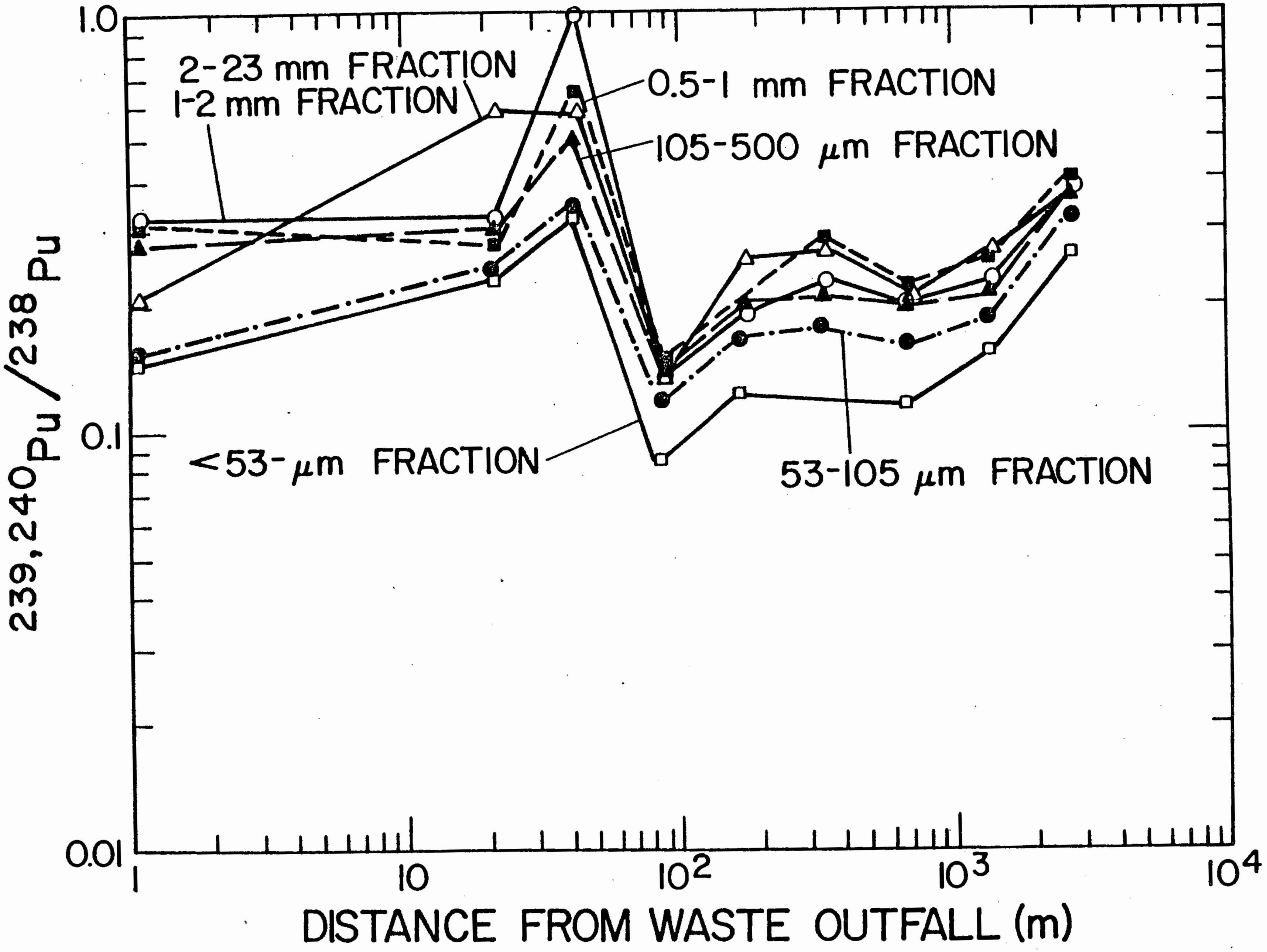

FIGURE 6. Relationship of $^{239,240}Pu$-^{238}Pu Ratios of Soil Size Fractions to Distance from the Waste Outfall in Effluent-Mortandad Canyon

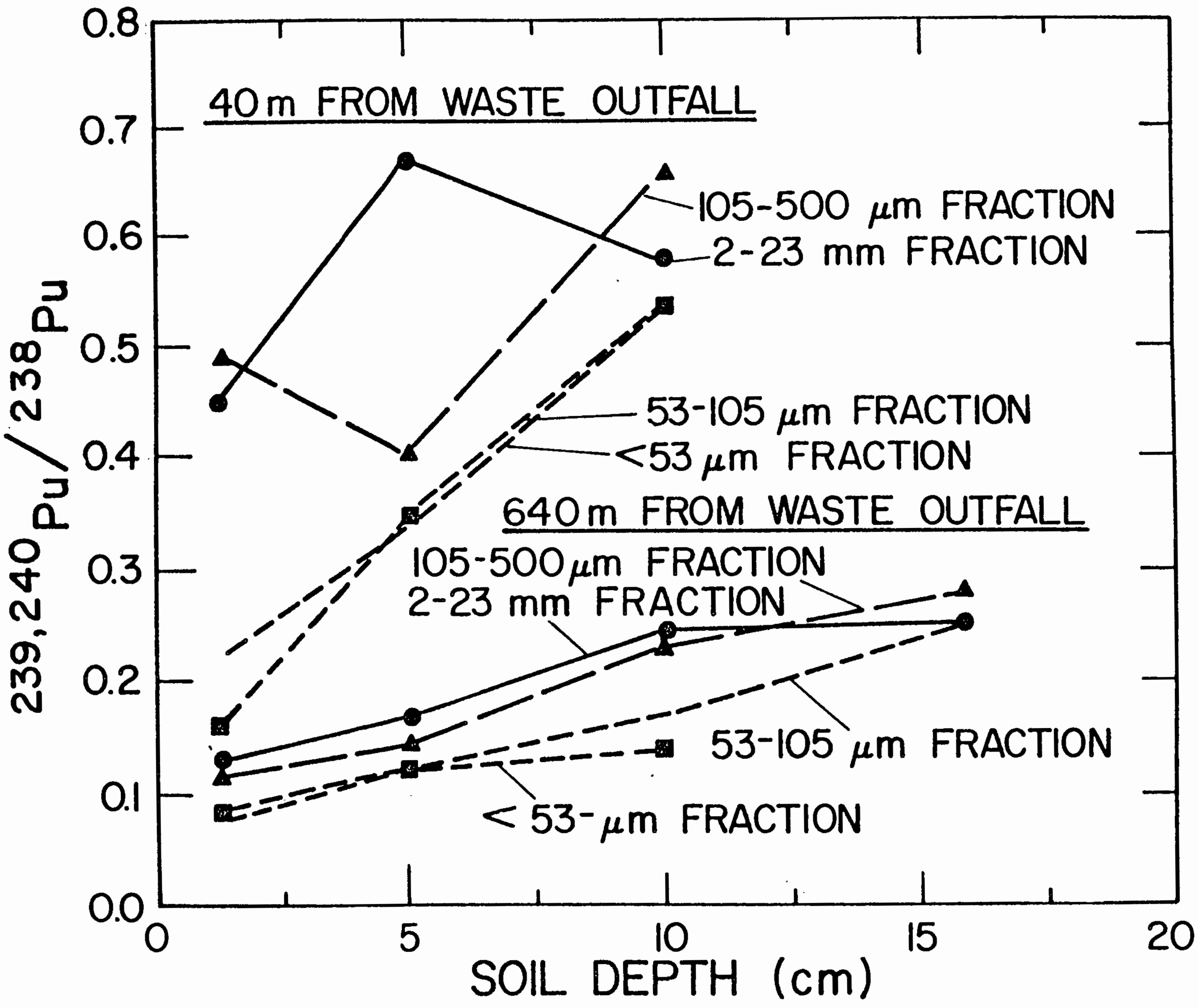

FIGURE 7. Relationship of ^{239,240}Pu-^{128}Pu Ratio of Particle Size Fractions to Soil Depth for Samples Collected 40 and 640 m from the Waste Outfall in Effluent-Mortandad Canyon

recently added ^{238}Pu was associated with the smaller soil particles than with the larger size fractions of Effluent-Mortandad Canyon soils during the spring months. Although isotopic differences between ^{238}Pu and ^{239,240}Pu could result in a distribution pattern such as found in these size fractions, a more comprehensive explanation would take into account the mean residence times of soil particles within each of the discharge areas. The distribution of plutonium isotopes observed in Effluent-Mortandad Canyon soils could also have occurred if large tuff fragments moved through this discharge area more slowly than small soil particles, which would then more nearly reflect the ^{239,240}Pu/^{238}Pu ratios in the current effluents.

Transport of Soil Plutonium in Rainstorm Runoff

Information relating to the physical transport of radionuclides down Effluent-Mortandad Canyon was obtained on September 15, 1974, following a rainfall of 2.9 cm on the upper portion of the watershed (Hakonson et al., 1976). A total estimated discharge of 3530 m^3 (3.53 x 10^6 liters) of water occurred during a 4.5 h period. Samples of water were collected throughout the event to relate the radioactivity transported by the runoff to the aqueous and suspended particulate fractions. Measurements on stream velocity and channel cross-sectional area were used in conjunction with the radionuclide data to estimate the total radioactivity transported by the runoff event, as previously reported for similar events in DP Canyon (Purtymun, 1974).

The runoff event demonstrated several interesting flow characteristics which seem to be typical of late summer rainstorms in the west. The maximum flow rate through the lower gaging station (1.28 km from the waste outfall) was 0.3 m^3/sec, corresponding to a velocity of 1.5 m/sec (4.8 ft/sec). This waterflow sustained a water depth of 21 cm in the center of the stream channel over a maximum surface flow width of 1.1 m. Maximum suspended sediment concentrations of 17±0.5 (SD) g/ℓ (17,000 ppm) and 74±12 g/ℓ were measured 15 minutes after the event began, in samples from the surface and bottom of the flow, respectively. Higher sediment concentrations were consistently measured in the bottom samples, reflecting the presence of suspended sand size fractions in the sample that probably resulted from turbulent flow. The relative particle size distribution in suspended sediment was not determined, although inspection of the samples confirmed that coarse materials comprised a higher percentage of bottom than surface samples. Sediment concentrations in all samples decreased at a relatively rapid rate from 15 to 55 minutes after the event began, corresponding to the rapid decrease in flow rate.

The concentrations of ^{238}Pu and ^{239,240}Pu in runoff samples exhibited very similar patterns with time (Tables 8 and 9). The filtered water contained low concentrations of all radionuclides (about 1% of the radionuclide inventory in each sample); levels ranged from about 2-5 pCi ^{238}Pu/ℓ and 0.21pCi ^{239,240}Pu/ℓ. Concentrations of the radionuclides in water were variable and did not exhibit a consistent pattern with time. On the other hand, levels of all three radionuclides in the suspended sediments ranged from 10-100 pCi ^{238}Pu/g and 1-10 pCi ^{239,240}Pu/g. Significantly higher ($P<0.05$) concentrations of the radionuclides in the suspended sediment were measured in samples collected near the surface of the flow compared to those from near the bottom. This observation was to be expected since a greater proportion of fine particle sizes comprised the surface samples and higher concentrations of plutonium were associated with relatively small soil size fractions (Table 4).

The relationship between flow rate and mean total radionuclide and suspended sediment concentrations in water samples is presented in Figure 8. The radionuclide and suspended sediment concentrations were relatively constant for flow rates in the range 0.07-0.25 m^3/sec, possibly indicating that all available fine materials were in suspension at these flow rates. However, radionuclide and suspended sediment concentrations were directly correlated with increasing flow

TABLE 8. Mean ^{239,240}Pu Concentrations in Runoff Samples Collected from Effluent-Mortandad Canyon

	^{239,240}Pu Concentrations				
	Suspended Sediment				Water
	pCi/g		pCi/ℓ		
Time (min)	Top	Bottom	Top	Bottom	(pCi/ℓ)[a]
5	3.4	1.3	48	73	0.25 (0.10)[b]
15	2.8	1.9 (1.4)	47 (1.4)	131 (84)	0.67 (0.76)
40	4.4 (1.5)	2.9 (2.1)	56 (20)	79 (26)	0.39 (0.29)
55	5.7	4.2 (1.8)	51 (3.5)	51 (29)	0.67 (0.64)
120	5.6 (1.3)	2.9 (2.3)	25 (5.7)	45 (5.7)	0.56 (0.38)
160	6.2 (3.2)	5.1 (1.6)	26	33 (16)	0.51 (0.34)
185	8.3 (0.1)	5.6 (1.0)	28 (0.71)	37 (0.71)	0.17 (0.11)
210	4.9	--	16	--	0.21
233	13	--	22	--	0.22
245	8.8 (0.35)	--	22 (0.71)	--	0.40
260	7.9 (1.7)	--	18 (1.4)	--	1.3 (1.3)

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[a] Averages for suspended sediment based on 2 samples; averages for water based on 4 samples (2 top and 2 bottom), filtered through 0.45 μm membrane.

[b] Parenthetic value represents ±1 S.D.

TABLE 9. Mean ^{239}Pu Concentrations in Runoff Water Collected from Effluent-Mortandad Canyon

	^{238}Pu Concentrations				
	Suspended Sediment[a]				Water[a]
	pCi/g		pCi/ℓ		
Time (min)	Top	Bottom	Top	Bottom	(pCi/ℓ)
5	25	7.3	350	410	2.5 (0.14)[b]
15	19 (0.71)	12 (9.3)	310 (2.1)	790 (550)	4.9 (5.5)
40	30 (11)	18 (15)	390 (150)	460 (220)	3.1 (1.6)
55	41 (2.1)	37 (23)	360 (7.1)	460 (340)	5.1 (2.9)
120	41 (17)	18 (15)	190 (80)	270 (20)	3.3 (1.3)
160	44 (21)	33 (9.2)	180 (7.8)	210 (110)	3.9 (3.2)
185	59 (5.0)	36 (3.5)	190 (11)	230 (11)	1.9 (1.0)
210	36	--	120	--	3.0
233	91	--	152	--	2.4
250	67 (0.71)	--	160 (9.9)	--	3.2
260	64 (9.2)	--	150 (2.8)	--	6.2 (3.6)

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[a] Averages for suspended sediment based on 2 samples; averages for water based on 4 samples (2 top and 2 bottom), water filtered through 0.45 μm membrane.

[b] Parenthetic value represents ±1 S.D.

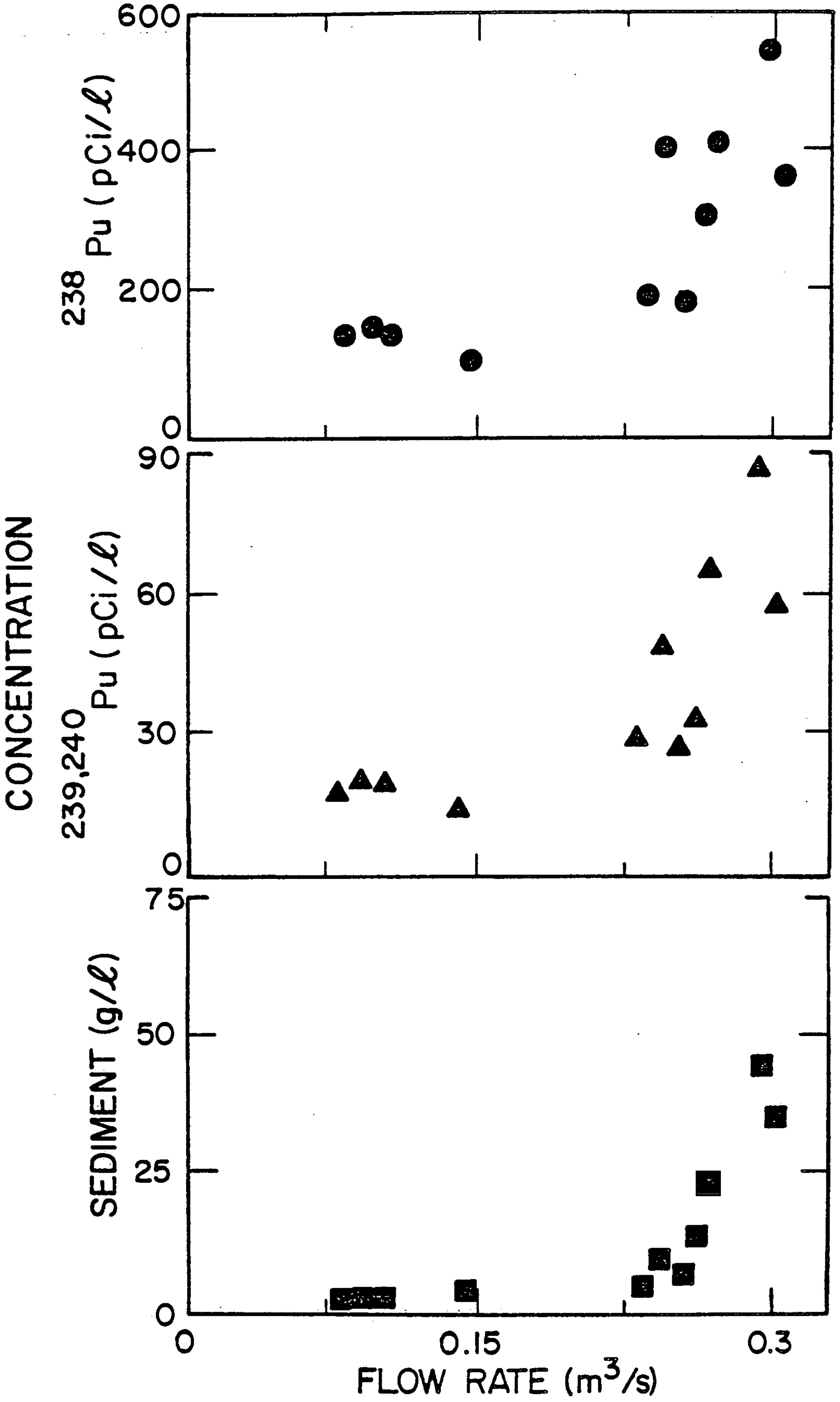

FIGURE 8. Concentration of Sediment and Radioactivity in Unfiltered Runoff Water from Effluent - Mortandad Canyon as a Function of Runnoff Flowrate

in the range 0.25-0.3 m^3/sec. Rates in excess of about 0.25 m^3/sec probably resulted in the suspension of coarse particles (>105 μm), which contained over 95% of the sediment mass and 90% of the radionuclide inventory.

The total amount of radioactivity transported by the event was calculated from average total radionuclide concentrations and cumulative runoff through the event. The estimated transport was 1.1 mCi ^{238}Pu and 0.2 mCi ^{239,240}Pu, which represented from 1-2% of the total added to the canyon since the first release in 1963. In the 11 years since Effluent-Mortandad Canyon has received contaminated wastes, over 50% of the radioactivity has been transported into the normally dry portion of the canyon by snowmelt and storm runoff (Table 1) indicating that on the average, annual losses of radioactivity to the dry portion of the stream are probably about 50%.

PLUTONIUM IN TRINITY SOILS

Soils investigations of plutonium in the fallout pathway of Trinity, were initiated more than 20 years ago (Larson et al., 1951b and 1951c; Olafson et al., 1957; Olafson and Larson, 1961) and continued in 1972 (Hakonson and Johnson, 1974) and in 1973 (Nyhan et al., 1976a). The primary objective of the 1972 study was to sample the soils and biota inside the fallout study was to sample the soils and biota inside the fallout pathway at 8-km increments to a distance of 56 km from Ground Zero (Figure 2). The objective of the 1973 studies (Nyhan et al., 1976a) was to determine the distribution and variation of $^{239,240}Pu$ in whole and fractionated soil samples collected along the fallout pathway as a function of soil depth and distance from Ground Zero. Soil radionuclide data from both studies were compared with similar data collected at the Trinity Site nearly 20 years ago and with soil physical-chemical properties influencing the distribution of plutonium in these soils.

Plutonium in Trinitite and Unfractionated Soils

The Trinitite particles collected at Ground Zero (GZ) contained about 2.0 nCi Pu/g and had an average $^{239,240}Pu$-^{238}Pu ratio of 21±0.8 (one SD). Comparable GZ soil samples contained about an order of magnitude lower levels of plutonium than the Trinitite samples (Table 10). The soil plutonium data from the GZ area cannot be compared with the data for the remainder of the transect because the area around GZ was mechanically disturbed shortly after the detonation and covered with at least 15 cm of uncontaminated soil, and the area around the 0.1 km station was scraped to remove the Trinitite lying on the ground surface. The high Pu concentration in the 0-2.5 cm segment of the GZ soil sample (Table 10) indicates either: 1) the overburdening was not successful; 2) that the

TABLE 10. Levels of Pu Found in Trinitite and Soils at Ground Zero of Trinity Site in 1972

Sample Description	Pu Concentration (pCi/g)
Trinitite	2000[a]
Soils:	
0-2.5 cm	250
2.5-7.5 cm	260
7.5-30 cm	62

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[a] Average Pu Concentration in 3 samples of Trinitite.

covered Pu had migrated to the soil surface; or 3) that the overburden had blown away over the last 27 years, thus exposing the contaminated soil.

The soils from the fallout pathway (Figures 9-11) generally had higher levels of ^{239,240}Pu than the control site soils (Figure 12). The ^{239,240}Pu levels found in the surface 0-2.5 cm of soil of the three sites within the fallout pathway averaged 21 times higher than the 9.8 femtocuries per gram (fCi/g) measured in the topsoil of the control site. Plutonium was generally nondetectable below 2.5 cm in the control site soils, whereas elevated levels of plutonium were found to depths of 25, 15, and 33 cm at the 1.6, 16 and 44 km sites, respectively.

The vertical distribution of ^{239,240}Pu in Trinity soils collected in 1973 (Figures 9-11) was compared with similar data collected nearly 20 years ago (Olafson et al., 1957; Olafson and Larson, 1961). Whereas the plutonium in the soil along the fallout pathway was detected exclusively in the upper 5 cm of soil nearly 20 years ago, only 42% and 57% of the ^{239,240}Pu inventory was found at this depth in 1973 at the 1.6 and 44 km sites, respectively, reflecting considerable downward migration of plutonium into the soil in the intervening 20 years. In contrast, the soils at the 16 km site still contained 78% of their ^{239,240}Pu in the upper 5 cm of the profile 28 years after the detonation. The total amount of

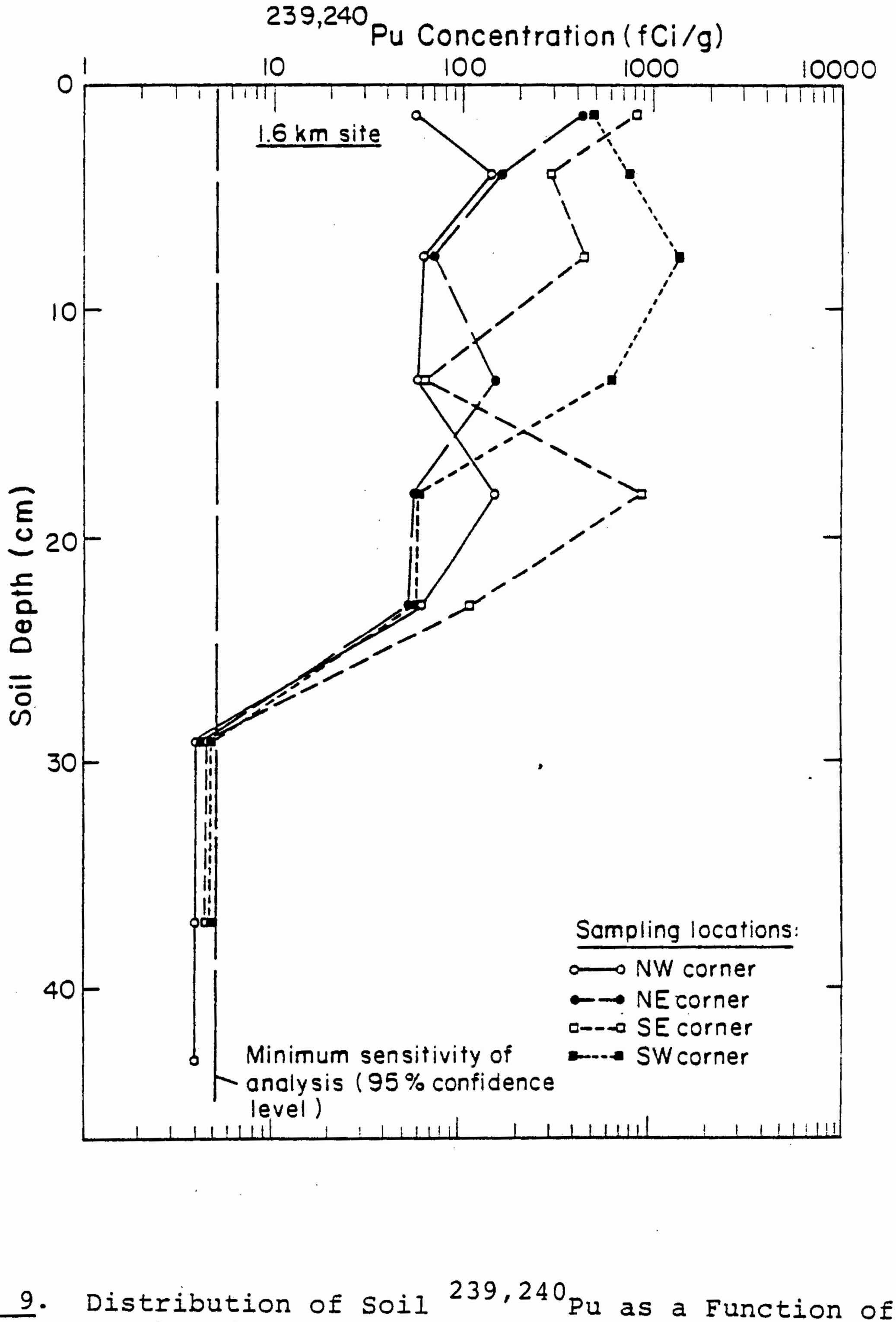

FIGURE 9. Distribution of Soil ^{239,240}Pu as a Function of Depth 1.6 km from Ground Zero. Plutonium Concentrations at each Depth Represent the Average of 2 Core Segments

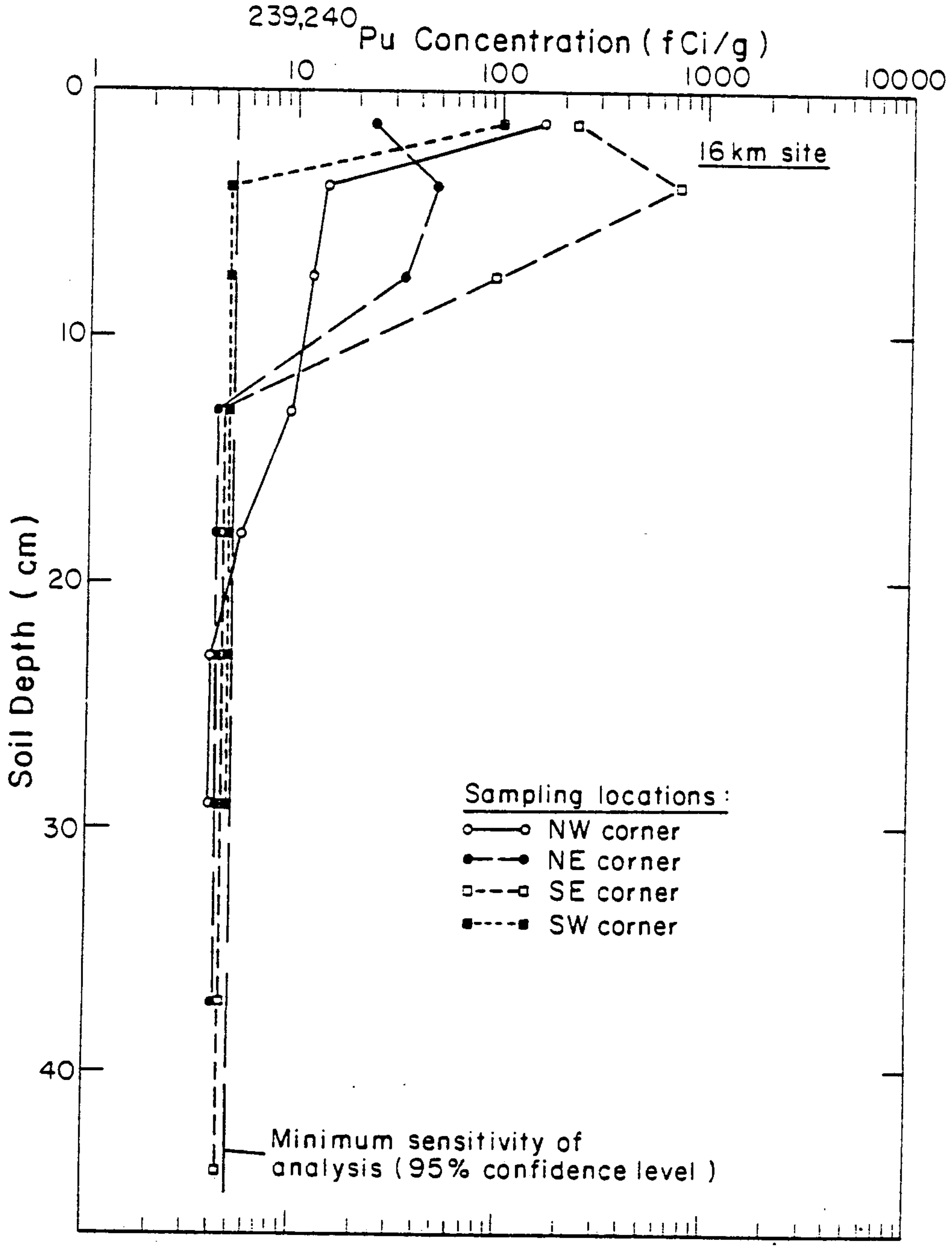

FIGURE 10. Distribution of Soil ^{239,240}Pu as a Function of Depth 16 km from Ground Zero. Plutonium Concentrations at Each Depth Represent the Average of 2 Core Segments

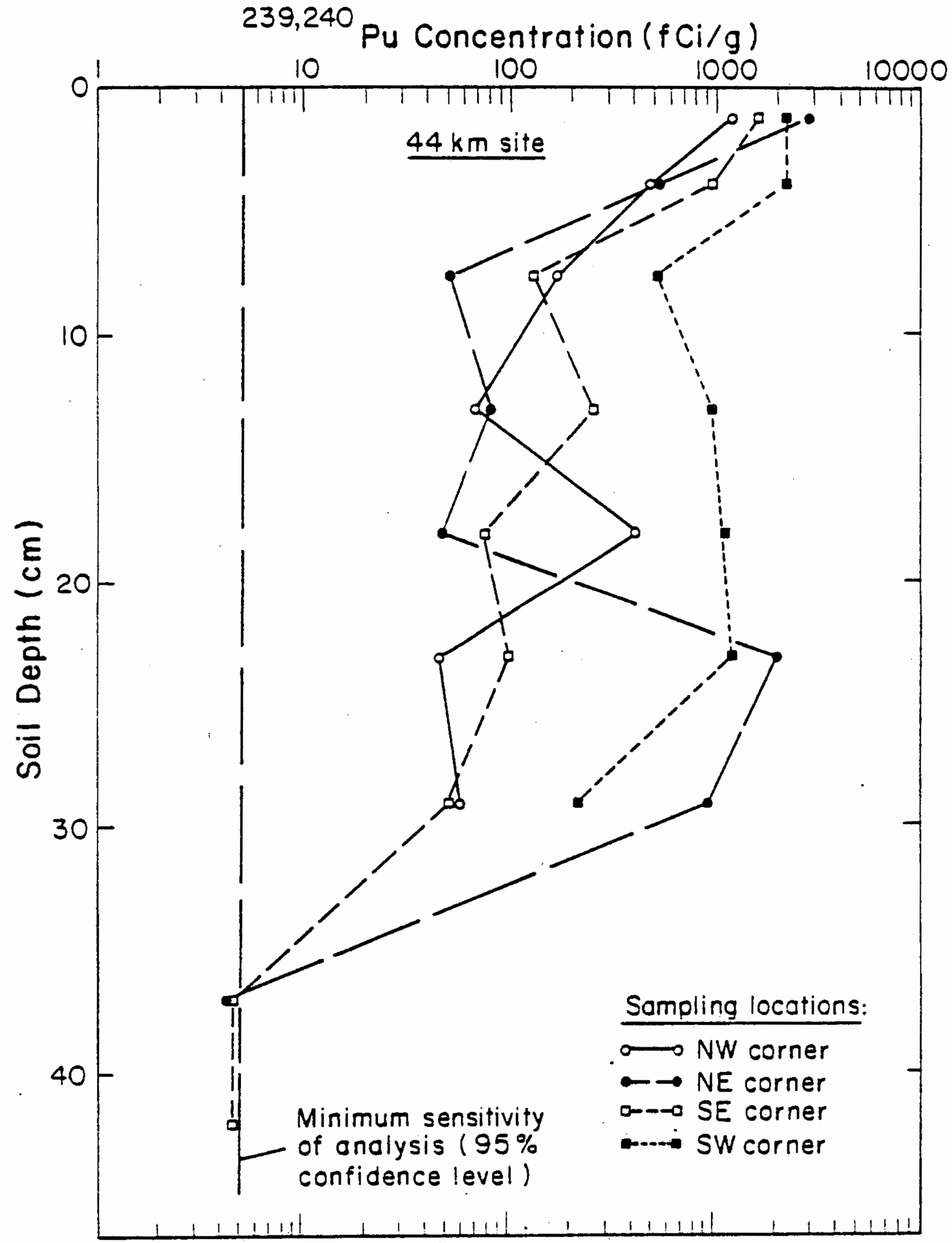

FIGURE 11. Distribution of Soil ^{239,240}Pu as a function of Depth 44 km from Ground Zero. Plutonium Concentrations at Each Depth Represent the Average of 2 Core Segments

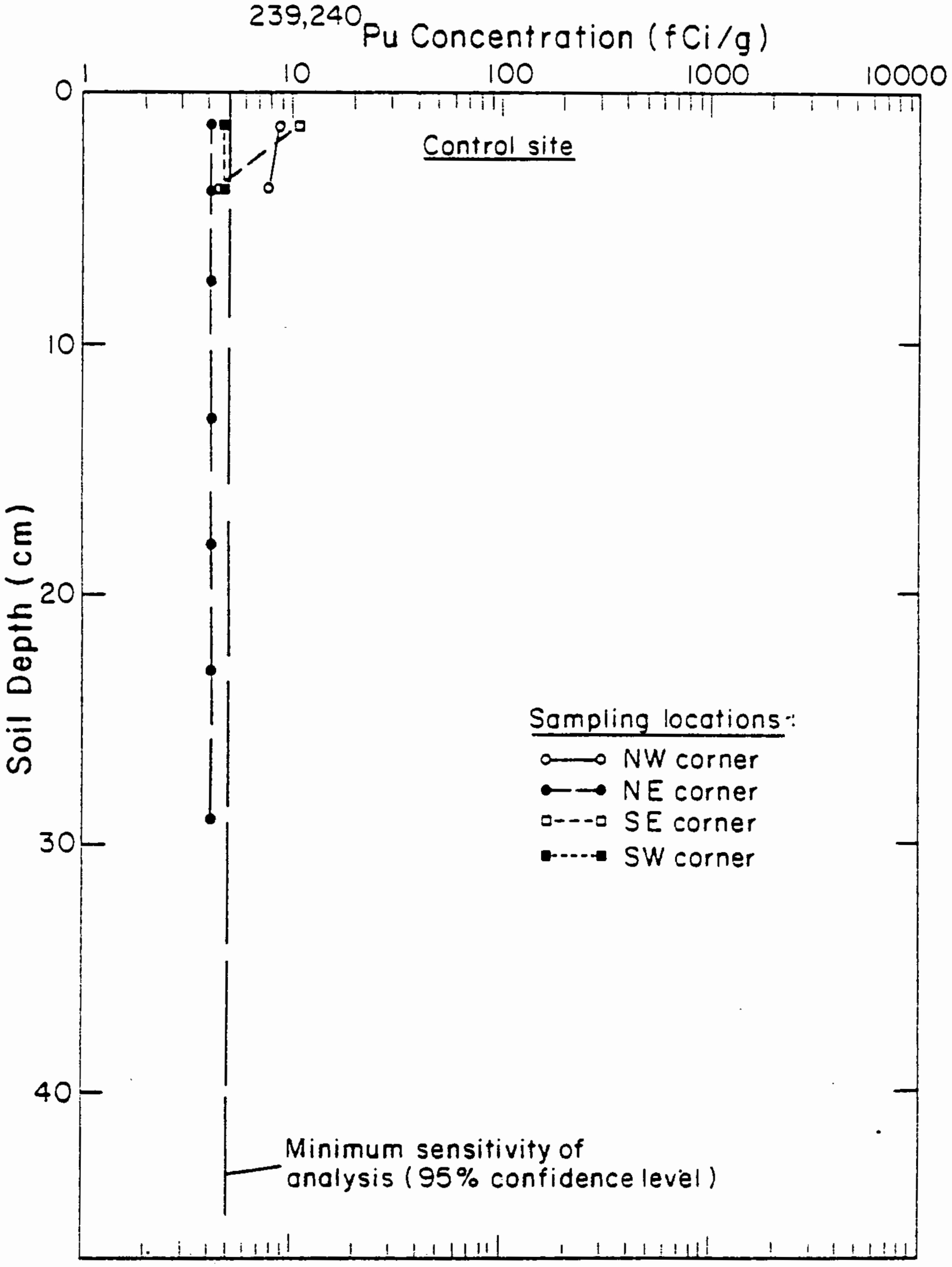

FIGURE 12. Distribution of Soil ^{239,240}Pu as a Function of Depth at the Control Site. Plutonium concentrations at Each Depth Represent the Average of 2 Core Segments

^{239,240}Pu measured in the 1.6 and 44 km soil profiles was greater than the inventory found in the profiles at the 16 km site, suggesting that appreciable downward movement of plutonium could only be detected in field locations which were relatively highly contaminated initially (Figure 2). A similar observation was made relative to the downward movement of fission products into these soils in 1949 and 1950 (Larson et al., 1951a and 1951b).

The soil plutonium data were compared with the morphology and classification (Figure 13) of the Aridisols at the 1.6 and 16 km sites and the Entisols located at the 44 km site on the Chupadera Mesa to further elucidate the vertical distribution of ^{239,240}Pu in Trinity soils. Plutonium was not detected in either the B_{3ca} horizon of the Dona Ana sandy loam at the 1.6 km site or the B_{2ca} horizon of the La Lande sandy loam at the 16 km site. These soil horizons represent the first strongly calcareous horizons encountered in the subsoil in these areas (Figure 13). The observed relationship between the vertical distribution of ^{239,240}Pu and soil horizonation would be expected since the zone of calcium carbonate accumulation is closely related to amounts of rainfall and the average maximum extent of water penetration into the solum (Jenny and Leanord, 1934).

Plutonium concentrations within the soil profiles exhibited considerable variation at all of the intensive study areas.

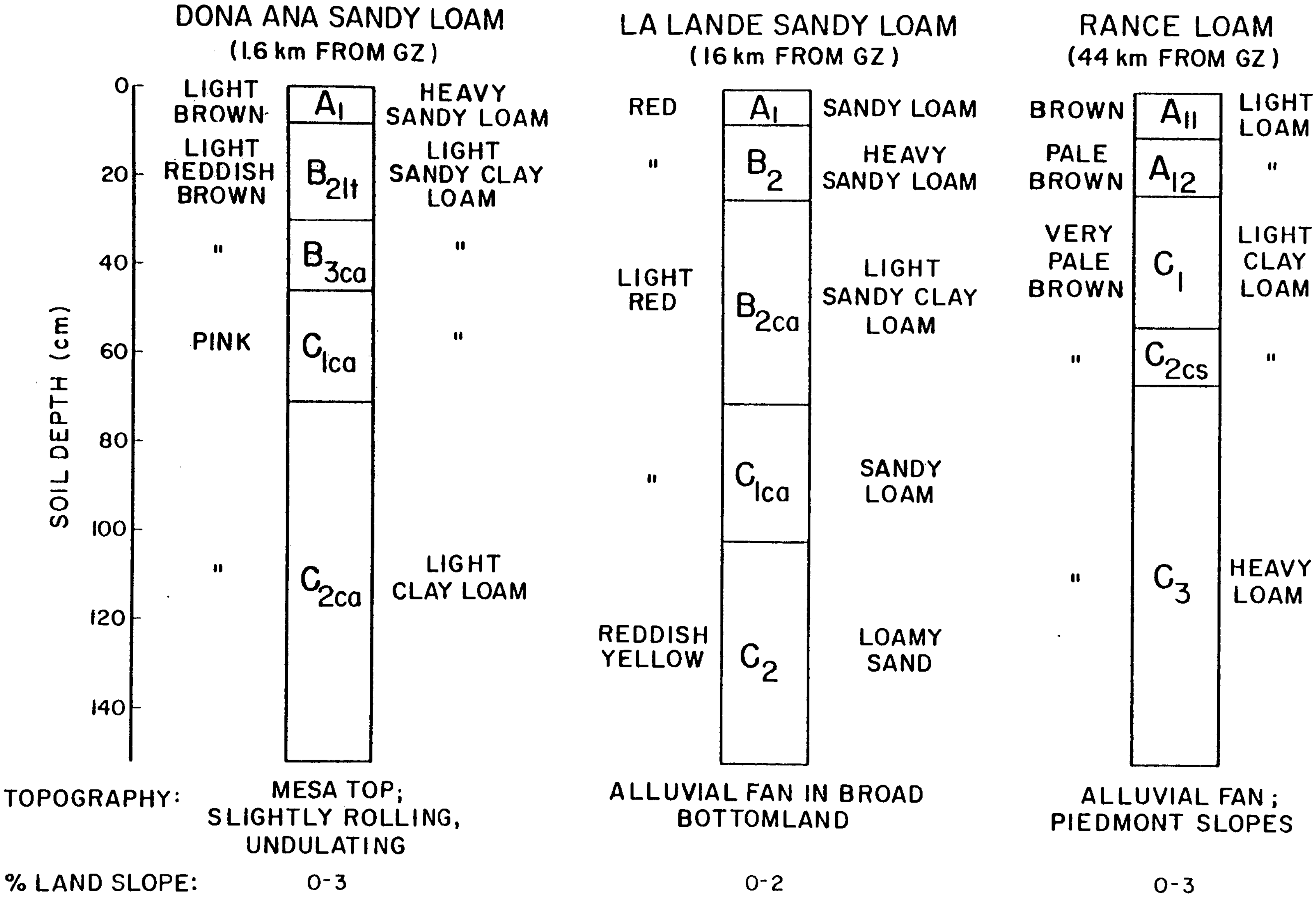

FIGURE 13. Soil Profile and Physiography Descriptions of Trinity Soils as a Function of Distance from Ground Zero (GZ)

Coefficients of variation (C.V. = SD/mean) of soil plutonium levels varied from 0.48 to 1.9, but were generally greater than 1.2 (Table 11). Variation due to aliquoting procedures generally resulted in C.V.'s of plutonium levels which were less than 0.35 and samples were counted for sufficiently long periods of time such that C.V.'s due to counting were usually less than 0.15. Thus, since most of the samples had C.V.'s > 1.2, the largest component of the variation in soil plutonium levels was generally attributed to spatial variation of plutonium within the soils at each intensive site. Since C.V.'s increased with depth in most cases (Table 11), part of the spatial variation of plutonium in soils may be due to differential penetration depths of plutonium into the soil, even in closely-spaced soil samples.

Plutonium in Soil Size Fractions

The distribution of ^{239,240}Pu in various size fractions of the topsoil (Nyhan et al., 1976a) varied considerably between sampling locations (Table 12). The highest plutonium concentrations were found in the <53 μm fraction at the 44 km site, while the 1.0-2.0 mm and 100-500 μm fractions exhibited the highest concentrations at the 1.6 and 16 km sites, respectively (Table 12). The lowest ^{239,240}Pu concentrations were consistently found in the 2-23 mm size fraction in soil samples collected in the fallout pathway; this separate

TABLE 11. Mean Concentrations and Coefficients of Variation of $^{239,240}Pu$ Levels in Intensive Site Soils in 1973

Soil Depth (cm)	Mean Soil $^{239,240}Pu$ Concentrations (fCi/g)[a]	Coefficient of Variation of $^{239,240}Pu$ Concentrations[b]	Number of Samples
	1.6 km Site		
0 - 2.5	440	0.82	8
2.5 - 5.0	340	1.0	8
5.0 - 10	510	1.5	8
10 - 15	220	1.7	8
15 - 20	220	1.8	8
20 - 25	200	1.8	7
	16 km Site		
0 - 2.5	130	1.2	8
2.5 - 5.0	380	1.9	4
5.0 - 10	56	1.4	5
	44 km Site		
0 - 2.5	2000	0.48	8
2.5 - 5.0	1000	0.96	8
5.0 - 10	220	1.4	8
10 - 15	340	1.3	8
15 - 20	310	1.5	8
20 - 25	820	1.7	8
25 - 33	350	1.8	7
	Control Site		
0 - 2.5	9.8	1.0	6

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[a] Samples containing nondetectable levels of soil plutonium (<5.0 femtocuries/g [fCi/g], 95% confidence level) were not included in the calculation of mean concentration.

[b] Represents standard deviation of mean divided by mean soil plutonium concentration.

TABLE 12. Distribution of Plutonium in Soil Size Fractions of Trinity Soils at the 0-2.5 cm Depth in 1973

Parameter Studied	Soil Size Fraction					
	<53 μm	53-100 μm	100-500 μm	0.5-1.0 mm	1.0-2.0 mm	2.0-23 mm
			1.6 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	70	50	920	2100	5300	8.9
Weight & Soil	8.9	11	49	23	6.1	2.0
% ^{239,240}Pu in Fraction	0.78	0.43	36	38	25	0.01
			16 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	660	98	790	140	67	20
Weight % Soil	10	19	65	4.0	0.42	1.6
% ^{239,240}Pu in Fraction	11	3.0	85	0.92	0.05	0.03
			44 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	3800	1700	420	640	1600	230
Weight % Soil	36	18	25	4.2	2.9	14
% ^{239,240}Pu in Fraction	73	16	5.5	1.4	2.4	1.8
			Control Site			
^{239,240}Pu Concentration (fCi/g)	20	25	7.3	56	ND[a]	20
Weight % Soil	13	17	49	13	4.1	4.4
% ^{239,240}Pu in Fraction	14	23	19	39	0.0	4.9

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[a] Less than minimum sensitivity of analysis (95% confidence level) of 5.0 fCi ^{239,240}Pu/g soil.

contained from 0.2 to 5% of the maximum $^{239,240}Pu$ concentrations observed in smaller size fractions, reflecting the overall low potential reactivity of the 2-23 mm fraction with fallout plutonium.

The percent of the total $^{239,240}Pu$ in each size fraction of each soil sample was calculated from the $^{239,240}Pu$ concentration data (Table 12) and the mass of the soil in each size fraction for each site. Only 1.2% of the $^{239,240}Pu$ and 20% of the soil mass was found in the <100 µm fractions at the 1.6 km site. The <100 µm size fractions from the 16 km site contained 14% of the $^{239,240}Pu$ inventory and 29% of the soil mass, whereas this fraction contained 89% of the total $^{239,240}Pu$ and 54% of the soil mass at the 44 km site. Thus, relatively larger amounts and high concentrations of plutonium were associated with smaller particles with increasing distance from Ground Zero.

The plutonium data for the single core segments presented in Table 11 should not be compared to the data presented in Tables 12 and 13, where a composite of four soil core segments were fractionated and assayed for plutonium. However, if the products of the plutonium concentration and the fractional soil mass are summed for all six size fractions, a total soil plutonium concentration can be calculated for the fractionated samples (Tables 12 and 13) and compared with the data in

TABLE 13. Distribution of Plutonium in Soil Size Fractions of Trinity Soils at the 5.0-10 cm Depth in 1973

	Soil Size Fraction					
Parameter Studied	<53 μm	53-100 μm	100-500 μm	0.5-1.0 mm	1.0-2.0 mm	2.0-23 mm
			1.6 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	11	37	72	27	10	ND[a]
Weight % Soil	10	12	41	21	9.4	6.6
% ^{239,240}Pu in Fraction	2.7	10	71	14	2.3	0.0
			16 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	320	76	42	17	ND	ND
Weight & Soil	12	16	58	11	0.55	2.5
% ^{239,240}Pu Fraction	49	17	32	2.0	0.0	0.0
			44 km From Ground Zero			
^{239,240}Pu Concentration (fCi/g)	270	240	89	33	ND	ND
Weight % Soil	28	19	30	8.8	2.2	12
% ^{239,240}Pu in Fraction	50	30	18	2.0	0.0	0.0

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[a] Less than minimum sensitivity of analysis (95% confidence level) of 5.0 fCi ^{239,240}Pu/g soil.

Table 11. If this comparison is made for soils from the surface 2.5 cm of soil, the plutonium concentration calculated from the size fraction data generally has a larger value than the average plutonium concentration values reported in Table 11. This observation is probably partially due to the propagation of variation in both plutonium concentrations and fractional soil mass in the size fractions, two factors which were not determined in these experiments.

The distributions of $^{230,240}Pu$ in the soil size fractions from the 5.0-10 cm depth (Table 13) can be compared with similar data from the 0-2.5 cm depth (Table 12). The soils at all of the sampling locations contained larger amounts of $^{239,240}Pu$ in small size fractions with increased depth. For example, only 1.2% of the total $^{239,240}Pu$ inventory at the 1.6 km site was found in <100 μm soil size fractions at the 0-2.5 cm depth, whereas this fraction accounted for about 13% of the soil plutonium inventory at the 5.0-10 cm depth. This pattern may reflect dissolution of $^{239,240}Pu$ originally deposited in the topsoil, which was subsequently leached by rainfall into the subsoil, where the plutonium was adsorbed on small soil particles with large surface areas.

SUMMARY

Soil plutonium concentrations were determined as a function of distance from either the liquid effluent outfalls at Los Alamos or from Ground Zero at Trinity Site and soil depth. Although most of the soil plutonium inventory in the intermittent streams at Los Alamos was located within about 2 km of the waste outfalls, runoff events were important in downstream transport of radioactivity beyond this point into the normally dry portion of these intermittent streams. Vertical mixing to the alluvium by hydrologic transport processes at Los Alamos were also responsible for the inconsistent plutonium-soil depth relationships observed at most sampling locations. In contracts, the horizontal distribution of plutonium in Trinity soils was related to the 1945 fallout deposition pattern and plutonium concentrations generally decreased with soil depth.

The distribution of plutonium was determined for a variety of size fractions as large as 2-23 mm in Los Alamos alluvium and Trinity soils. The 2-23 mm fractions of Los Alamos and Trinity soils generally had at least 10-fold lower Pu concentrations than smaller soil size fractions. The <105 μm size fractions in the coarse-textured alluvium at Los Alamos accounted for up to 96% of the soil mass and 80% of the plutonium. Although Trinity soils close to Ground Zero also fit this pattern, up to 90% of the plutonium was associated with the small (<105 μm) size fractions with increases in soil depth and distance from Ground Zero.

The distribution of plutonium in Los Alamos and Trinity soils was also compared with several physical, chemical and hydrologic properties of soil. Increased cation exchange capacities and levels of soil organic carbon and calcium carbonate were significantly correlated with elevated plutonium levels in the alluvium at Los Alamos. The fractional distribution of plutonium was correlated with surface area in Los Alamos soils, but this relationship did not hold true for most of the Trinity soils, signifying that other unidentified causal factors were influencing the distribution of plutonium in soil separates at Trinity Site. The maximum penetration depths of ^{239,240}Pu into Trinity soils were related to carbonate accumulations in the subsoil and the maximum extent of rainwater penetration into these soil profiles.

Temporal changes in the distribution of plutonium in the Los Alamos and Trinity Site soils were also considered. After the isotopic composition of the effluents added to Effluent-Mortandad Canyon was changed in 1968, soil size fractions could still be collected in this canyon 5 years afterwards, which reflected the isotopic composition of the pre-1968 liquid effluents. The spatial distribution of plutonium in the alluvium of Acid-Pueblo Canyon indicates that dilution and loss of plutonium from the upper soil layers has occurred since the liquid effluents were last added to this canyon in 1963. Whereas the plutonium in Trinity soils was only detected in the upper 5 cm of soil nearly 20 years ago, plutonium had migrated as far as 33 cm into these soils at some sampling locations.

CURRENT SOIL ACTINIDE RESEARCH PROGRAMS

A variety of soil trenching and coring techniques for sampling soils for radionuclides are being evaluated at Los Alamos and the Trinity environs to determine contributions to variation in actinide concentrations observed in the field.

Actinide-related activities within the effluent-receiving areas at Los Alamos currently involve obtaining more comprehensive radionuclide inventory estimates and further evaluating the transport of soil and actinides in these intermittent streams. We have sampled stream bank soils and the alluvium below our previous sampling depths (maximum of 30 cm) to determine inventories of transuranics at these locations. Seasonal changes in radionuclide concentrations and soil movement are being routinely monitored at several locations within Effluent-Mortandad Canyon.

Wind erosion of Trinity soils is being evaluated as an actinide transport vector, as well as the distribution of plutonium on soil size fractions. Bagnold dust collectors have been installed at our intensive study areas to evaluate amounts of soil and plutonium resuspended at each site as a function of distance above the soil surface and season of the year. Individual soil size fractions are being further examined relative to the distribution of plutonium particles on soil particles using alpha-track techniques.

LITERATURE CITED

Bellamy, A. W., J. L. Leitch, K. H. Larson, and S. L. Warren. 1949. The 1948 radiological and biological survey of areas in New Mexico affected by the first atomic bomb detonation. USAEC Report UCLA-32, Univ. of California, Los Angeles. 95 pp.

Blair, W. F. 1943. Ecological distribution of mammals in the Tularosa Basin, New Mexico. Contr. Lab. Vert. Biol. Univ. of Michigan 20:1-24.

Carrigan, P. H. and R. J. Pickering. 1976. Radioactive materials in bottom sediment of Clinch River; Part B, Inventory and vertical distribution of radionuclides in undisturbed cores. Final Oak Ridge Health Physics Division Report. Oak Ridge National Laboratory, Oak Ridge, TN, ORNL-3721, 80 pp.

Hakonson, T. E., J. W. Nyhan, L. J. Johnson and K. V. Bostick. 1973. Ecological investigation of radioactive materials in waste discharge areas at Los Alamos. LA-5282-MS. Los Alamos Scientific Laboratory, Los Alamos, NM, 47 pp.

Hakonson, T. E. and L. J. Johnson. 1974. Distribution of environmental plutonium in the Trinity Site ecosystem after 27 years. pp. 242-247. In USAEC Report CONF-730907-P1, Office of Information Services, Technical Information Center, Oak Ridge, TN.

Hakonson, T. E., L. J. Johnson and W. D. Purtymun. 1974. The distribution of plutonium in liquid waste disposal areas at Los Alamos, pp. 248-253. In USAEC Report CONF-730907-P1, Office of Information Services, Technical Information Center, Oak Ridge, TN.

Hakonson, T. E. and K. V. Bostick. 1976. Cesium-137 and plutonium in liquid waste disposal areas at Los Alamos. Proc. of the Fourth National Symposium on Radioecology (In Press).

Hakonson, T. E., J. W. Nyhan, and W. D. Purtymun. 1976. The accumulation and transport of soil plutonium in liquid waste discharge areas at Los Alamos. Proc. IAEA Symposium on Transuranics in the Environment, IAEA-SM-199/99 (In Press).

Hanson, W. C. 1975. Ecological considerations of the behavior of plutonium in the environment. Health Phys. 28:529-537.

Jenny, H. and C. D. Leanord. 1934. Functional relationships between soil properties and rainfall. Soil Sci. 38:363-381.

Kornegay, B. H., W. A. Vaughan, D. K. Jamison and J. M. Morgan (eds.). 1963. Transport of radionuclides in fresh water systems. Office Information Services, Technical Information Center, Oak Ridge, TN., TID-7664. 406 pp.

Larson, K. H., J. H. Olafson, J. W. Neel, W. F. Dunn, S. H. Gordon and B. Gillooly. 1951a. The 1949 and 1950 radiological soil survey of fission product contamination and some soil-plant interrelationships of areas in New Mexico affected by the first atomic bomb detonation. USAEC Report UCLA-140, Univ. of California, Los Angeles, CA. pp. 1-83.

Larson, K. H., W. F. Dunn, J. W. Neel and J. H. Olafson. 1951b. Soil studies with respect to radioactivity in the Alamogordo area. USAEC Report UCLA-104, Univ. of California, Los Angeles, CA. pp. 50-53.

Larson, K. H., J. L. Leitch, W. F. Dunn, J. W. Neel, J. H. Olafson, E. E. Held, J. Taylor, W. J. Gross, A. W. Bellamy and L. Baurmash. 1951c. Alpha activity due to the 1945 atomic bomb detonation at Trinity, Alamogordo, NM. USAEC Report UCLA-108, Univ. of California, Los Angeles, CA. pp. 1-45.

Neher, R. E. and O. F. Bailey. 1970. Soils and vegetation inventory of White Sands Missile Range, White Sands, NM. USDA Soil Conservation Service, West Regional Technical Service Center, Portland, OR. 166 pp.

Nyhan, J. W., F. R. Miera, Jr., and R. E. Neher. 1976a. Distribution of plutonium in Trinity soils after 28 years. J. Environ. Qual. 5 (In Press).

Nyhan, J. W., F. R. Miera, Jr., and R. J. Peters. 1976b. The distribution of plutonium and cesium in alluvial soils of the Los Alamos environs. Proc. of the Fourth National Symposium on Radioecology (In Press).

Nyhan, J. W., F. R. Miera, Jr., and R. J. Peters. 1976c. Distribution of plutonium in soil particle size fractions of liquid effluent-receiving areas at Los Alamos. J. Environ. Qual. 5 (In Press).

Olafson, J. H., H. Nishita, and K. H. Larson. 1957. The distribution of plutonium in the soils of central and northeastern New Mexico as a result of the atomic bomb test of July 16, 1945. USAEC Report UCLA-406, Univ. of California, Los Angeles, CA. pp. 1-25.

Olafson, J. H. and K. H. Larson. 1961. Plutonium, its biology and environmental persistence. USAEC Report UCLA-501, Univ. of California, Los Angeles, CA. 32 pp.

Pickering, R. J. 1969. Distribution of radionuclides in bottom sediment of the Clinch River, Eastern Tennessee. Geological Survey professional paper 433-H, U.S. Government Printing Office, Washington, DC. 25 pp.

Purtymun, W. D., G. L. Johnson, and E. C. John. 1966. Distribution of radioactivity in the alluvium of a disposal area at Los Alamos, NM. U.S. Geol. Survey Prof. Paper 550-D, U.S. Government Printing Office, Washington, DC. 3 pp

Purtymun, W. D. 1971. Plutonium in stream channel alluvium in the Los Alamos area, New Mexico. LA-4561, Los Alamos Scientific Laboratory, Los Alamos, NM. 7 pp.

Purtymun, W. D. 1974. Storm runoff and transport of radionuclides in DP canyon, Los Alamos County, NM. LA-5744, Los Alamos Scientific Laboratory, Los Alamos, NM. 9 pp.

Schiager, K. J. and K. E. Apt. 1974. Environmental surveillance at Los Alamos during 1973. Los Alamos Scientific Laboratory, Los Alamos, NM. LA-5586. 57 pp.

Shields, L. M. 1956. Zonation of vegetation within the Tularosa Basin, NM. The Southwest Naturalist 1:49-680.

U.S. Department of Agriculture, Soil Conservation Service, Soil Survey Investigations Section. 1972. Soil survey laboratory methods and procedures for collecting soil samples. U.S. Government Printing Office, Washington, DC. 63 pp.

FOLLOWING J. W. NYHAN'S PRESENTATION

QUESTIONS AND ANSWERS

Wildung: How did you measure particle size distribution?

Nyhan: We used a dry sieving technique. We usually took about 20 g of soil, dry-sieved it into the six fractions and analyzed these fractions for plutonium.

Wildung: How good are you at separating the small particles from the larger particles with the dry-sieving technique?

Nyhan: I suppose there are pretty intricate ways you could do this. After we sieved the materials, we typically ended up with a product on one sieve. In order to minimize contamination we took an air hose and essentially blew the finer particles off of the larger particles. In addition, most of the soils that we were studying were relatively coarse-textured, i.e., about 96% of the weight of the Los Alamos soils comprised particles that were very large. Since we found the highest concentrations of plutonium in the fine soil particles, the latter factor would also help to minimize cross contamination of large soil particles with small soil particles containing large concentrations of plutonium.

Wildung: Of course it wouldn't take too much fine particle contamination at the levels that you are working.

Nyhan: I thought originally that we might not be able to see differences greater than about three orders of magnitude for these samples. However, we used the same technique with Trinity soils as we did with Los Alamos soils, and some of those samples clearly showed nondetectable levels of plutonium in some of the fractions versus a couple thousand femtocuries per gram [fCi/g] in some of the smaller size fractions of the same soil.

Wildung: At the Trinity site at the 30-cm depth, that is, the depth of rainfall penetration, did you have carbonate deposition?

Nyhan: At the 44-km site, at 30 cm, did we have carbonate? No. This soil is classified as an entisol, which has an A and a C horizon, with no accumulation of carbonates in the C horizon. The soil was derived from a gypsum deposit, so calcium sulfate was there, not calcium carbonate.

Wildung: You showed a correlation of plutonium levels with calcium carbonate in. . .

Nyhan: Oh, that was in the Los Alamos soils.

Wildung: I understand that, but you did show a correlation of plutonium with calcium carbonate in the canyons and you stated that this may have some implication with respect to other ecosystems because at certain concentrations plutonium carbonates are soluble. But I wonder if the real reason you see this correlation is because calcium carbonate is one of the predominant factors involved in plutonium insolubilization. That is the reason I asked if carbonates were present at sites of plutonium localization in the Trinity site profiles.

Nyhan: Yes. Besides you could have a situation where you've got a precipitate which might tend to make plutonium less mobile, but on the other hand, the precipitate is a plutonium compound that's more soluble. Thus, you might expect to see greater vertical penetration of the plutonium with the carbonates present. There are some interesting things that we have seen in one of the effluent-receiving areas that are related to this phenomenon. We've got coarse alluvium on top of the massive tuff which I showed you at the start of this presentation. I think that Acid Pueblo Canyon, which hasn't been used as an effluent-receiving area since 1963, is currently more or less equilibrated with the environment. Many of the plutonium distributions with depth in this particular canyon show a relative increase as soon as you encountered the tuff. The alluvium probably has a half-life of something like two to three years years in the shallow, intermittent streams at Los Alamos, so that there's only a certain depth of alluvium that is exchanged annually. Indeed, you've got plutonium concentrations in the tuff that are now acting as a reservoir for the plutonium in these soils.

Rai: You mentioned the spatial variation in the plutonium distribution. How heavily can you rely upon comparison based upon the data collected 20 years ago?

Nyhan: The comparisons are made with some of Kermit Larson's work and some work done by UCLA personnel at a Trinity site in the 50's. These people actually collected core samples and had them analyzed for plutonium. Their detection limits were not as good as ours are today, but we have obtained some of these old samples from Kermit Larson and NAEG to help answer this question.

Rai: I was wondering whether it is possible that due to spatial variation the researchers 20 years ago missed a site where plutonium was present down to 30 cm. You might make mention of the spatial distribution.

Nyhan: There is, and it's quite large. I'm not a statistician, but I think you could pretty easily show that there was a significant difference over time. Most of the samples that they took 20 years ago had some signs of activity in the surface inch of soil, but none of the samples taken below this depth showed any detectable levels of activity.

Rai: Did Larson go any deeper than 30 cm in very many places?

Nyhan: He had one set of cores that I think went down to about 60 cm, and here he is only showing significant signs of activity in the top 2 inches. These core samples were broken down into 1-inch increments all the way to about 2 feet.

Price: When you are coring, are you sure that you're not carrying down contamination from the surface, or when you analyze do you take away the portion that has been in contact with the corer? How do you control that possibility?

Nyhan: When we are taking a sample, we drive the core tube down into the soil and then compare the depth of the soil inside the corer with the soil depth outside of the corer. We would typically come out with about 10% compaction integrated over the entire soil core. Immediately upon taking the sample we place a rubber stopper in one end of the core tube, place the tube in a plastic bag, and double wrap this package. This sample would then be placed upright in a freezer chest with dry ice in it.

Price: You don't have anything like smear along the sides?

Nyhan: I can answer that for cesium. I know that if you contaminate the surface of a bucket of sand from one of the effluent-receiving areas with cesium, and then take a core sample in this bucket just like you would do out in the field, there isn't any smearing along the side of the core. I tried tubes that had varying diameters and the 1-inch diamter core that I finally ended up with would hold the soil inside it when you removed the core from the soil, something that I couldn't accomplish with the larger sampling tubes because everything fell out of them. There was no aliquoting error introduced into the analysis because after we froze the sample and cut it up, the total amount of soil that was in each depth segment was analyzed for plutonium.

Rai: It seems to me you could avoid all those problems just be taking sample by standard procedure, like soil scientists do. Just dig a pit and take samples from the side of the pit, that way one could avoid the mixing problems encountered in tube sampling.

Nyhan: That's possible in some locations, but not where I'm sampling at Los Alamos. The trench in the alluvium would immediately collapse, i.e., it would be like digging a hole in a sandbox full of dry sand.

Lini: What is the rainfall at the Trinity Site? How far into the ground does it penetrate?

Nyhan: We're getting about 7 to 9 inches of rain a year at Trinity Site. Typically in the West you get most of that rain occurring in less than 1/10 of an inch rainstorms. Where you reach the depth of maximum carbonate concentrations in a lot of the western soils, that also represents the maximum extent of rainwater penetration into that soil such as at the Trinity Site. Three-inch rainstorms would roughly penetrate about 30 inches into one of the Trinity Site soils. That would be the maximum extent, but you hardly ever get a 3-inch rain.

Serne: You did mention for the site 44-km from Ground Zero, that you felt that the rainwater was reaching 30-cm depth as its maximum penetration. You stated that as you went deeper, more plutonium was found in finer and finer particles, and you hypothesized solubilization at the surface and resorption below. Is there any justification for your hypothesis over a totally physical mechanism in terms of downward movement of fine particles of plutonium oxide with time and water percolation, i.e., just physical transport of fine plutonium particles down to that depth. I wonder if anyone can show that it's actually a chemical dissolution-resorption instead of just the PuO_2 particles finally, through more wettings and dryings, transporting down.

Nyhan: That's a good question. One of the things that we're doing now will answer that question. I don't have the answer right now, but we're looking at alpha-track analysis, and trying to look at the distribution of plutonium particles in the soil, as compared with the distribution of soil particles that are there. It would seem to me that if there was any type of a surface area-dependent reaction, the pattern that I observed of increased plutonium concentrations in finer size fractions with increasing depth would seem to be reflecting a chemical dissolution rather than a physical absorption.

Serne: Maybe the fine plutonium oxide particles end up in your fine fraction. It could be just a filtering mechanism of the soil profile.

Nyhan: But if it was a filtering mechanism of the soil profile you'd expect a similar concentration of plutonium on each one of the size fractions, wouldn't you?

Serne: Not if they're discrete particles of PuO_2.

Bondietti: With density of 10. Not the same density as your soil. You're using dry sieving. Using wet sieving you'd have that other problem involved, where the Pu would sink faster than a 2.6 g/cm^3 particle.

Nyhan: Like some of Tamura's work.

Rai: In soils, clay particles which are less than 2 micrometers in size may leach down to great depths (60 inches or even down farther than that). Thus, if the plutonium particles are small enough and durable enough, it is possible that these particles would also move down the profile.

Nyhan: Yes, it's possible, however, using that same argument, it has probably taken the Trinity soils about 2 to 3 hundred years or maybe up to a thousand years to develop a B horizon, which results in migration of submicron clay particles from the upper soil layers to a subsoil layer. Along these same lines, if the soil and plutonium particles are migrating at these slow rates, why did I see a change in the vertical distribution of plutonium at Trinity Site in about 20 years?

Glover: I did a preliminary experiment to figure out a way to get a good PuO_2 soil slurry. I mixed some soil and PuO_2 (diameter of 10 μ and less) and put it on top of a soil column. The column was rinsed with 1 liter of distilled water and the water collected in fractions. In the very first fraction of water that came through, high alpha activity was detected which indicated that the PuO_2 particles had passed through. With particles as large as 10 microns I couldn't do a fission track analysis on it because of the amount of radiation associated with it. The PuO_2 particles did, indeed, come out in the effluent. So it's moving, whether it was physical movement or not. PuO_2 in a matter of a couple of days or so moved down through the 3 cm of soil. So it's possible that even in a short period of time that PuO_2 might somehow move through the soil.

Nyhan: We tend to be field oriented, and I had nothing to look at to compare against time except the older analyses that were done at Trinity Site. But all the old vertical distributions of plutonium taken in the late 40's and early 50's had similar vertical distributions of plutonium.

Rogers: That fallout has been there such a long time that these original fallout particles may have attached themselves to the larger size fraction of the soil and therefore are not so mobile any more. I think some of Tamura's data indicate that most of the plutonium is associated with the larger particles and not so much with the smaller particle size batch. Therefore over this period of time maybe the migration process may stop, or becomes more difficult to proceed because of fixation.

Glover: Of course, if you have a system where water is constantly being added, it is possible that the fallout (PuO_2) would move, maybe not very much. In your situation, where you don't have very much rainfall you have a static system. The PuO_2 does have a chance to attach itself to the soil and get to some point where it would stop.

Rai: Like a series of steps . . .

Glover: Yes, but in my situation where I'm constantly running water through the soil column, there is a possibility of a PuO_2 particle that just does not become attached to anything and moves constantly until it is trapped at some point. So, I agree with you that it would be possible.

Nyhan: What you were just saying is similar to what they found at Argonne with the Los Alamos tuff. That's what they mean by saturated flow.

Glover: So you get both of those things working. This is probably one thing to consider when you look at all different kinds of soils. It would be difficult to actually say this is what will happen all the time, because it would depend on how much rainfall you have in the area, what kind of soil you've got, and what kind of conditions exist to say whether or not the movement is physical or if an ion exchange mechanism influences movement.

Bruns: We're finding some verification of this too, incidentally, in our field studies of Hanford soil. We had a Redox facility. It was the second fuel reprocessing facility established at Hanford and has been down for 15 or 20 years. We were looking at a dried up low level waste pond originating from Redox and at Analytical Laboratory low level wastes, and there the plutonium activity is still increasing at 30 cm depth in a particular region that channeled down through the pond. We haven't gone deeper than that and that's why I was curious as to how far it's going to keep increasing. With time, it apparently seems to be going down a little bit. Possibly the plutonium polymer species is a fine particle size or possibly a soluble, elutriable species. A lot of liquid went into this pond, and so it has washed down and it still may be going on down with rainfall. In Z-9 that Ms. Sue Price is working on, we found activity at about 30 meters.

Price: At least 30 feet . . .

Bruns: Thirty feet. That's right; 30 feet is the furtherest we've core sampled there. It's getting on the nanocurie range at that depth, but it's above 100 nanocuries/gm, so it is a concern.

Rai: It seems to me that one way of resolving this problem is to compare the size of the plutonium particles and the sizes of soil pores and then determine whether it is physically possible for the plutonium particles to go through the soil pores.

Nyhan: For Trinity soils, I calculated this knowing the specific activity of the plutonium particles. I took the maximum concentration of ^{239}Pu (about 1,000 fCi/g ^{239}Pu) and knowing the specific activity of pure $^{239}PuO_2$, I calculated the size of the particle that could be contained in an entire soil sample if all the ^{239}Pu were contained in one particle. This calculation showed that we were looking at soil sizes less than 53 μ with submicron particles of plutonium on these soil particles. This distribution is not the same as working at higher concentrations where you have what Claude Sills calls the hot particle problem. We're looking at sort of a piggyback effect where the plutonium particles are "piggy-backing" on much larger soil particles. That is the overall impression you get of almost any size fraction distribution that I looked at under environmental conditions.

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ACTINIDE-SOIL INTERACTIONS IN WASTE MANAGEMENT AT THE SAVANNAH RIVER PLANT

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INTRODUCTION

Three aspects of the transuranium (TRU) nuclide-soil interaction were studied in connection with Savannah River Plant (SRP) burial ground operations. Results of the studies are reported as three separate parts of this report.

RADIONUCLIDE CONTENT OF AN EXHUMED CANYON VESSEL

The long-term hazard potential associated with burial of process equipment from radiochemical separations plants is being evaluated. As part of this evaluation, a feed adjustment tank was exhumed 18 years after burial. The tank had been in service in the fuel reprocessing plant for 29 months before it was retired. Assay of the exhumed tank indicated that 7 mg of ^{239}Pu and 1 mCi of ^{137}Cs remained on its surfaces. Less than 1 μCi of ^{239}Pu was found in the soil under the tank.

VOLUME REDUCTION OF PLUTONIUM-CONTAMINATED SOIL

A series of laboratory tests was aimed at reducing the volume of plutonium-contaminated soil in the SRP burial ground. The tests showed that the volume of plutonium-contaminated soil could be reduced to one-third by scrubbing and separating a clay silt fraction containing about 95% of the plutonium. Only the plutonium-rich fraction would then require storage in durable containers; the remaining two-thirds (plutonium-depleted fraction) of the soil could be returned to the burial trenches.

MOVEMENT OF ORGANICALLY BOUND PLUTONIUM IN SOIL

A safety evaluation of underground storage of spent Purex solvent (tri-n-butyl phosphate, TBP, in hydrocarbon diluent) was made. In this evaluation, laboratory tests showed that small volumes of organic-complexed plutonium are effectively sorbed and immobilized in dry (ground surface) soil. But moist (subsurface) soil would permit extensive migration of postulated large volumes of solvent-complexed plutonium until the plutonium transfers to the water phase with subsequent absorption on the soil.

RADIONUCLIDE CONTENT OF AN EXHUMED CANYON VESSEL

H. P. Holcomb

To assess the long-term hazard potential associated with the burial of retired, intensely contaminated process equipment, an emplacement of canyon equipment was excavated. During the previous 20 years, failed or obsolete process equipment, amounting to 10^5 cubic feet, from radiochemical separations processes have been placed in earthen trenches at the SRP burial ground. Radionuclides associated with this waste are principally the fission products ^{95}Zr-^{95}Nb, $^{141-144}Ce$, and $^{103-106}Ru$. These species have short to moderate half-lives and present no significant requirements for control and surveillance of the burial site beyond a time span of a few decades. However, this type of waste also includes longer-lived contaminants, such as ^{90}Sr, ^{137}Cs, and $^{238-239}Pu$. These species greatly influence planning for future control and surveillance criteria of the burial site. The TRU nuclide content of this equipment was not measured prior to burial because of the intense beta-gamma radiation associated with the equipment, generally several tens of R/hr at distances of a few feet.

One vessel, a Purex feed adjustment tank from the hot canyon of a separations plant, has been exhumed and studied. This piece of equipment was retired from service and buried in 1957. This part of the study describes the exhumation and assay methods. The assays showed that 7 mg of ^{239}Pu and 1 mCi of ^{137}Cs remain on the surfaces of the vessel; the amount of radionuclides in the nearby soil is substantially less.

DETAILS

Pre-excavation Work

Before the contaminated vessel was unearthed, the following steps were taken:

- Criteria for selection of buried equipment were set
- Records for available equipment were examined
- A candidate vessel was selected
- The buried vessel was located by drill probing
- A Test Authorization was prepared
- Adjacent soil was sampled
- Laboratory leaching experiments were designed
- A job plan was written and approved

The first choice of a candidate for the exhumation test was a first-cycle Purex feed tank. This tank was an 8-ft-diameter by 8-ft-high vessel that had been buried after it was retired from service in 1957.

The first task was to find the buried process vessel by drill probing (Figure 1) in a high-level waste trench. The location of the feed tank was shown on an old burial ground map with a feed adjustment tank noted as being nearby in the same trench. However, probing the chosen area of the burial trench indicated the presence of only one vessel, an 8-ft-diameter vessel that was buried about 3 1/2 ft beneath the surface.

FIGURE 1. Drill Probing for Buried Process Vessel

Soil samples were taken as shown in Figure 2 by vertically coring as close to the vessel as possible. Another series of cores was taken at a distance of 1 ft foot from the vessel wall. After the vessel was exhumed, soil that had been beneath the vessel was also sampled.

Trench Excavation and Vessel Exhumation

The remaining steps in the test procedure, beginning with the exhumation of the vessel, are listed below.

- Soil around vessel was excavated
- Vessel was removed and transported to test site
- Soil beneath vessel was backfilled and sampled
- Vessel contents were sampled
- Adhering and contained soil were removed from vessel
- Temporary hut was constructed around vessel
- Radiation surveys and measurements of vessel and surrounding soil were conducted
- Sample coupons were cut from vessel
- Leach tests and soil analyses were performed in laboratory
- Report was written

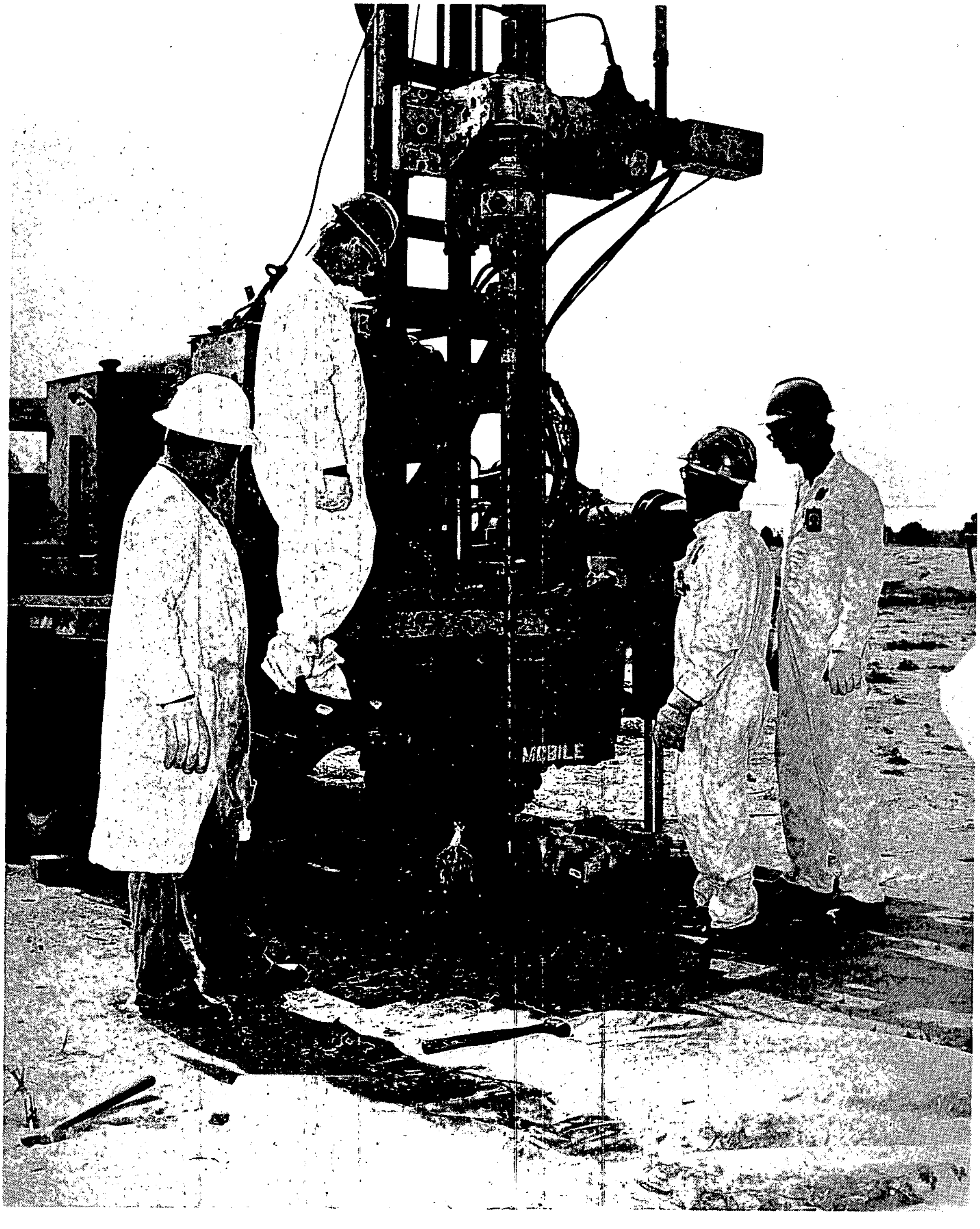

FIGURE 2. Core Sampling Soil Surrounding Buried Process Vessel

This was not the first piece of equipment to be exhumed from the SRP burial ground. Previously, five batch evaporators and a process centrifuge were reclaimed, reworked, and returned to service; but this is the first attempt at SRP to recover buried equipment for the purpose of measuring contamination levels.

A clam shell was used to uncover the vessel. Figure 3 shows the first portion of the vessel wall that was uncovered.

FIGURE 3. First Portion of Buried Vessel to be Uncovered
Dead Root Immediately Adjacent to Vessel

A dead root was immediately adjacent to the vessel. On this uncovered portion of the vessel wall, the alpha contamination was 10^4 dis/(min)(75 cm^2). Radioactivity in the root was almost exclusively that of ^{90}Sr, about 10^5 pCi/g, with only 6 pCi/g of plutonium.

As excavation and soil removal from around the vessel continued, the serial number, painted on the side, was exposed (Figure 4). On reviewing the records, the vessel being exhumed was found to be the Purex feed adjustment tank instead of the feed tank originally sought. For this test, however, either vessel would suffice because their process histories were very similar. The feed adjustment tank had been in hot canyon service for 29 months, from October 1954 to March 1957. Health Physics records at the time of burial showed a radiation level of 22.5 R/hr at 1 ft. Calculations indicated that the current radiation level would be about 2 mR/hr at 3 in., sufficiently low for extended periods of close work.

When the overburden was removed, it was confirmed that the tank had been buried with the agitator opening uncovered, allowing the tank to be filled with soil and water. Figure 5 shows the mud-filled tank, with clods being supported at the opening. The tank and its contents weighed about 18 tons. A 75-ton crane (Figure 6) lifted the tank from the emplacement and placed it in a transport box on a trailer for moving to the test site.

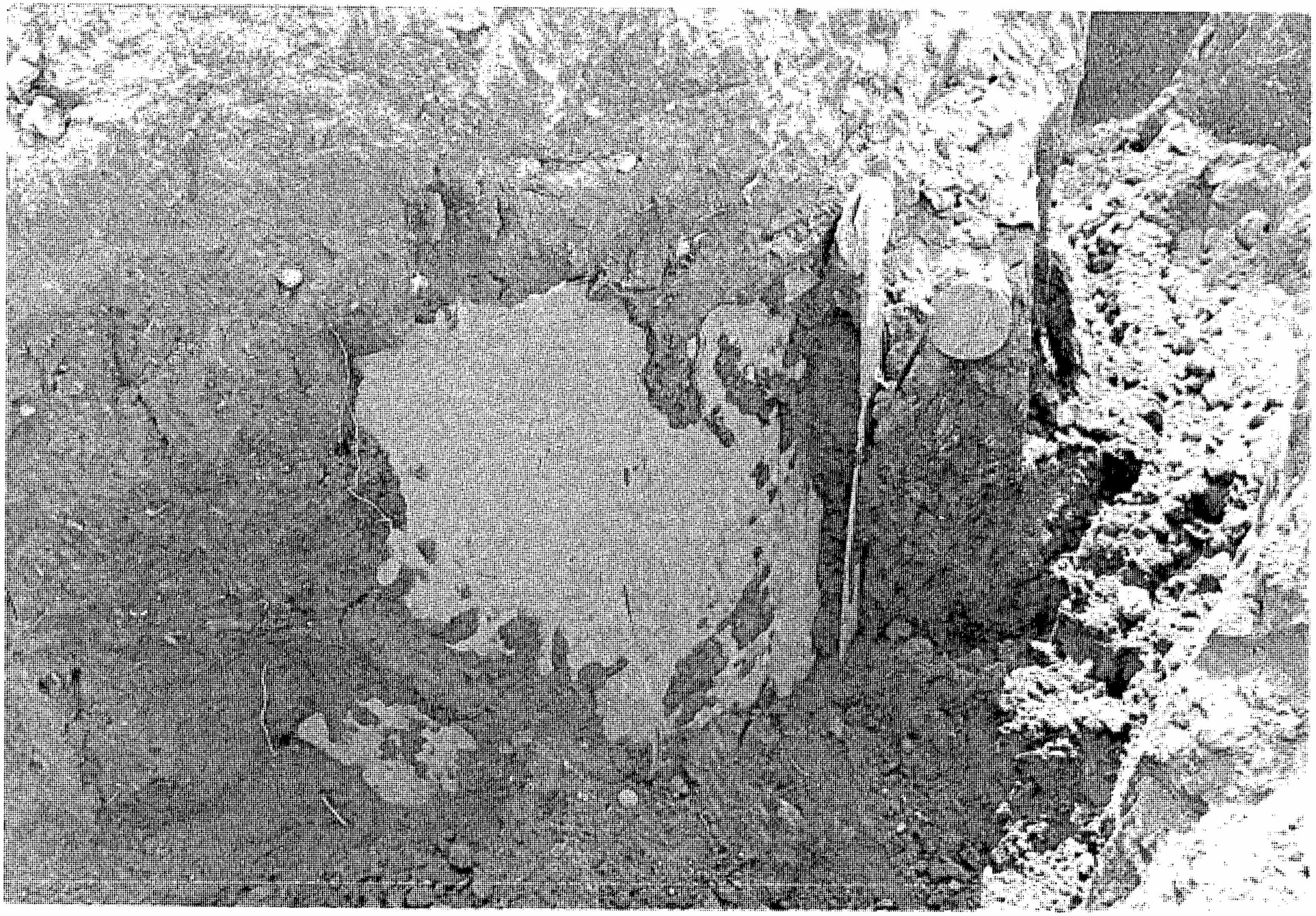

FIGURE 4. Wall of Exhumed Purex Feed Adjustment Tank Showing Serial Number

FIGURE 5. Buried Purex Feed Adjustment Tank Filled With Soil and Water

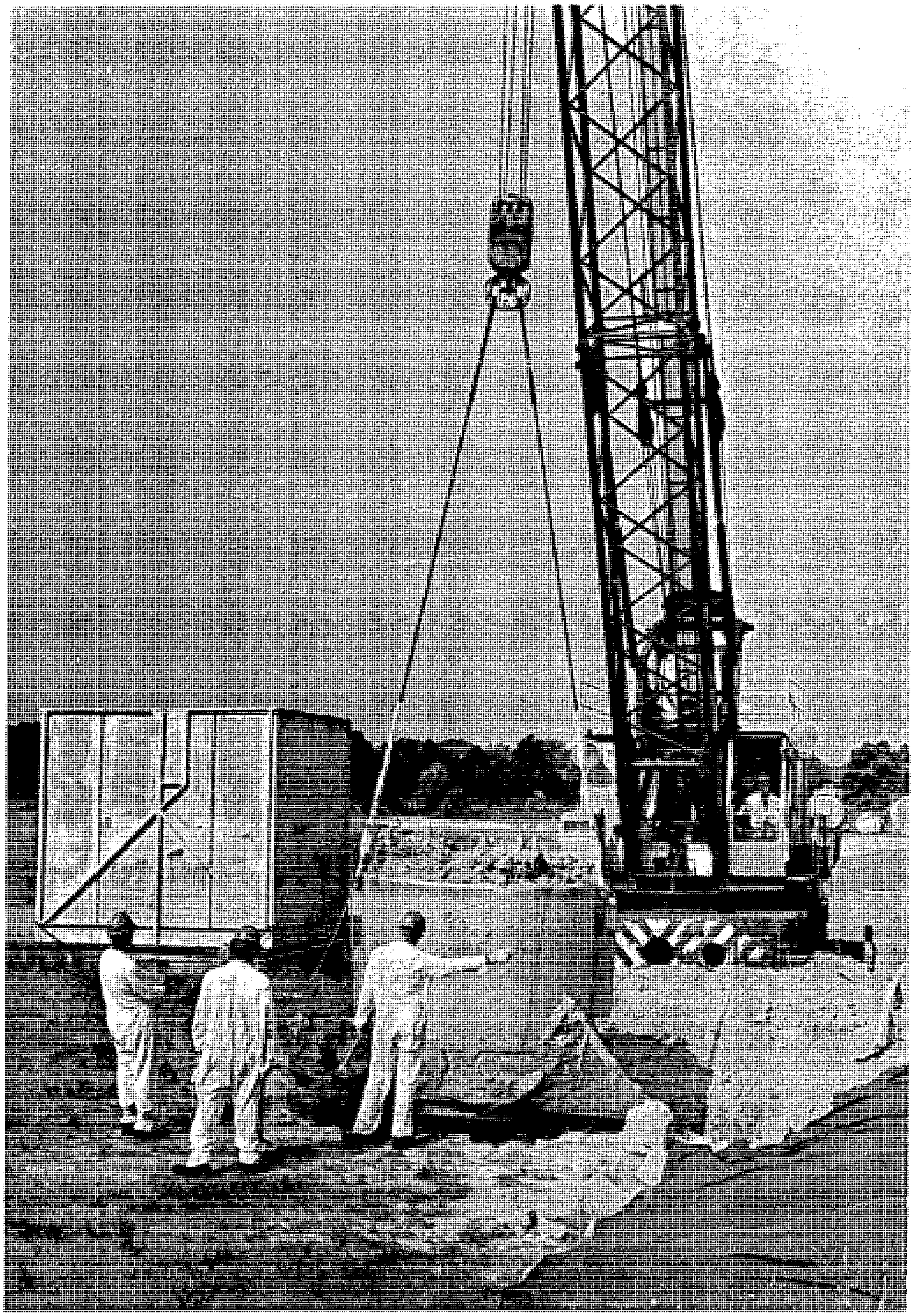

FIGURE 6. Purex Feed Adjustment Tank Being Lifted from Emplacement and Placed in Transport Box

Cleaning and Assaying Exhumed Tank

At the test site, a platform was constructed to permit working over the tank that was still contained in the transport box. About 350 gal of water was removed and sampled, leaving a mud cake that was core-sampled. The tank was lifted from the box and suspended over the adjacent open trench. The exterior soil was removed by washing as shown in Figure 7, and the interior mud cake was then washed out as shown in Figure 8. When contained soil was removed from the tank, cursory visual inspection revealed that the cooling coils were still intact. A closer view, Figure 9, revealed that the coils and interior of the vessel were bright and shiny, indicating that the vessel was in excellent metallurgical condition, as more thorough visual inspection later indicated.

After the tank was cleaned and visually inspected, radiation measurements began. These included beta-gamma measurements with a Cutie Pie (Figure 10); comprehensive alpha surveys of both exterior and interior as shown in Figure 11; and a gamma pulse height analysis using portable equipment (Figure 12). The beta-gamma activity averaged 3 mrad/hr at 1 ft from the tank. Figure 12 also shows the plastic hut that was used to prevent the spread of contamination from the tank.

Six 2-in.-diameter coupons were cut from the 3/8-in.-thick stainless steel tank wall (Figure 13) and bottom. These coupons

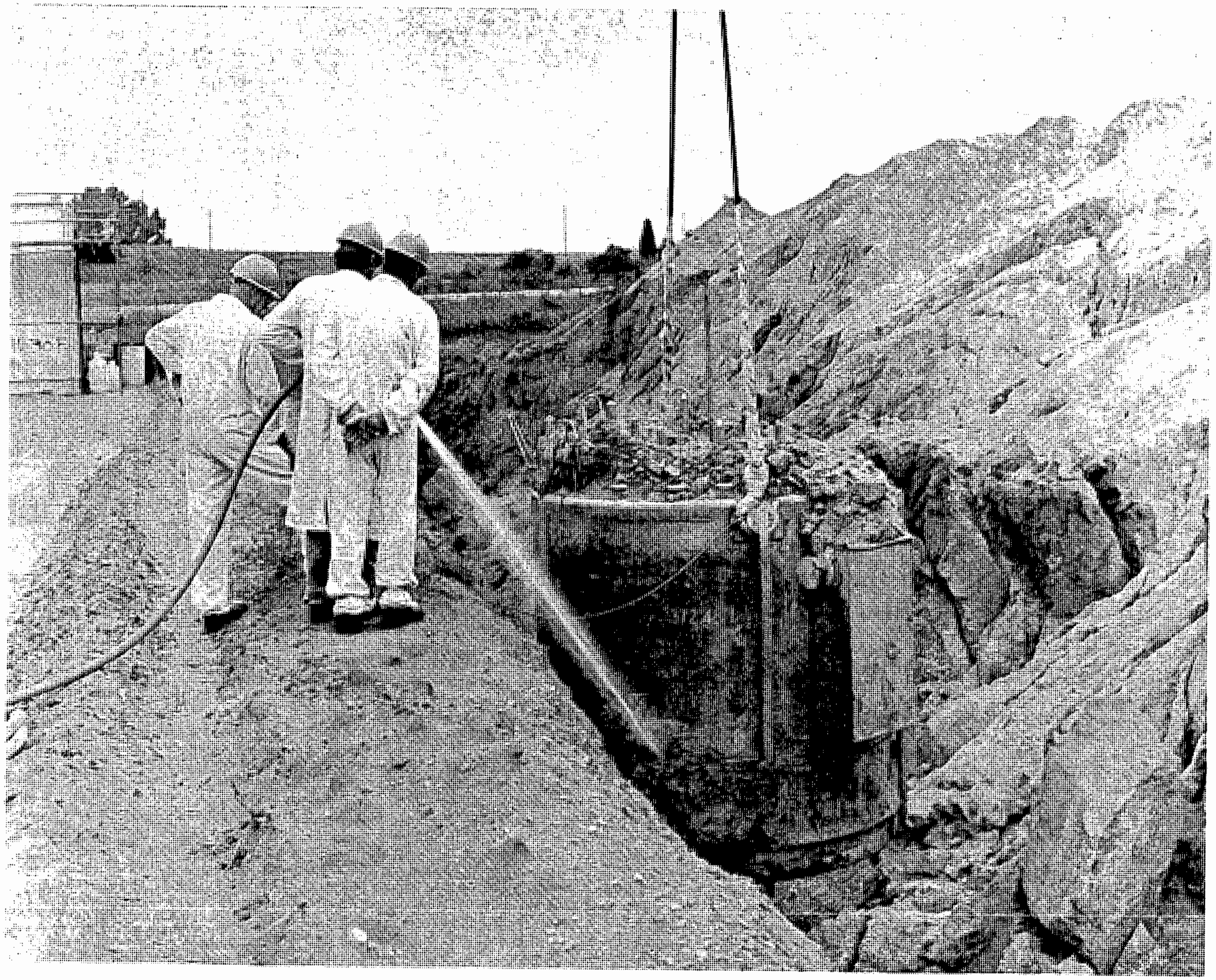

FIGURE 7. Washing Exterior of Exhumed Purex Feed Adjustment Tank

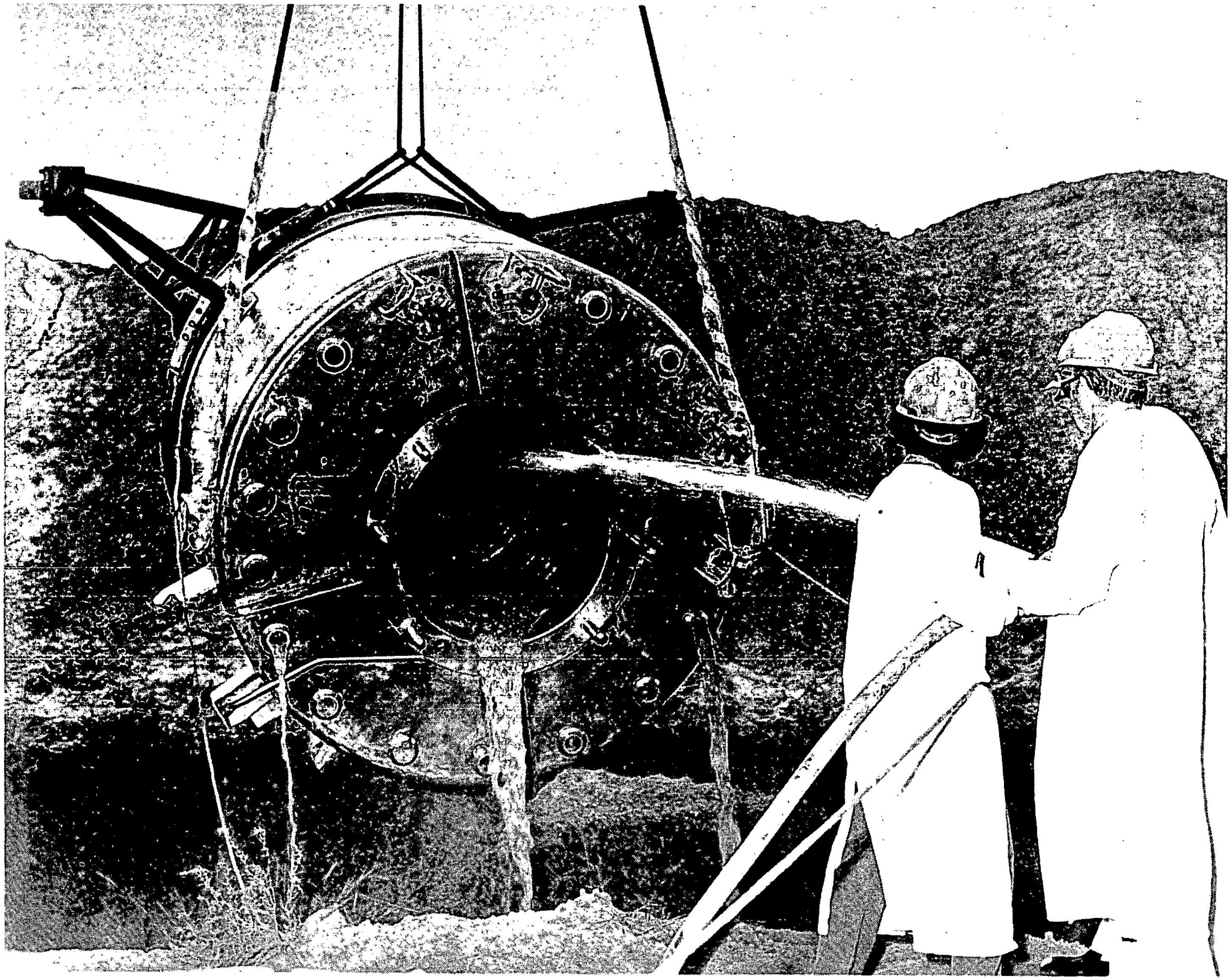

FIGURE 8. Washing Interior of Exhumed Purex Feed Adjustment Tank

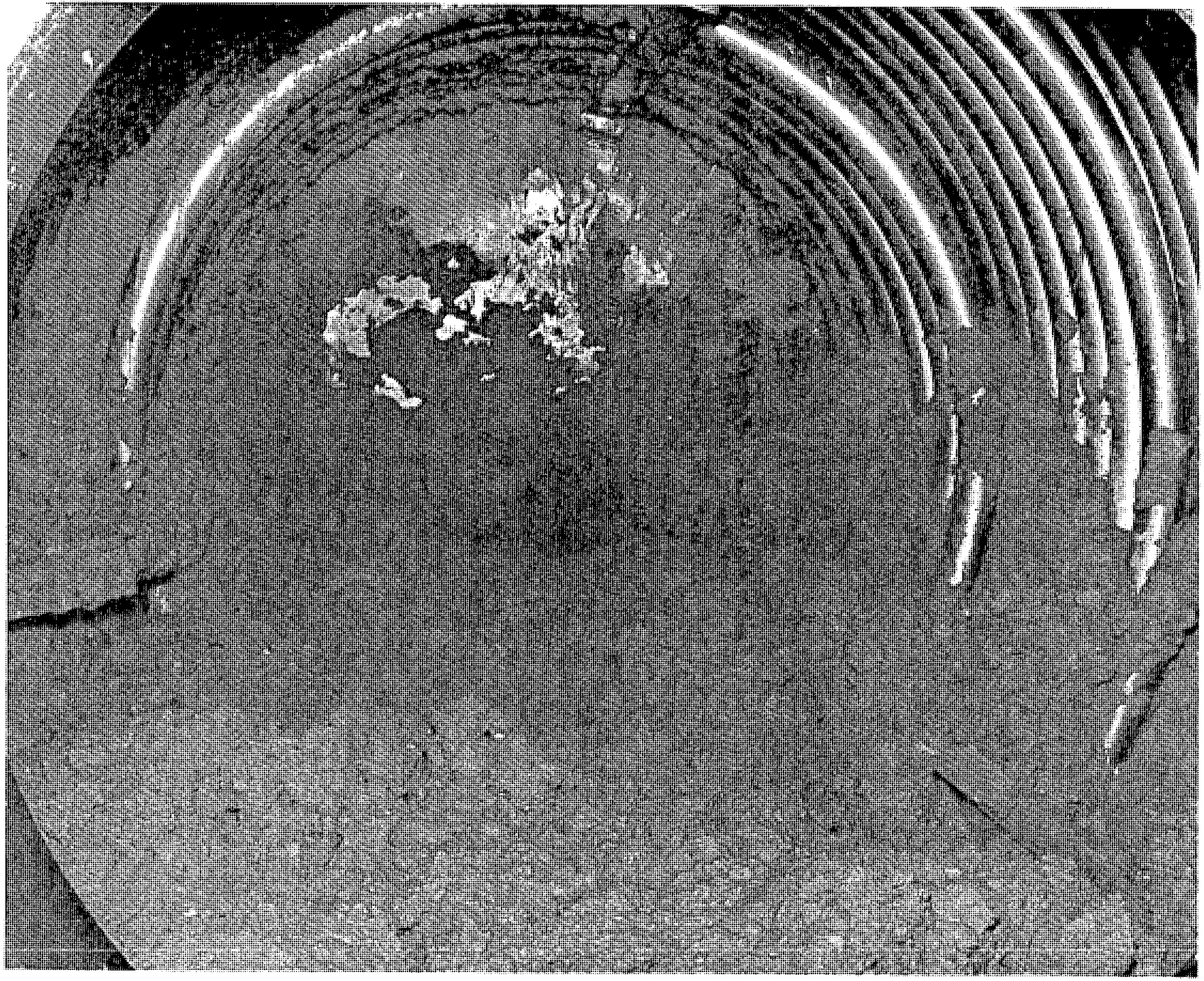

FIGURE 9. Interior of Exhumed Purex Feed Adjustment Tank

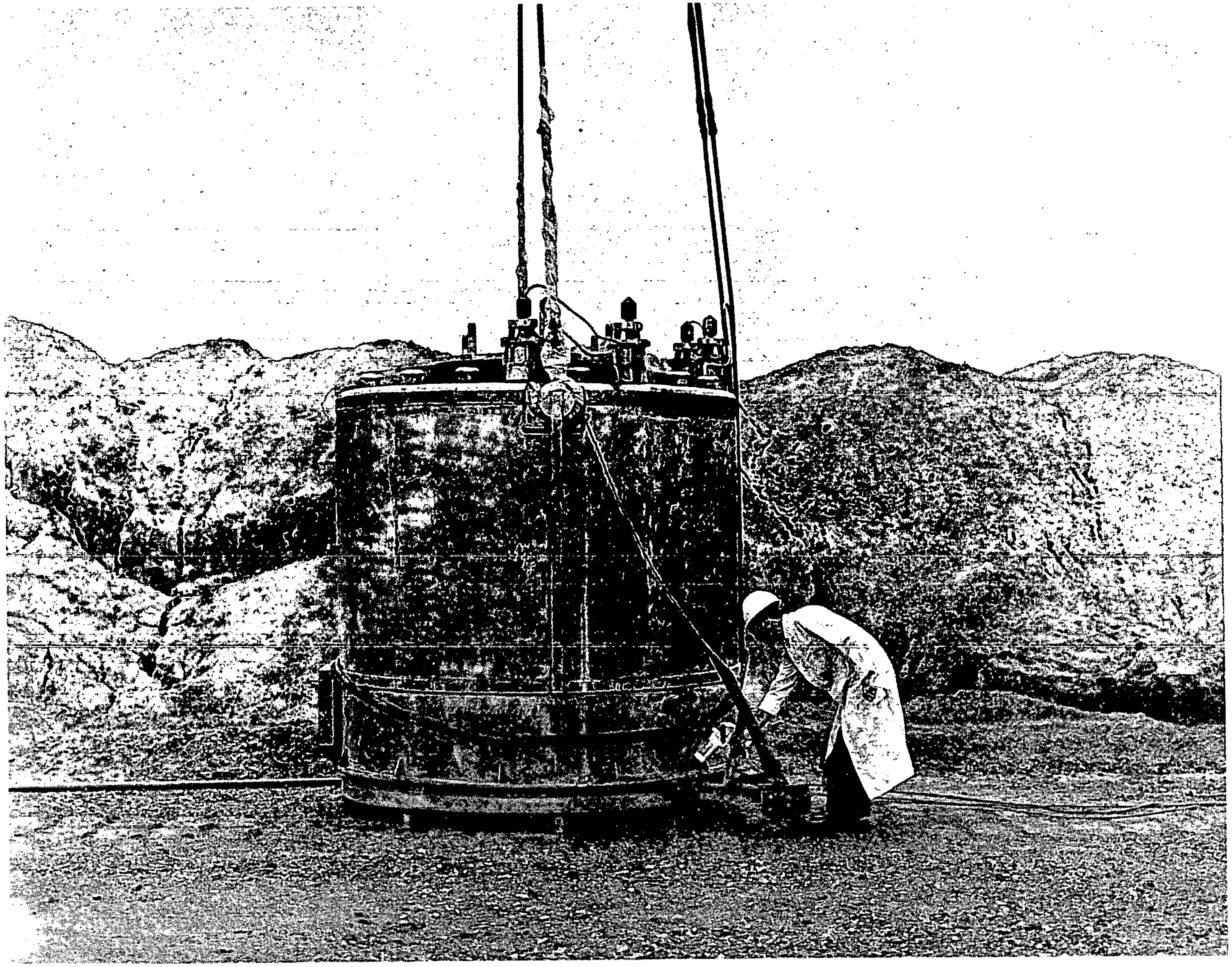

FIGURE 10. Beta-Gamma (Cutie Pie) Survey of Exhumed Purex Feed Adjustment Tank After Tank Was Washed

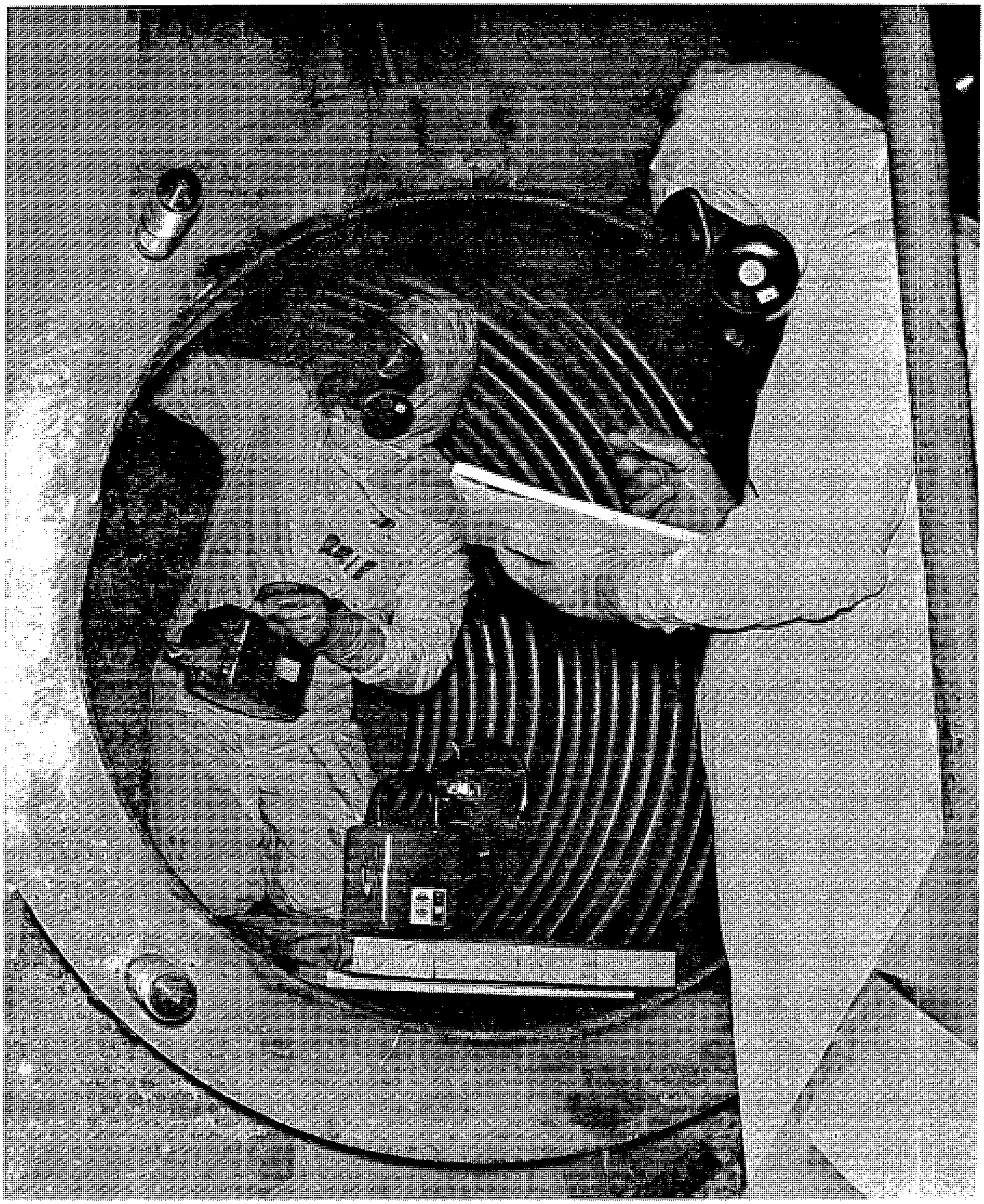

FIGURE 11. Alpha Activity Survey of Interior of Exhumed Purex Feed Adjustment Tank After Mud Removal

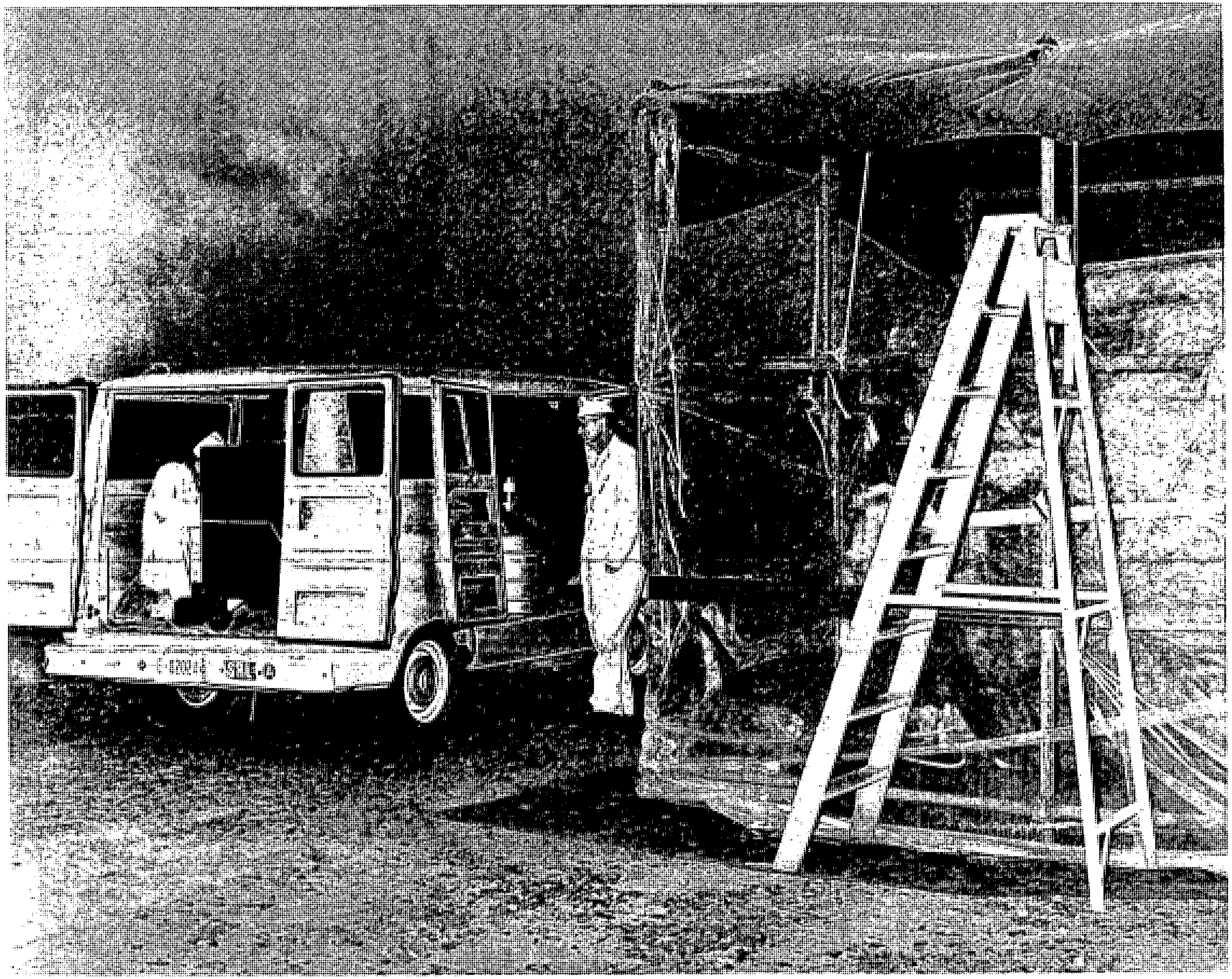

FIGURE 12. Gamma Pulse Height Analysis of Exhumed, Cleaned Purex Feed Adjustment Tank

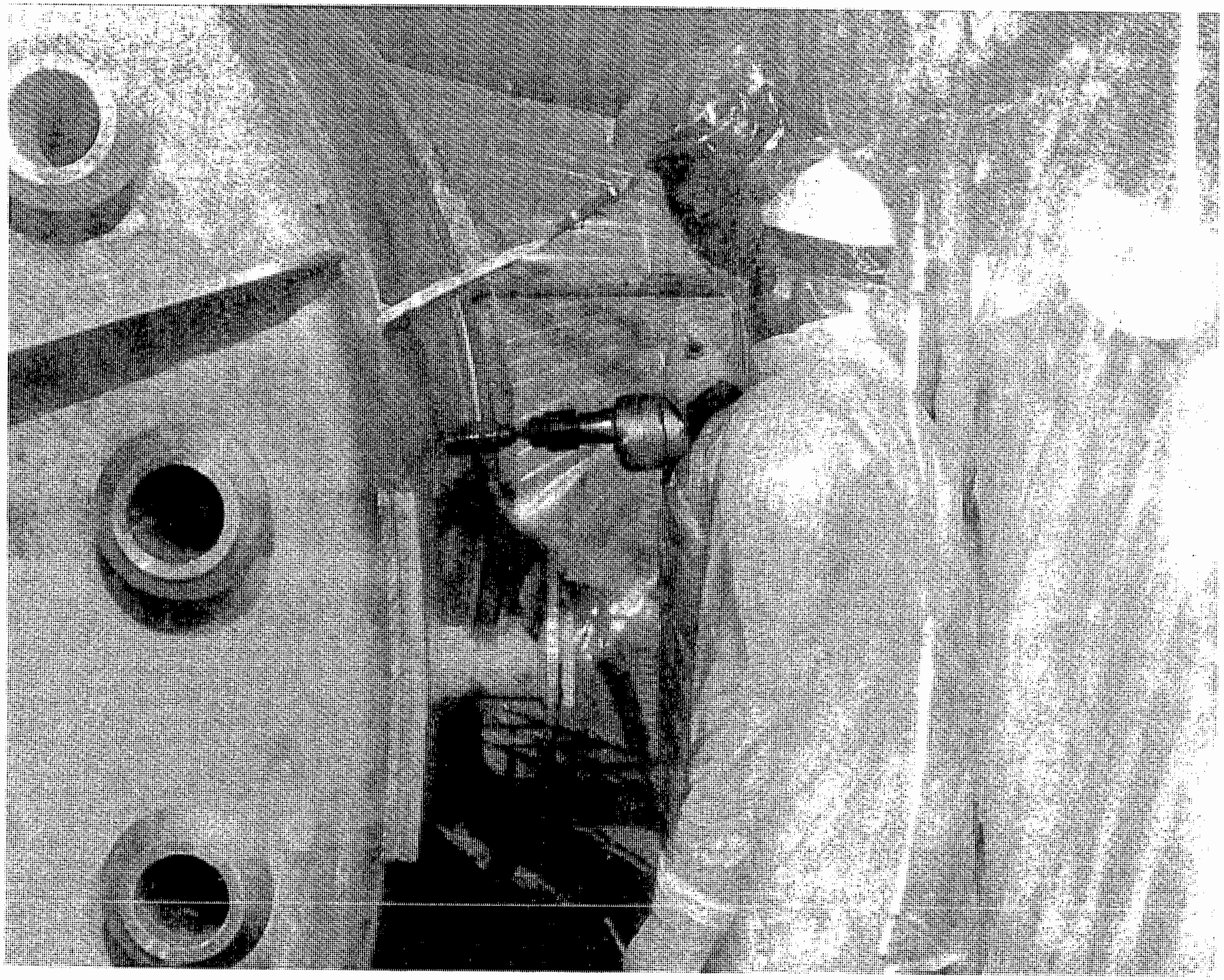

FIGURE 13. Cutting Sample Coupons from Exhumed Purex Feed Adjustment Tank

have been assayed for alpha and gamma emitters and are undergoing long-term leach testing in the laboratory.

Reburial of the feed adjustment tank in a lysimeter was originally planned, so radionuclidic leaching could be studied under natural conditions. Excavation of the lysimeter pit is shown in Figure 14. The pit is 16 to 18 ft deep with a sloping bottom and is 12 ft long and 13 ft wide. Installation of the 20-mil-thick polyvinyl chloride liner is shown in Figure 15. A standpipe to house a pump was installed, and a base was prepared with sand, gravel, and soil layers to support the vessel and to serve as a sump. However, when the TRU contamination level of the vessel was found to be lower than expected, a decision was made to rebury the vessel in the adjacent trench. Use of the lysimeter is planned for other exhumed equipment with higher contamination levels.

RESULTS

Table 1 summarizes the residual ^{239}Pu contamination found on individual surfaces of the exhumed tank. More than half of the contamination was found on the outside top surface; contamination on the mild steel trunion guides and supports contributed about 20% of the total of 7 mg of ^{239}Pu found. Under ERDA guidelines, waste with a TRU content of greater than 10 nCi/g must be stored retrievably. However, discarded bulky process equipment with a TRU content above 10 nCi/g is presently

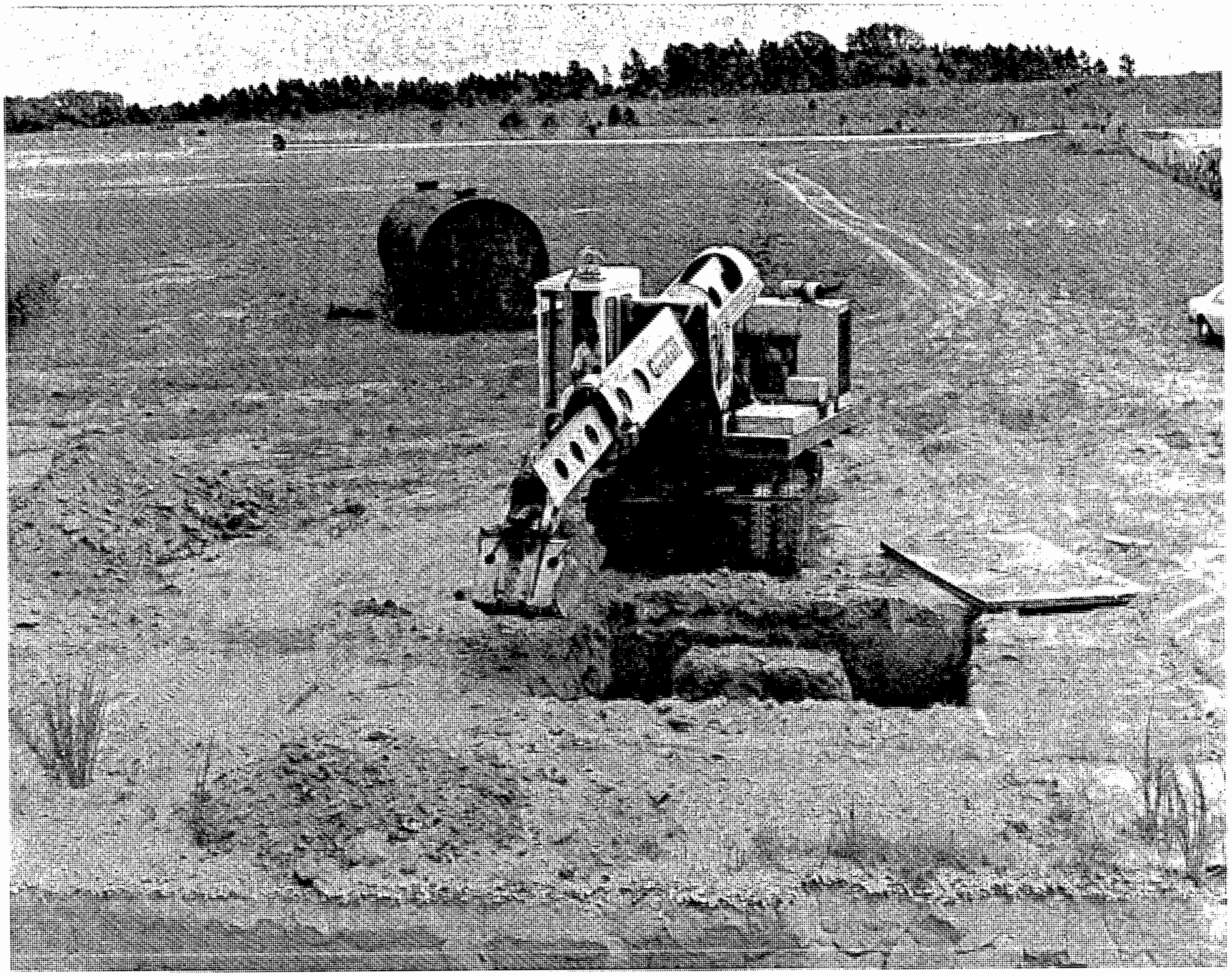

FIGURE 14. Excavation of Lysimeter Pit

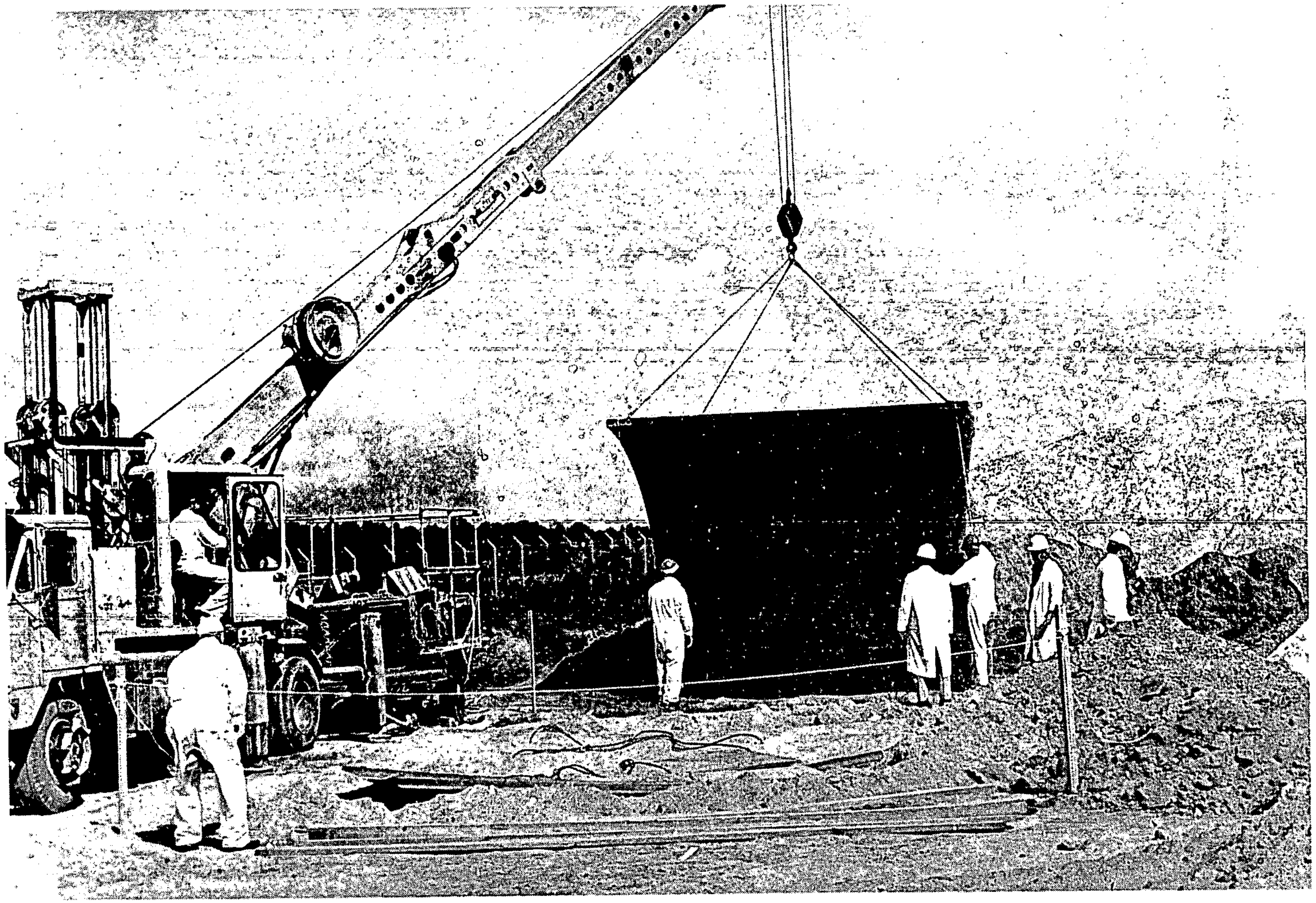

FIGURE 15. Installing Lysimeter Liner (20-mil-thick Polyvinyl Chloride)

exempted from retrievable storage at Savannah River. So, although the exhumed tank would be classified as bulky equipment, its low TRU content places it in the nonretrievable storage category. Table 2 shows that the total surface contamination is only about 1% of the guideline limit (10 nCi/g). Table 3 summarizes the quantities of ^{239}Pu found in the mud cake and water contained in the vessel upon exhumation. The mud, i.e., the soil and interstitial water, contained only 0.08 mg of plutonium, about 1% of the quantity found on the vessel surfaces; the 356 gal of water contained less than 0.01 mg of plutonium. A gamma pulse height analysis showed that ^{137}Cs was the only detectable gamma-emitting fission product on the tank surfaces; a total of 1 mCi of ^{137}Cs was determined to be present on the surfaces of the empty tank.

CONCLUSION

The primary conclusion so far from this continuing test is that this process vessel, a Purex feed adjustment tank, when buried 18 years ago, contained less plutonium than the 10 nCi/g that ERDA waste management standards currently define as TRU-contaminated, retrievable waste. However, this is only the first bit of information thus far obtained from an overall program to assess the long-term hazards of equipment burials. To provide a better data base for hazard assessment in planning for future surveillance and control of the burial ground site,

TABLE 1. Contribution of Individual Surfaces to Residual ^{239}Pu[a] in Exhumed Purex Feed Adjustment Tank

Vessel Surface	Area, ft^2	Total ^{239}Pu on Surface, dis/min	% of Total ^{239}Pu on Vessel
Wall, inside	201	7.0×10^7	7.4
Wall, outside	201	4.0×10^7	4.2
Bottom, inside	50	1.1×10^7	1.2
Bottom, outside	50	3.8×10^7	4.0
Top, inside	43	5.4×10^6	0.6
Top, outside	56	5.2×10^8	54.7
Top flange	5.5	9.6×10^6	1.0
Annular opening	7.1	3.3×10^6	0.3
Coils	307	6.1×10^7	6.4
Trunion guides and supports	11	1.9×10^8	20.0

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a. Total = 9.5×10^8 dis/min
Total ^{239}Pu = 7.0 mg
Total ^{239}Pu = 4.3×10^5 nCi

TABLE 2. ^{239}Pu Contamination in Exhumed Purex Feed Adjustment Tank, on Weight Basis

Total Empty Weight	7300 lb
Weight of Coils	1820
Total Weight	9120
or	4.14×10^6 g

$$\text{nCi/g} = \frac{4.30 \times 10^5 \text{ nCi}}{4.14 \times 10^6 \text{ g}} = 0.1 \text{ nCi/g}$$

TABLE 3. ^{239}Pu in Soil and Water Contained in Exhumed Purex Feed Adjustment Tank

SOIL (and interstitial water)

Layer Depth	^{239}Pu, pCi/g	^{239}Pu in Layer, pCi
0 - 1'	0.529	7.09×10^5
1' - 2'	0.072	9.65×10^4
2' - 3'	0.110	1.47×10^5
3' - 4'	0.094	1.26×10^5
4' - 4'10"	0.229	2.56×10^5
4'10" - 5'9"	0.667	8.20×10^5
5'9" - 5'10"	4.963	2.53×10^6

TOTAL = 4.68×10^6 pCi
= 1.04×10^7 dis/min
= 0.076 mg

WATER

Emptied from vessel = 356 gal or 1.35×10^6 ml
Analysis of composite sample = <1 dis/min/ml ^{239}Pu
Total ^{239}Pu in water = <1.35×10^6 dis/min
= <0.01 mg

further exhumations and testing of other equipment, potentially more highly contaminated, is being contemplated. Therefore, this program will not likely conclude with the study of only this one piece of buried, bulky equipment.

VOLUME REDUCTION OF PLUTONIUM-CONTAMINATED SOIL

J. H. Horton

A laboratory study was conducted to determine if plutonium in soil at the SRP burial ground is primarily associated with the sand, silt, or clay fractions. Approximately three million cubic feet (maximum) of soil and waste in burial ground trenches may be contaminated with plutonium; this contaminated soil and waste may be retrieved in the future for long-term storage. Separation of the sand, silt, and clay components would reduce the volume of soil requiring further treatment and storage if the plutonium is primarily associated with one of these fractions.

A series of simple laboratory experiments involving water-scrubbing and washing was designed to determine the value of such a step in a conceptual process for volume reduction of soil from plutonium waste trenches in the SRP burial ground. By water washing and scrubbing the soil, the clay-silt fraction containing about 95% of the plutonium, but comprising only one-third of the total soil, was separated from the sand fraction that contained about 5% of the plutonium. The concept of simple water washing or scrubbing was also attractive because wet soil would substantially reduce atmospheric resuspension of plutonium particles during exhumation and because the technology of sand cleaning by water is widely used and relatively inexpensive.

DETAILS

A sample of soil removed from a burial ground trench filled with TRU waste in 1964 was used for these tests. A gamma pulse height analysis showed the soil contained 93 nCi of ^{238}Pu per gram of soil; ^{238}Pu was the only significant alpha emitter found.

The mining industry has developed water-based processes for sorting granular materials. Production of sand meeting ASTM specifications involves scrubbing and washing to remove "fines." Because burial ground soil is about two-thirds sand, this simple operation suggested the possibility of reducing the volume of plutonium-contaminated soil to about one-third of the original volume provided the plutonium is associated with the silt and clay fractions of the soil. This method was tested with the equipment shown in Figure 16. The magnetic stirrer provided scrubbing, and the flow rate of the water could be varied to remove different particle sizes. The plastic pipe was attached to the flask to dampen the stirring action before the particles flowed out of the system and to provide a uniform cross section so that the size of particles removed could be more accurately calculated with Stoke's law. The effluent from the system was collected in 150-ml aliquots. To determine the quantity of plutonium removed in each aliquot, 3 ml was removed while the sample was stirred with a magnetic stirrer. The 3-ml aliquot was used for alpha activity measurements.

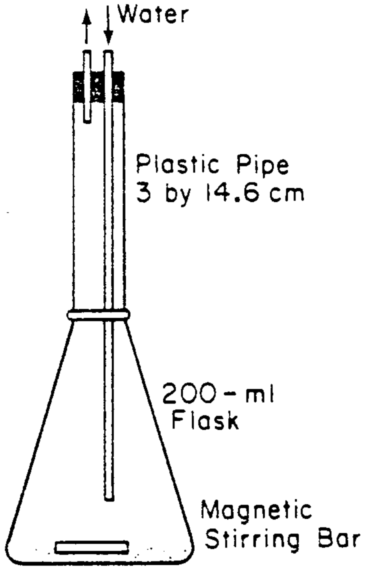

FIGURE 16. Laboratory Equipment for Scrubbing and Washing Soil

The plutonium concentration in the effluent decreased exponentially so that the results could be described by the following equation:

$$\frac{C}{Co} = e^{-bv}$$

where

C_o = concentration in effluent when flow began

C = concentration in effluent after a flow of volume v

b = elution constant, v^{-1}

v = volume of flow

The data from each test was fitted to a straight line by the least squares method. The results are presented as straight lines calculated with $C_o = 1.0$. Various stirring times before flow began and various flow rates were compared to determine their influence upon the removal of plutonium and the residue of plutonium in the washed sand.

A comparison of ^{238}Pu removal at various flow rates is summarized in Figure 17. In these tests, the soil sample was placed in the flask, and 50 ml of water was added. The total volume of wash water was 1500 ml. Scrubbing time before washing was 10 min. With increasing flow, the rate of plutonium removal increased. As shown in Table 4, the plutonium removed in the clay-silt fraction increased as the flow rate increased. Also, the increased flow rate leaves a smaller amount of washed sand.

The effect of prewash scrubbing times on washing of ^{238}Pu is summarized in Figure 18. The flow rate in these tests was

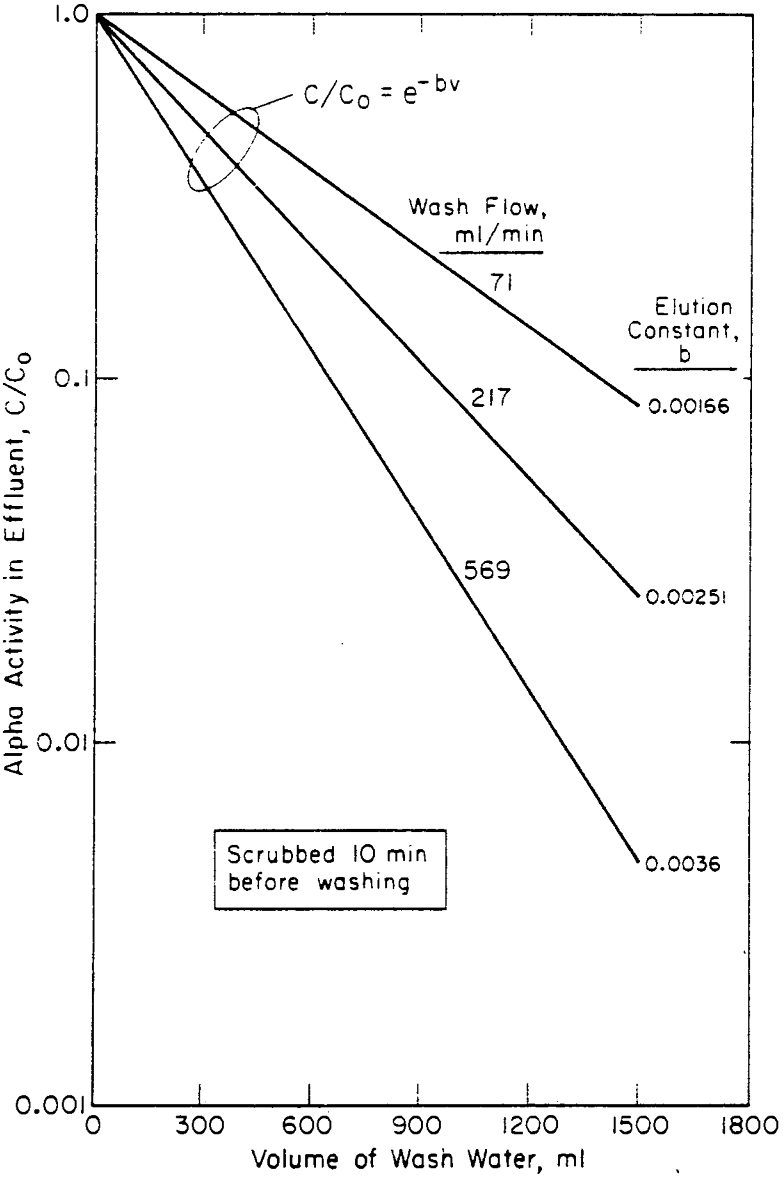

FIGURE 17. Removal of ^{238}Pu from Burial Ground Soil by Scrubbing and Washing at Various Flows

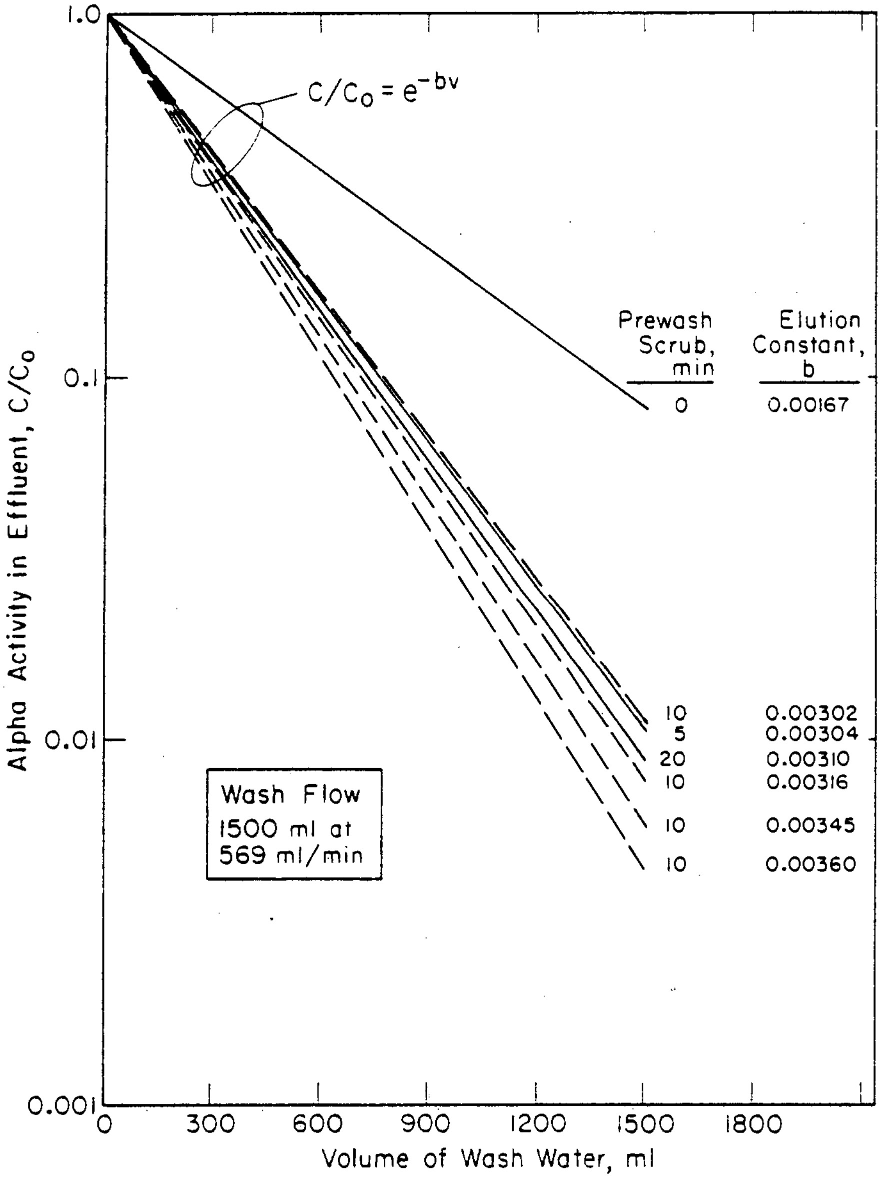

FIGURE 18. Effect of Prewash Scrubbing Time and Washing of ^{238}Pu from Burial Ground Soil

569 ml/min, and the total flow was 1500 ml. Scrubbing continued throughout the elution of fines. The elution rate of fines increased considerably with scrubbing times of 5 to 20 min before washing. The test was repeated four times with a 10-min scrubbing time to determine the variation between samples. These results are shown by the dashed lines. The variation is so great that little would be gained by continued study in the laboratory because scrubbing times using one type of equipment are not comparable with scrubbing times using another type of equipment. The amount of scrubbing required can best be determined using full-scale equipment because the amount will be different for each type of experiment. However, these data do indicate that no reasonable amount of scrubbing will remove all of the plutonium from the sand. Other data from these tests are summarized in Table 5 which again shows that in this particular experiment, scrubbing beyond 10 min does not improve the removal of plutonium in the clay-silt fraction.

To determine if additional washing would be worthwhile, two tests were made in which the total flow was 3000 ml, or double the volume used previously. The scrubbing time before washing was 10 min, and the flow rate was 569 ml/min. However, the extended washing had no effect on the elution constant. The washed sand was 60 and 63% of the total soil, and 97.3% of the plutonium was removed in the fines in both tests.

TABLE 4. Effects of Wash Flow on Soil Classification

Scrubbed 10 min before washing; wash volume 1500 ml

Wash Flow, ml/min	Washed Sand, % of soil	Largest Particle Eluted, µm	Plutonium in Clay-Silt Fraction, % of initial
71	88	38	29.9
217	82	66	88.4
569	76	110	96.3

TABLE 5. Effects of Pre-Wash Scrubbing on Soil Classification

Wash flow 560 ml/min; wash volume 1500 ml

Pre-Wash Scrubbing Time, min	Washed Sand, % of soil	Plutonium in Clay-Silt Fraction, % of initial
0	81	79.6
5	69	93.3
10	76	96.3
10	64	97.1
20	62	95.6

During the course of the scrub tests, there were indications that the ^{238}Pu was present in the soil as tiny particles. This was verified by radioautographs. For the radioautographs, a suspension of fines, washed from the burial ground soil during the scrubbing and washing test, was deposited on a steel disk, dried, and coated with collodian. The results of an 8-day exposure to X-ray film is shown in Figure 19. Sample 1 contained 2800 pCi, and Sample 2 contained 950 pCi.

Commercial scrubbers are expected to decontaminate the sand much more effectively than the laboratory apparatus, and commercial classifiers can remove any specified range of particle sizes.

Little water would be needed because it can be recirculated. The clay-silt did not peptize but settled rapidly. After standing overnight, the alpha activity of the wash water was only 0.5 pCi/ml. Eventually the recycled water will become turbid and must then be purified or discarded. Filtration

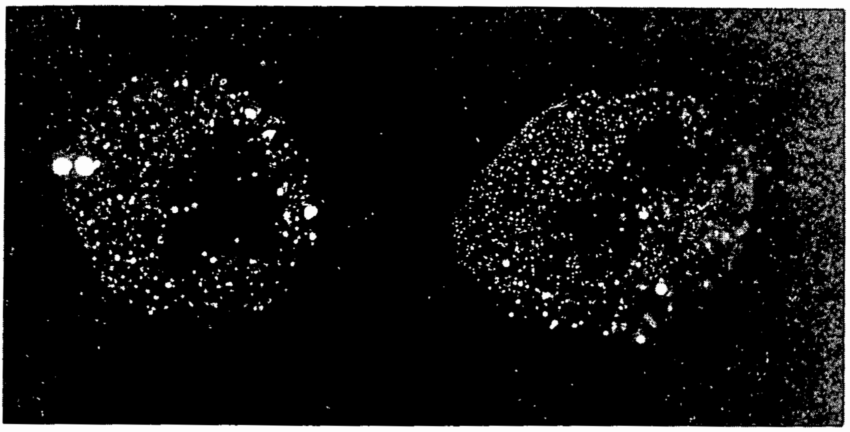

FIGURE 19. Autoradiograph of Clay-Silt from Burial Ground Soil

should provide adequate purification. This phase of the study can probably not be evaluated in the laboratory but could be performed with pilot scale or production equipment using clean soil.

The method should be applicable to any soil containing a large fraction of quartz and sand regardless of the method of contamination with plutonium.

MOVEMENT OF ORGANICALLY BOUND PLUTONIUM IN SOIL

E. L. Wilhite

At SRP, irradiated fuel elements are chemically reprocessed by the Purex process. This process uses tri-n-butyl phosphate (TBP) dissolved in a hydrocarbon diluent in the solvent extraction step for separation and purification of plutonium and uranium. During the process, the TBP-hydrocarbon solution is attacked and degraded by reagents used in the process and by radiation from fission products. Degradation products are removed by washing during processing, but eventually some species accumulate that resist removal by washing and adversely affect solvent extraction performance. When the solvent is no longer usable in the process, it is transferred to the burial ground for storage in underground tanks.

The safety of SRP burial ground operations is being reviewed. As a part of the safety analysis, the consequences of a massive leak of stored spent process solvent from the underground tanks at the burial ground were evaluated. A laboratory study was completed to determine the movement of organically bound plutonium in soil as part of an evaluation of the environmental risk of storing contaminated solvent in underground tanks at the burial ground. The maximum credible release of stored solvent was defined as the release of the entire contents of Solvent Storage Tank 2. This tank contains 27 Ci of plutonium (88% ^{238}Pu) in 8025 gal of solvent, the largest amount of plutonium in any tank.

DETAILS

Spent Solvent Storage

Spent solvent has been stored at the burial ground since 1955. The burial ground is situated between the two chemical reprocessing areas (Figure 20). The solvent storage tanks are situated roughly at the center of the burial ground about 0.7 mi from the nearest surface stream (Four Mile Creek). There are currently 22 solvent storage tanks, two of which (Tanks 8 and 17) are no longer in service because of past leaks. Before 1972, the solvent inventory was reduced by burning.(1) Burning resulted in very low emission of airborne radioactivity

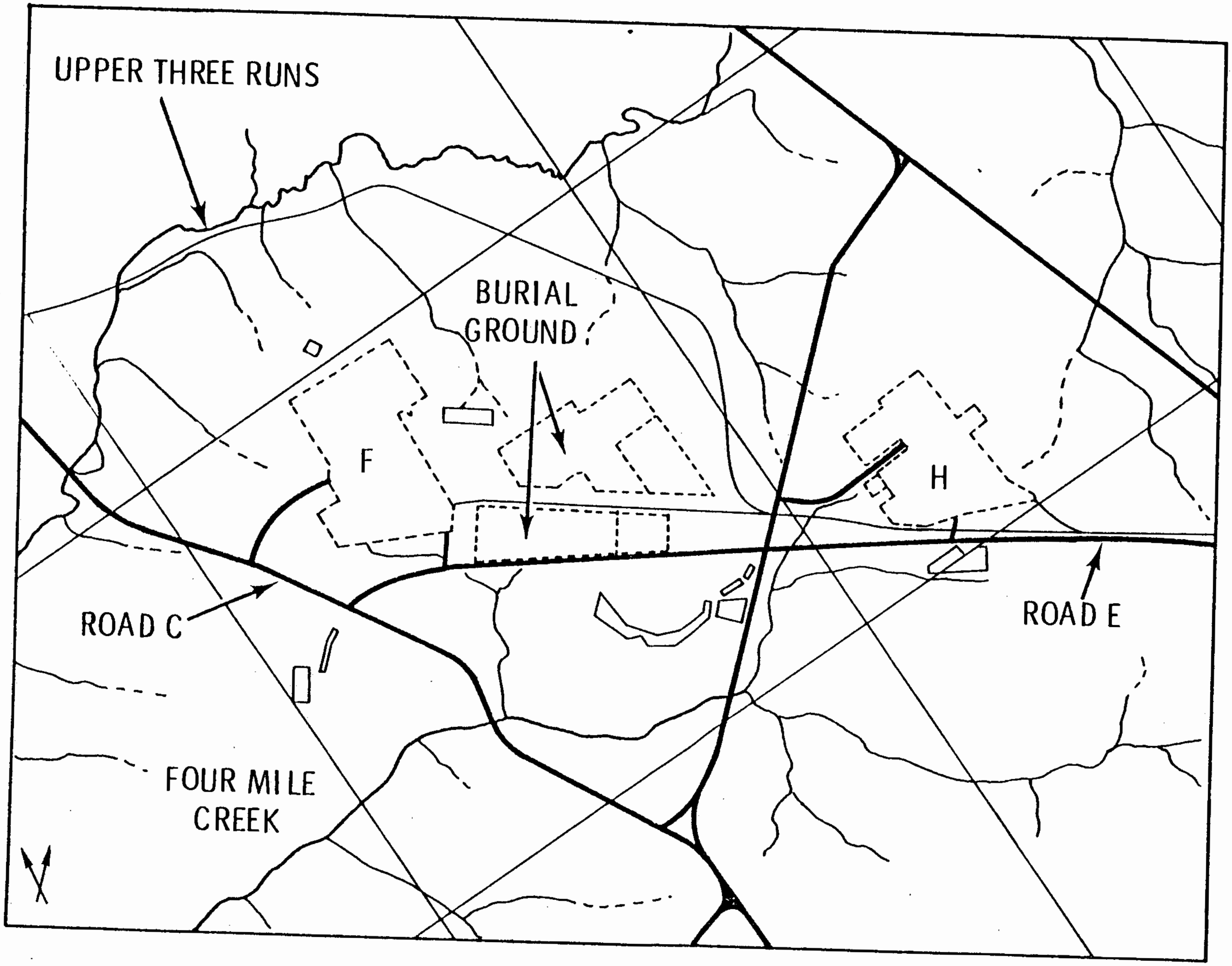

FIGURE 20. Chemical Separations Areas - Savannah River Plant

but did release copious quantities of black smoke. Environmental restrictions on smoke emissions caused burning operations to cease in 1972. During 16 years of solvent incineration, about 370,000 gal of spent solvent were burned.

The current inventory of solvent is shown in Table 6. The 150,000 gal of solvent contains 45.6 Ci of TRU nuclides and about 46.2 Ci of fission products. Plutonium-238 is the predominant TRU nuclide in the solvent, and the primary fission product is ^{106}Ru.

Solvent-Soil Plutonium Transfer

The characteristics of plutonium transfer from spent solvent to soil and ground water were investigated in a series of laboratory tests. The interaction of solvent-bound plutonium and dry soil is shown in Table 7. In this test, 1.0 ml of solvent from Tank 2 [2.1×10^6 alpha dis/(min)/(ml)] was sorbed on dry soil and placed at the top of each of two columns of soil. The columns were then eluted by down-flow with ground water. After 2 months of operation, the columns were dismantled, and the soil was sectioned into 0.1-in. segments for analysis. During the course of the experiment, no plutonium was detected in the effluent from the columns. In each column, little movement of the plutonium was noted (∿95% retained in the top 1/2 in.). K_d(a) is estimated at 6000 for the short column and

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(a) K_d = sorbed Pu (per gram soil)/unsorbed Pu (per ml of equlibrated water).

3000 for the long column. Earlier studies[(2)] at SRL have shown that K_d for plutonium is on the order of 1000 to 8000 for a pH range of 5.5 to 7.0.

TABLE 6. Solvent Inventory

Tank	Solvent Volume, gal	TRU Content, Ci	Major TRU Nuclide (alpha percent)	Fission Product Content, Ci
1	6,100	0.5	^{244}Cm (66%)	3.5
2	8,025	27.0	^{238}Pu (88%)	5.2
3	8,400	0.02	^{238}Pu (70%)	0.013
4	275	0.006	^{238}Pu (67%)	0.001
5	9,780	17.0	^{244}Cm (93%)	11.0
6	19,350	0.06	^{244}Cm (80%)	0.26
7	2,075	0.01	^{238}Pu (77%)	0.014
8[a]	Contains no liquid			
9	4,135	0.006	^{239}Pu (30%)	2.0
10	1,365	0.003	^{238}Pu (50%)	0.05
11	6,190	0.2	^{244}Cm (56%)	0.6
12	5,025	0.15	^{238}Pu (63%)	0.5
13	11,500	0.08	^{238}Pu (97%)	0.2
14	22,700	0.15	^{238}Pu (98%)	0.15
15	7,550	0.18	^{244}Cm (63%)	1.4
16	2,000	0.003	-	0.0007
17[a]	100	0.013	^{239}Pu (60%)	0.29
18	965	0.007	^{239}Pu (30%)	3.5
19	19,500	0.1	^{244}Cm (65%)	2.6
20	7,900	0.06	^{238}Pu (60%)	15.0
21	3,100	0.001	-	0.013
22	2,900	0.0008	^{244}Cm (70%)	0.004
Total	148,935	45.6	^{238}Pu (54%)	46.2

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[a] Tank no longer in service due to past leak.

TABLE 7. Columns Treated with 1.0 ml Tank 2 Solvent (2.1×10^6 dis/min/ml) Sorbed on Dry Soil

Column Length, in.	Effluent Collected	
	Liters	Bed Volumes
2.6	48.5	1450
5.8	24.5	330

Movement Down Column, in.	Gross Alpha in 0.1 in. soil, dis/min	
	2.6 in. Column	5.8 in. Column
0.1	6.2×10^5	-
0.2	2.4×10^5	4.1×10^5
0.4	1.1×10^5	2.1×10^5
0.5	1.7×10^5	2.8×10^5
0.6	2.1×10^4	1.3×10^4
0.8	5.2×10^3	8.4×10^3
0.9	2.6×10^3	1.1×10^4
1.0	3.0×10^3	3.4×10^3
1.1	-	1.2×10^3
1.2	-	<10
1.4	-	<10
1.5	-	<10
1.6	-	<10

The sorption of solvent-bound plutonium in moist soil is shown in Figure 21. In this test, Tank 18 solvent was passed through a previously water-saturated soil column (25-ml bed volume). The effluent was analyzed for plutonium. Although there is some scatter in the data, the results clearly show little retention of plutonium on wet soil. Plutonium K_d for this test is estimated to be less than 10.

In other tests (Table 8), ground water was equilibrated with solvent from Tanks 2 and 20 to determine the transfer of plutonium from solvent to water. The distribution coeffi-

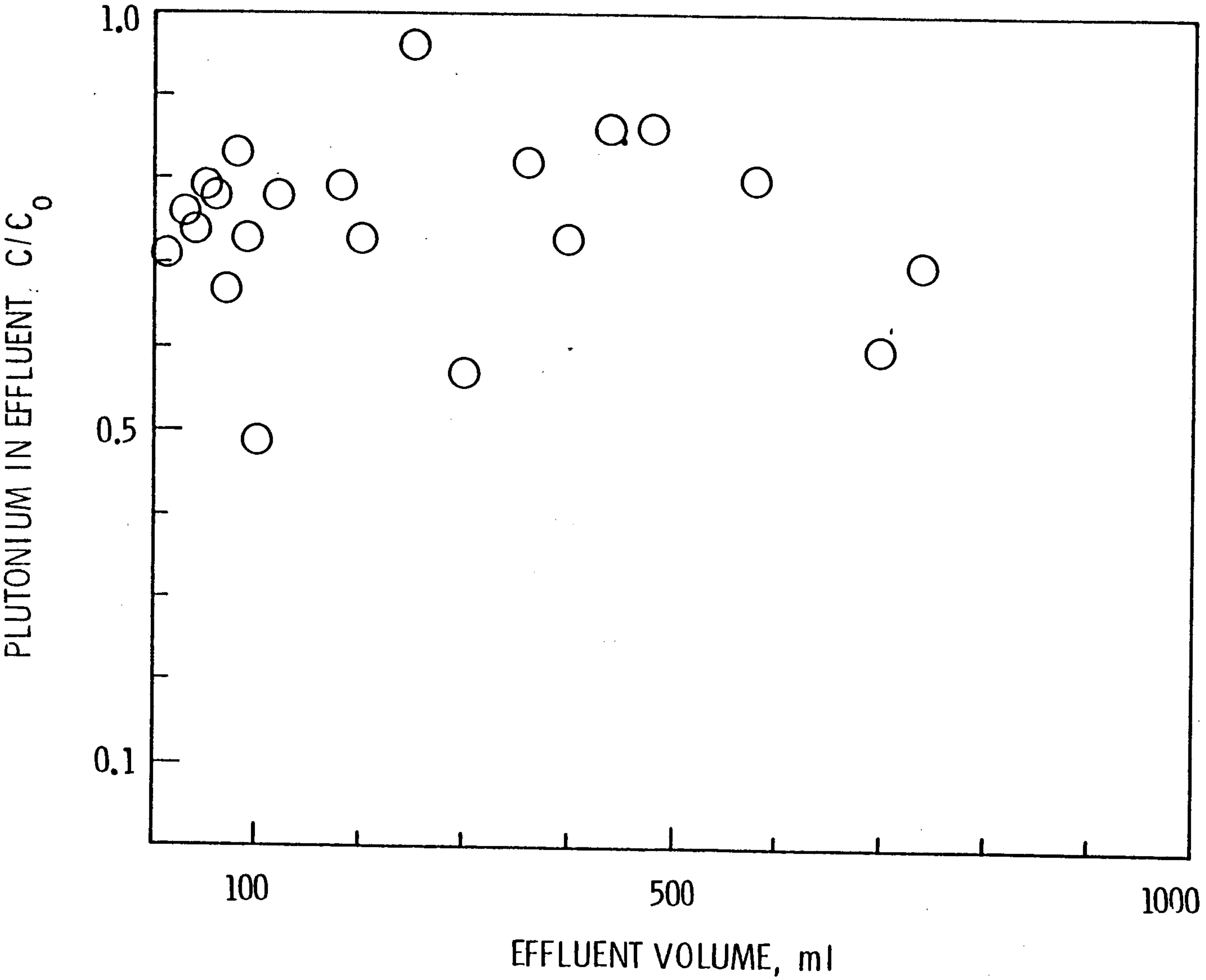

FIGURE 21. Column Test with Tank 18 Solvent and Water-Saturated Soil

plutonium from solvent to water. The distribution coefficients[a] were 0.001 to 0.01. The degree of absorption by soil of plutonium transferred to water from Tank 2 solvent was found to be moderate (K_d = 150 + 60).

TABLE 8. Transfer of Plutonium from Solvent to Water

Solvent Sample	Distribution Coefficient
Tank 2	0.001 ±0.0005
Tank 20	0.01 ±0.01

Retention of Plutonium (transferred from Solvent to Water) by Soil

Solvent Sample	K_d
Tank 2	150 ±60

The laboratory tests show that solvent released to moist, subsurface soil will not be effectively sorbed, and plutonium will be mobile. Thus, in the event of a leak in one of the underground tanks, solvent may migrate to the water table with little loss of plutonium to the soil. At the water table, the solvent will tend to spread as a thin film over the soil water surface. The rate and extent of this spreading action has not been defined. However, laboratory tests verify that solvent-bound plutonium will transfer to soil water with subsequent

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(a) Distribution coefficient - Pu in water (dis/min/ml)/Pu in equlibrated solvent (dis/min/ml).

transfer of plutonium to soil. Thus, the amount of plutonium remaining in solvent after spreading on water is estimated as outlined in Figure 22.

The calculated distribution of plutonium between solvent and soil is shown in Table 9. The area of solvent spreading was estimated by assuming plutonium interaction with a 2-in. depth of water-saturated soil (bulk density = 1.5 g/cm^3). The fraction of plutonium remaining in the solvent was calculated iteratively to account for plutonium transfer to soil as solvent spreading occurs.

TABLE 9. Calculated Distribution of Plutonium Between Solvent and Soil[a]

Soil Mass, g	Area, acres	Fraction of Plutonium Remaining in Solvent	Fraction of Plutonium Remaining in Soil
1×10^5	0.0003	0.9975	0.0025
1×10^7	0.03	0.802	0.198
1×10^9	3.0	0.039	0.961
1×10^{10}	30.0	0.004	0.996

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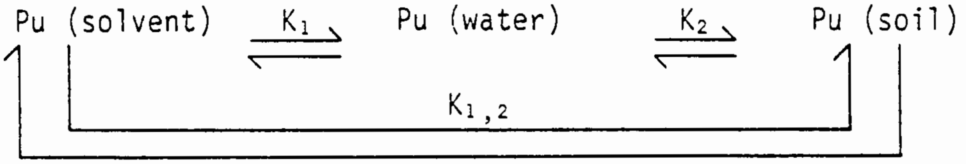
a. See Figure 22.

Although solvent released to the subsurface water table may spread to a considerable extent, plutonium will be removed from the solvent and become fixed on the soil as a result of interaction with soil water. In spreading over about 3 acres of water table, approximately 96% of the plutonium originally in the solvent will have become fixed on the soil. After spreading to 30 acres, greater than 99% of the plutonium will have been sorbed.



K_1 = distribution coefficient

K_2 = K_d

$K_{1,2}$ = $K_1 \cdot K_2$

$$K_{1,2} = \frac{\text{Pu on soil, pCi/g}}{\text{Pu in solvent, pCi/ml}}$$

$$K_{1,2} = \frac{f_{soil}}{f_{solvent}} \cdot \frac{V_{solvent}}{M_{soil}}$$

where: f_{soil} = fraction of plutonium sorbed on soil

$f_{solvent}$ = fraction of plutonium remaining in solvent

$V_{solvent}$ = volume of solvent, ml

M_{soil} = mass of soil, g

FIGURE 22. Plutonium Transfer from Solvent to Soil

The maximum amount of plutonium that could be released from a leaking tank is the 27 Ci contained in Tank 2 (Table 10). If the entire quantity of solvent in Tank 2 were to leak from the tank, about 30 acres of soil at the water table would be contaminated with plutonium at an average concentration of about 2600 pCi/g. The maximum soil concentration would be approximately 9×10^4 pCi/g over 0.3 acre. A proposed interim standard for plutonium in soil is 400 pCi/g for inhabited areas.(3) The maximum concentration of plutonium in soil water over a 0.3-acre extent would be 6×10^5 pCi/l. Soil water over a 30-acre extent would contain an average plutonium concentration of 17,600 pCi/l. The current ERDA standard for plutonium in water is 5000 pCi/l for an uncontrolled area.(4)

TABLE 10. Consequences of Postulated Leaking Tank (Release of 27 Ci of Plutonium in 8025 Gal of Solvent)

Distribution of Plutonium Released to the Environment

Average soil concentration:	2600 pCi/g over 30 acres
Maximum soil concentration:	9×10^4 pCi/g over 0.3 acre
Average water concentration:	17,600 pCi/ℓ
Maximum water concentration:	6×10^5 pCi/ℓ
Long-term release of ^{239}Pu:	500 pCi/ℓ at ground water outcrop <1 pCi/ℓ in Four Mile Creek

Plutonium sorbed on soil as a result of the postulated solvent tank leak would move slowly through the soil-water system. At least 50,000 years would be required for the plutonium to reach Four Mile Creek. During this time, almost all of the ^{238}Pu will decay, leaving only about 0.8 Ci of ^{239}Pu. Extrapolated concentrations of ^{239}Pu in water would be approximately 500 pCi/l at the ground water outcrop and less than 1 pCi/l after dilution in Four Mile Creek.

CONCLUSION

In summary, although a postulated massive leak of solvent would result in soil and ground water being contaminated with plutonium, most of the plutonium (∿90% ^{238}Pu) will decay within the SRP boundaries. Any transport of plutonium to local surface streams will result in releases below the present operating guides for normal SRP operation.

To minimize the probability of the release of large volumes of waste solvent to the subsurface environment, six new storage tanks with liquid level monitors and leak detectors have recently been installed at SRP. Stored solvent will be transferred to the new tanks early in 1976. After removal of solvent, the old tanks will be abandoned in place. To reduce the solvent inventory, a two-stage solvent incinerator equipped with an exhaust gas scrubber is being designed. The incinerator will process the current inventory in less than 2 years of operation. With expected waste solvent receipts of less than 5000 gal/year, storage inventory will be minimal after incineration of the present inventory.

REFERENCES

1. Tharin, D. W., Burning of Radioactive Process Solvent, USAEC Report DP-942, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC, 1965.
2. Prout, W. E., "Adsorption of Radioactive Wastes by Savannah River Plant Soil," Soil Science 86, 13, 1958.
3. Healy, J. N., A Proposed Interim Standard for Plutonium in Soils, USAEC Report LA-5483-MS, Los Alamos Scientific Laboratory, Los Alamos, NM, 1974.
4. "Standards for Radiation Protection," Chapter 0524 in USERDA Manual, Washington, DC, 1975.

FOLLOWING H. P. HOLCOMB'S PRESENTATION

QUESTIONS AND ANSWERS

Nyhan: Why do you think you saw differences in the soil: water ratio in the two experiments where you reacted the dry soil versus the wet soil with the plutonium solvent?

Holcomb: I'm not really sure. Mr. Wilhite I'm sure could answer that question for you. I don't really know, unless it is due to the physical presence of the water layer on the soil.

Bondietti: It's been shown with pesticides that sorption is much greater in a drier system. When water is added it displaces the organic molecule away from the soil.

PLUTONIUM AND AMERICIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT

I. SORPTION OF PLUTONIUM AND AMERICIUM BY SOILS

P. A. Glover
F. J. Miner
W. L. Polzer

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INTRODUCTION

Plutonium has made its way into the environment through accidental releases and nuclear weapons testing. Since it is known to be harmful to man, it is of vital importance to obtain as much information as possible on plutonium behavior in the environment.

The specific goal of this investigation is to obtain information about the behavior of plutonium and americium--specifically information about their movement--in the soil/water environment.

To meet this goal the following objectives were developed:

1. Select soils of wide ranging physical and chemical characteristics and measure their sorption and elution characteristics for plutonium and americium.
2. Determine whether there are significant relationships between the physical and chemical characteristics of the soils and their sorption of plutonium and americium. Relationships that do exist will provide insight to mechanisms of movement of the two actinides in the soil.

Equilibrium sorption measurements have been completed using 17 soils with plutonium and americium nitrates as the source of the actinides. Relationships between certain physical and chemical characteristics of the soils and sorption have been identified and observations made relating the mechanisms of sorption to the chemical behavior of plutonium and americium in the soil/water system.

Column elution studies have been made using plutonium nitrate as the source of plutonium. Elution characteristics have been determined and observations made relating these characteristics to certain physical and chemical characteristics of the soils.

MATERIALS AND METHODS

SOIL SELECTION AND SAMPLING

Several criteria were developed initially for selecting the soils to be investigated, including: 1) confining the investigation to a manageable number of soils (12 to 15); 2) restricting selection of soils to areas that now have, or soon will have, facilities for handling plutonium; and 3) collecting surface samples (top down to 8-10 in.) and, if required, a subsurface sample (approximately 2 ft down).

The location for the original 13 samples obtained based on the above criteria are as follows: Los Alamos, New Mexico; Hanford, Washington; Barnwell, South Carolina (Allied Gulf Nuclear Services); West Valley, New York (Nuclear Fuel Services); Oak Ridge, Tennessee; Idaho Falls, Idaho (Idaho National Engineering Laboratory); and Rocky Flats, Colorado.

Three additional soils were obtained from Arkansas and one from Illinois. These soils do not meet the second criteria (plutonium handling facility), but were obtained in order to get a better cross section of soils in the United States.

SOIL CHARACTERIZATION

The following characteristics were measured on each of the original 13 soils:

- Cation Exchange Capacity
- Soluble Carbonate
- Organic Carbon ("Oxidizable Matter")
- % Sand, Silt, and Clay
- Particle Size Distribution
- Soluble Salt Content
- Inorganic Carbon (Lime
- pH
- Eh
- Relative Permeability
- Mineralogical Analysis

All of these characteristics were also measured on each of the four additional soils except particle size distribution, Eh, and relative permeability.

Particle size distribution, relative permeability, Eh, and some pH measurements were made at Rocky Flats. Mineralogical analyses were made at Rocky Flats with the assistance of the Colorado School of Mines. The remaining parameters and the soil textures were measured by the Soil Testing Laboratory, Colorado State University, and later at the Front Range Environmental Laboratory.

Results obtained from the chemical and physical analyses of the soils are given in Table 1.

PLUTONIUM SOURCE (SOLUBLE)

Plutonium in a nitric acid solution was selected as the source of "soluble" plutonium. Three concentrations of the soluble plutonium were prepared by diluting a standard plutonium solution with 0.5M HNO_3. These solutions have to be acidic to prevent hydrolysis and polymerization of the plutonium. In addition, the acidity has to be low so that the pH of the soil/water slurry will not be affected by the addition of the plutonium source. Therefore, the standard plutonium solutions were prepared to contain the required total amount of plutonium in 10 μl.

The concentrations of the resultant standard plutonium solutions are shown in Table 2. When 10 μl of the standard plutonium solutions are added to 30 ml of water (the quantity of water used in the experimental equilibrium sorption procedure), the total plutonium activity of samples containing the 9,600 d/min/10 μl standard was approximately 10^{-8}M; those with the 103,000 d/min/10 μl standard, 10^{-7}M; and those with the 972,000 d/min/10 μl, 10^{-6}M.

TABLE 1. Physical and Chemical Characteristics of Soil

Source	Soil Code	CEC (meg/100 g)	Soluble Salts (mmhos/cm)	Soluble Carbonate (meg/l)	Inorganic Carbon (% $CaCO_3$)	Organic Matter %	pH	% Sand	% Silt	% Clay	Texture
Colorado A (Rocky Flats)	CO-A	20.0	3.6	5.97	0.4	2.4	5.7	44	20	36	Clay loam
Colorado B (Sugar Loaf)	CO-B	17.5	0.4	0.97	0.3	3.4	5.6	64	14	22	Sandy clay loam
Colorado C (Rocky Flats)	CO-C	29.6	0.4	1.98	2.4	0.7	7.9	5	31	64	Clay
Idaho A (ERDA)	ID-A	15.5	0.5	2.71	17.2	0.8	7.8	16	50	34	Silty clay loam
Idaho B	ID-B	13.8	0.8	2.51	7.9	0.2	8.3	44	24	32	Clay loam
Idaho C	ID-C	8.2	1.0	2.52	5.2	0.3	8.0	66	41	23	Sandy clay loam
Idaho D	ID-D	17.5	1.2	4.90	0.0	0.1	7.5	38	32	30	Clay loam
Washington A (Hanford)	WA-A	6.4	0.9	2.60	0.6	0.3	8.0	74	12	14	Sandy loam
Washington B	WA-B	5.8	0.4	2.30	0.0	0.1	8.2	74	12	14	Sandy loam
Tennessee (Oak Ridge)	TN	20.5	0.4	0.30	0.0	1.0	4.8	32	32	36	Sandy loam
South Carolina (Barnwell)	SC	2.9	0.4	0.50	0.2	0.7	5.4	78	2	20	Sandy loam-silty clay loam
New York (West Valley)	NY	16.0	1.2	1.40	0.0	2.7	5.4	32	32	36	Clay loam
New Mexico (Los Alamos)	NM	7.0	1.7	2.80	0.2	0.7	6.4	48	48	18	Loam
Arkansas A	AR-A	34.4	0.5	0.10	0.9	3.2	6.2	10	34	56	Silty clay
Arkansas B	AR-B	3.8	0.4	0.10	0.7	0.6	4.8	82	9	9	Fine sand
Arkansas C	AR-C	16.2	0.3	0.10	0.6	2.3	2.3	9	54	37	Silty clay loam
Illinois	IL	17.4	0.5	0.10	0.7	3.6	3.6	31	53	16	Loam

TABLE 2. Standard Plutonium Solutions

Solution	Pu, M	Pu, g/l	H^+, M	Activity, d/min/10 µl
1	2.4×10^{-5}	5.9×10^{-3}	0.54	9,600
2	2.0×10^{-4}	6.3×10^{-2}	0.43	103,000
3	2.5×10^{-3}	6.0×10^{-1}	0.65	972,000

AMERICIUM SOURCE (SOLUBLE)

Americium in a nitric acid solution was selected as the soluble source of americium. Two concentrations of the soluble americium were prepared by diluting a standard solution of americium with 0.5M HNO_3. The solutions were prepared so that the required amount of americium will be contained in 10 µl of solution.

PLUTONIUM SORPTION MEASUREMENTS

For the equilibrium sorption measurements, 6 g of soil and 30 ml of distilled water were added to 50 ml polycarbonate centrifuge tubes. Four replicates were prepared for each soil. To this mixture, 10 µl were added of the required concentration of the standard plutonium solution. The centrifuge tubes were sealed with plastic friction-fit pipe caps and the caps taped to prevent leakage. The tubes were then placed on a Tube Rotator and rotated at a slightly canted, vertical axis at approximately 25 rpm. The plutonium samples were agitated by this method for time intervals varying from 10 min to 48 hr, depending on the experiment.

After agitation was completed, the tubes were removed and placed in an International Equipment Company Model HT Centrifuge with a Model 856 rotor, and centrifuged for 19 min at 4000 rpm. These conditions were calculated to settle particles with a diameter greater than 0.1 μm. For these calculations, a soil particle density of 2.5 was used.

After centrifugation, 4 ml of the aqueous phase was removed for plutonium analysis and the remainder used for pH and Eh measurements.

The distribution of plutonium between the soil and water was expressed in two ways. The first was % Pu Sorbed. This was calculated as follows:

$$\% \text{ Pu Sorbed} = \frac{Pu_s}{Pu_i} \times 100$$

where Pu_s = d/min in the soil phase = $Pu_i - Pu_{aq}$

Pu_i = total d/min added initially to the soil

Pu_{aq} = total d/min in the aqueous phase after equilibration.

The % Pu Sorbed data were used to determine rates at which sorption equilibrium was attained.

When % Pu Sorbed data indicated that sorption equilibrium had been attained, the equilibrium that exists was expressed by conventional distribution coefficients calculated as follows:

$$K_{d(m)} = \frac{Pu_s}{Pu_{aq}} \times \frac{V}{M}$$

where Pu_s and Pu_{aq} have the same meaning as above

V = ml of aqueous phase after equilibration

M = g of soil.

AMERICIUM SORPTION MEASUREMENTS

The procedure used for americium sorption measurements was basically the same as used for the plutonium sorption measurements. Eight replicates of each soil were run using two americium concentrations (10^{-10} and 10^{-8}M) rather than the four replicates at three concentrations used for plutonium. The americium samples were rotated for 24 and 48 hours after preliminary experiments indicated equilibrium was attained between these two times for most of the soils.

After centrifugation, 5 ml of the aqueous phase were removed for americium analysis. The sample of the aqueous phase was placed in a 4-dram vial and the vial put in a well-type gamma counter. Each sample was counted for a total of 5000 counts. These counts were converted to disintegrations per minute per millilitre and then averaged. From these data, and the total amount of americium added initially to the sample, the amount of americium sorbed by the soil is calculated.

The sorption of americium was expressed in the same way as the distribution of plutonium, i.e., % Am Sorbed and conventional distribution coefficients [$K_{d(m)}$].

PLUTONIUM COLUMN ELUTION MEASUREMENTS

For the column elution study, 24 grams of soil were added to a specially designed glass column, 1 cm in diameter. One gram of the same soil was thoroughly mixed with 10 µl of a 10^{-3}M plutonium nitrate solution. This soil was then distributed evenly on top of the soil in the column. The column was then packed by dropping it two inches to a hard surface 40 times. Glass beads were placed on top of the packed column to prevent disturbance of the soil surface, then the column was washed with 1 liter of distilled water. This volume of water is equivalent to 54 in. of water being applied to the soil by rainfall or irrigation. The eluate from the column was collected in 20 ml aliquots using a fraction collector. Selected aliquots were analyzed for plutonium.

After washing the column with 1 liter of water, the detachable bottom of the column was removed and the soil pushed out through the bottom and cut into three equal sections (approximately 1.3 cm). Each section was oven dried for approximately 3 hr at 100°C, cooled, then weighed and analyzed for plutonium.

RESULTS AND DISCUSSION

EQUILIBRIUM PLUTONIUM SORPTION

Preliminary work with SC and CO-C soils showed that there was a variation between soils in the rate, and therefore in the time, at which equilibrium sorption was attained. As a result, a single equilibration time was not used for the initial 13 soils investigated. Instead, each soil was equilibrated for succeeding time intervals from 10 min to as long as 48 hr at each plutonium concentration until there was no difference, statistically, in the % Pu Sorbed for two consecutive equilibration times. The data from these runs indicated that the time required to attain equilibrium sorption varied from 5 to 48 hr. On the basis of this work, the last four soils investigated were equilibrated for 48 hr only.

Three observations were made from an inspection of the % Pu Sorbed versus time data. First, the initial concentration of plutonium does, in some cases, have an effect on the amount of plutonium sorbed, although on the basis of the percent of plutonium sorbed, this effect is small. The difference between the % Pu Sorbed at equilibrium sorption for any of the 13 soils at the three levels of plutonium concentration ranged from 0% to 7.5%. The average difference for all 13 soils was 1.9% Pu Sorbed.

The second observation from the % Pu Sorbed data is that the rate of plutonium sorption is relatively rapid although it does vary somewhat between soils. The time for equilibrium sorption to be reached ranged from 1 to 48 hr.

The third observation is that plutonium sorption is quite high. For 62% of the time, the equilibrium sorption is 99.1% or higher, and for 87% of the time, it is 96.1% or higher. Only for 5% of the time is the equilibrium sorption below 90% and in no case is it lower than 87%.

Distribution coefficients are the customary way of expressing equilibrium sorption in soil/water systems. These coefficients are conventionally associated in the chemical literature with a mechanism that involves the exchange of a simple ion, M^{n+}, in solution with a comparable ion, X^{m+}, in the solid exchange medium. But as noted above, at the acidities associated with soil/water/plutonium systems, plutonium does not exist, for the most part, as simple ions such as Pu^{n+}, but rather as a series of hydrolyzed species. These species have varying charges and sizes that are determined by parameters such as the concentration of plutonium, the pH and Eh of the soil/water systems, the presence and concentration of complexing ions, etc. Each of these plutonium species will have different sorption behavior with both the mineral and the organic components of the soil.

Because of this complex chemistry of plutonium, the mechanism for its sorption in a soil/water system is no doubt quite complicated. In order to differentiate, therefore, between this complicated mechanism and a simple mechanism that could be implicit in the use of K_d, the conventional notation for a distribution coefficient, a different notation--$K_{d(m)}$-- is used in this paper. It implies an experimentally measured sorption coefficient that is not necessarily related to any specific sorption mechanism and might indeed be the summation of a number of different mechanisms.

The $K_{d(m)}$ values for equilibrium sorption were determined for each of the 17 soils at the three levels of plutonium concentration. Their mean values and associated standard errors are tabulated in Table 3. The % Pu Sorbed values at equilibrium sorption are tabulated in Table 4.

Note the wide range of $K_{d(m)}$ values obtained--from a high of 14,100 for TN to a low of 35 for WA-A. Expressed as % Pu Sorbed, it is equivalent to 99.96% sorbed for TN to 87.55% sorbed for WA-A. This indicates the great sensitivity of $K_{d(m)}$ values to changes in plutonium concentration at high levels of plutonium sorption, a sensitivity not shared by % Pu Sorbed values.

Note also that the effect of the initial concentration of plutonium on the extent of plutonium sorption is much more apparent in the $K_{d(m)}$ values than in the % Pu Sorbed values.

TABLE 3. $K_{d(m)}$ at Equilibrium Sorption

Mean ±SE

Soil Code	Initial Pu Concentration, M		
	10^{-8}	10^{-7}	10^{-6}
CO-A	2200 ±460	2700 ±170	1200 ±190
CO-B	200 ±24	130 ±6	40 ±3
CO-C	1900 ±110	1800 ±100	2000 ±270
ID-A	1700 ±70	4300 ±160	5000 ±290
ID-B	320 ±26	330 ±12	140 ±11
ID-C	690 ±110	4100 ±150	4000 ±23
ID-D	2100 ±640	1500 ±80	310 ±42
WA-A	100 ±7	100 ±3	35 ±1
WA-B	430 ±27	600 ±44	680 ±16
TN	2600 ±640	1200 ±100	14000 ±2700
SC	280 ±5	870 ±52	1000 ±20
NY	810 ±130	1100 ±45	870 ±57
NM	100 ±5	200 ±8	220 ±12
AR-A	710 ±36	660 ±33	760 ±45
AR-B	80 ±3	230 ±9	260 ±35
AR-C	430 ±23	570 ±44	870 ±30
IL	230 ±10	630 ±95	320 ±130

TABLE 4. % Pu Sorbed at Equilibrium Sorption

% Pu Sorbed ±SE

	Initial Pu Concentration, M		
Soil Code	10^{-8}	10^{-7}	10^{-6}
CO-A	99.75 ±0.04	99.81 ±0.01	99.54 ±0.07
CO-B	97.35 ±0.33	96.13 ±0.18	89.42 ±0.44
CO-C	99.73 ±0.01	99.72 ±0.01	99.73 ±0.04
ID-A	99.71 ±0.01	99.88 ±0.01	99.90 ±0.01
ID-B	98.43 ±0.14	98.52 ±0.05	96.59 ±0.27
ID-C	99.23 ±0.10	99.88 ±0.01	99.87 ±0.01
ID-D	99.72 ±0.07	99.66 ±0.02	98.32 ±0.26
WA-A	95.16 ±0.31	95.12 ±0.14	87.55 ±0.36
WA-B	98.84 ±0.05	99.15 ±0.07	99.27 ±0.02
TN	99.77 ±0.05	99.59 ±0.03	99.96 ±0.01
SC	98.23 ±0.03	99.43 ±0.03	99.51 ±0.01
NY	99.34 ±0.10	99.53 ±0.02	99.42 ±0.04
NM	95.36 ±0.22	97.54 ±0.10	97.77 ±0.12
AR-A	99.37 ±0.03	99.32 ±0.04	99.47 ±0.08
AR-B	94.23 ±0.23	97.82 ±0.24	97.89 ±0.31
AR-C	98.95 ±0.05	99.20 ±0.05	99.49 ±0.02
IL	97.96 ±0.10	99.13 ±0.10	96.86 ±0.63

MATHEMATICAL RELATIONSHIPS BETWEEN EQUILIBRIUM SORPTION OF PLUTONIUM AND CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE SOIL

Regression analyses were used to determine whether or not significant relationships existed between plutonium sorption and the physical and chemical characteristics of the soils. These analyses were carried out using the independent variables in two forms. In the first, stepwise regression was performed using the chemical and physical characteristics of the soils (CEC, pH, % clay, etc.) as the independent variables. The dependent variables were the plutonium content of the aqueous phases at sorption equilibrium, expressed as count data (disintegrations/minute/ml). The relationships that resulted from this regression analysis on the first 13 soils are given in Table 5. (Calculations using data from the last four soils have not been completed.) These relationships are all statistically significant at a 95% or greater confidence level. The R^2 values, or coefficients of determination, are also included in Table 5. They indicate the percent of the total variance explained by the relationship. The larger the R^2 value, the less likelihood that significant variables or cause/effect relationships have been overlooked.

In the second regression analysis, the initial independent variables were grouped to form new independent variables. This was done by a principal component analysis technique. The purpose of the principal component analysis and subsequent regression analysis was to explore possible relationships among the set of independent variables that might have been overlooked in the initial regression analysis. These relationships, if they do exist, could provide additional clues to the processes that are involved in the sorption and movement of plutonium in the soil.

TABLE 5. Stepwise Regression Analysis

Independent Variables: CEC, pH, % clay, etc.
Dependent Variables: Count data (dis/min/ml)

Initial Pu Concn, M	Relationship[(a)]	R^2
10^{-8}	d/m/m = 14.880 - 0.3025 (% clay)	37.4%
10^{-7}	d/m/m = 125.154 - 5.904 (% clay) + 6.965 (CEC)	33.9%
10^{-6}	d/m/m = -249.68 + 34.85 (% sand) +233.41 (CEC) - 122.38 (% clay)	41.7%

(a) d/m/m = disintegrations/minute/ml.

The new independent variables that resulted from the principal component analysis consist of a linear combination of the original variables and have the form

$$Z_i = a_1X_1 + a_2X_2 + \ldots a_8X_8.$$

In these new variables, X_1, X_2, ... X_8 represent the original independent variables in the same order as they occur in Table 1, i.e., X_1 = CEC, X_2 = soluble salts, etc., except the X_8 = clay, not silt. Silt was eliminated in the principal component analysis for mathematical reasons. The relative absolute magnitude of the coefficients (a_i) indicates the relative importance of the original variable (X_n) in the new variable Z_n. The coefficients with the largest absolute values in each of the three new independent variables identified by principal component analysis are summarized in Table 6.

Stepwise regression analyses were performed using the new independent variables defined by the principal component analysis. The dependent variables were the count data. The results of the regression analysis are summarized in Table 7. Note that at all three plutonium concentrations, Z_1 is the only significant variable. And even though the values of R_2 are small, the relationship between the count data (plutonium concentration) and Z_1 is statistically significant at the 95% confidence level.

Of the original independent variables, the ones most significant in Z_1 are CEC, clay, and sand (Table 6). These variables were the ones that were also found to be most important from the initial regression analysis using the original independent variables (Table 5). The importance of these particular variables would indicate that a conventional ion exchange process is responsible for the sorption of plutonium. However, two points should be noted. First, R^2 values decrease, as indicated in Table 7, with an increase in plutonium concentration. This would indicate that the ion exchange process is becoming less important with an increase in plutonium concentration. Since the ion exchange capacity of the soil is orders of magnitude higher than the highest plutonium concentration investigated,

TABLE 6. Relative Importance of the Original Independent Variables in the New Independent Variables

New Independent Variable	Original Independent Variables and Their Associated Coefficients
Z_1	CEC (0.56), Sand (-0.53), Clay (0.54)
Z_2	Soluble salts (-0.34), Inorganic carbon (0.48), Organic carbon (-0.53), pH (0.56)
Z_3	Soluble salts (0.59), Soluble carbonate (0.72)

TABLE 7. Stepwise Regression Analysis

Independent Variables: Z_1, Z_2, Z_3

Dependent Variables: Count data (d/m/m)(a)

Initial Plutonium Concn, M	Relationship(a)	R^2
10^{-8}	d/m/m = 6.192 - 2.220 (Z_1)	32.2%
10^{-7}	d/m/m = 52.257 - 15.356 (Z_1)	14.7%
10^{-6}	d/m/m = 1097 - 361.05 (Z_1)	12.6%

(a) d/m/m = disintegrations/minute/ml

this does not seem logical. Second, as noted above, the nearer R^2 values are to 100%, the more assurance there is that significant variables or cause/effect relationships have not been overlooked. The R^2 values in Tables 5 and 7 vary from 12 to 42%, indicating that other variables and relationships are likely involved in the sorption. Additional work is planned to explore other possible relationships more fully.

EQUILIBRIUM AMERICIUM SORPTION

The mean % Am Sorbed values are summarized in Table 8. The sorption results follow the same general trend that was identified using soluble plutonium. Almost all of the americium had been sorbed by the soil in 48 hr. Sixty percent of the soils sorbed 99% of the americium at the low concentration and 71% of the soils sorbed 99% of the americium at the high concentration.

Distribution coefficients for americium in the soil were calculated after establishing that equilibrium had been reached. The mean values obtained are summarized in Table 9.

The sensitivity of the $K_{d(m)}$ values is obvious. For example, the $K_{d(m)}$ for CO-C soil at the high and low americium concentrations are 5200 and 8100 and the corresponding % Am Sorbed are 99.90 and 99.94. A difference in % Am Sorbed of 0.04 appears as an increase of approximately 3000 in the distribution coefficient.

TABLE 8. % Americium Sorbed at Equilibrium Sorption

Mean ±SE

Soil Code	Initial Am Concentration, M 10^{-10}	 10^{-8}
CO-A	99.81 ±0.04	99.83 ±0.01
CO-B	99.23 ±0.03	99.47 ±0.01
CO-C	99.90 ±0.02	99.94 ±0.01
ID-A	99.92 ±0.05	99.16 ±0.01
ID-B	95.49 ±0.09	99.20 ±0.06
ID-C	99.44 ±0.03	99.66 ±0.01
ID-D	99.94 ±0.02	99.95 ±0.004
WA-A	95.99 ±0.33	97.64 ±0.16
WA-B	98.01 ±0.04	98.89 ±0.07
TN	99.84 ±0.03	99.96 ±0.01
SC	94.43 ±0.59	97.50 ±0.11
NY	99.51 ±0.04	99.81 ±0.01
NM	98.86 ±0.04	98.84 ±0.02
AR-A	99.55 ±0.17	99.87 ±0.01
AR-B	98.80 ±0.06	99.40 ±0.05
AR-C	96.94 ±0.07	99.81 ±0.01
IL	99.70 ±0.03	99.76 ±0.01

TABLE 9. $K_{d(m)}$ at Equilibrium Sorption

Mean ±SE

Soil Code	Initial Am Concentration, M 10^{-10}	10^{-8}
CO-A	2500 ±210	2600 ±110
CO-B	600 ±24	840 ±20
CO-C	5200 ±970	8100 ±400
ID-A	5900 ±230	510 ±8
ID-B	300 ±10	610 ±86
ID-C	820 ±43	1300 ±31
ID-D	10000 ±1500	8500 ±660
WA-A	120 ±7	200 ±14
WA-B	230 ±5	430 ±28
TN	2600 ±470	9700 ±1100
SC	82 ±1	190 ±9
NY	920 ±79	2300 ±330
NM	400 ±11	420 ±7
AR-A	2900 ±1800	3300 ±240
AR-B	390 ±20	760 ±72
AR-C	1800 ±	2300 ±50
IL	1600 ±190	1900 ±22

MATHEMATICAL RELATIONSHIPS BETWEEN EQUILIBRIUM SORPTION OF AMERICIUM AND CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE SOIL

Regression analyses are being performed in the same way with the americium sorption data as with the plutonium sorption data to determine whether or not significant relationships exist between americium sorption and the physical and chemical characteristics of the soil. Although the analyses have not yet been completed, they indicate, as with plutonium, that a relationship exists between CEC, sand, and clay and the sorption of americium.

ELUTION CHARACTERISTICS OF PLUTONIUM

The transport of plutonium through soil by water was studied using columns of ID-B, CO-A, and ID-A soils. The rate of flow of the water through the columns was governed by the soil, and varied from approximately 15 min per 20 ml for CO-A to 90 min for ID-B and 180 min for ID-A.

Duplicate column elution runs were made for each of the three soils. The effluents were collected in 20 ml fractions and subsequently analyzed for plutonium. After each elution was completed, the soil column was sectioned and the soil analyzed for plutonium. The average plutonium content in each soil section, as well as the total amount of plutonium in the effluent, are summarized in Table 10 for each of the three soils.

TABLE 10. Elution Characteristics

Pu Source: Pu Nitrate

Initial Amount Pu on Column: 2.5×10^{-8} mole

Soil	$K_{d(m)}$	Depth, cm	% Total Pu
ID-B	144	0.0 - 1.3	93.9
		1.3 - 2.6	2.8
		2.6 - 3.9	1.5
		Eluate	1.8
CO-A	1180	0.0 - 1.3	98.3
		1.3 - 2.6	0.8
		2.6 - 3.9	0.5
		Eluate	0.4
ID-A	5020	0.0 - 1.3	99.5
		1.3 - 2.6	0.3
		2.6 - 3.9	0.2
		Eluate	<0.1

These data indicate that the soil with the lowest $K_{d(m)}$ (ID-B) retains the least amount of plutonium, while the soil with the highest $K_{d(m)}$ (ID-A) retains the most. In no case, however, was more than 2% of the original plutonium eluted from the column.

The fractions of the column effluents were analyzed for plutonium to determine its pattern of elution. In two of the soils, ID-B and CO-A, there were prompt pulses of plutonium occurring in the initial 20 ml effluent fractions. These pulses contained 0.9% of the original plutonium placed on the column for ID-B and 0.1% for CO-A. The remaining effluent fractions for these two soils contained continually decreasing amounts of plutonium.

The behavior of the ID-A soil was different. There was no pulse of plutonium throughout the entire elution. Instead, the plutonium concentration in the effluent fractions varied randomly between 0.001 and 0.004% of the original plutonium on the column throughout the entire elution.

The pH of the effluent fractions was measured. For all three soils, the pH of the effluent increased with an increase in the amount of water through the column. Generally, the increase in pH was greatest at the beginning of the elution. The total increase in pH varied with the soils for a minimum of 0.3 (8.3 to 8.6) for ID-A to a maximum of 1.4 (5.8 to 7.2) for CO-A.

FOLLOWING P. A. GLOVER'S PRESENTATION

QUESTIONS AND ANSWERS

Rogers: Did you get any insoluble clay particles or colloids down through your column?

Glover: Insoluble clay particles coming through? In a very preliminary study I took a portion of the first 20 ml aliquot and filtered it through a 0.01 μm filter and collected the small particles that had been washed out of the column. There was a filter on the column but the particles were still washed out.

Rogers: What kind of filter?

Glover: It was a glass fiber filter. We analyzed the water once we had filtered that solution, and we still found a measurable plutonium concentration in the filtrate, but it did decrease, indicating that some of the plutonium was attached or somehow fixed to the very small clay particles. The first three aliquots had the highest concentration of plutonium, so there is a possibility that the plutonium came down either associated with the clay particles and there was some ionic plutonium or something that came through in the first few aliquots.

Rogers: There is a possibility that some of the small clay particles actually infiltrated, just as we've postulated for the plutonium oxide particles, and this physical mechanism also may be a major method of plutonium transport down through the soil.

Glover: We did not want to retard the water flow very much because we knew the movement was already slow. Therefore the filter that we used was a glass fiber filter and then a stainless steel frit to hold the soil. Of course, the glass fiber filter is very porous, so it's possible to get soil particles through it. In most of the column elution studies we have done, you can visually see, after the tube has set for awhile, the settling of particles on the bottom of the tube. So the particles get through.

Wildung: What was the range of organic carbon contents of the soils?

Glover: Organic carbon ranged from about 0.1% to 3.6%.

Rogers: What was the range of pH?

Glover: The pH's ranged from 4.8 to about 8.

Nyhan: What were the pH's of some of the final soil-water solutions?

Glover: What were the final pH's?

Nyhan: Yes.

Glover: We did measure pH's. Will (Polzer) is going to talk about that. The pH's after equilibration did not change drastically from what they initially were. I don't have any of my data.

Polzer: They ranged from about 4.9 to 8.9.

Glover: They did not change drastically. Initially, we were adding a millimeter of the plutonium standards that was in 0.5 M nitrate solution and the pH was changed. But with 10 lambda, we could not see any difference initially in the pH.

Serne: Could you give me roughly what the cross section of these columns were so I can calculate a flow rate?

Glover: The soil column itself was approximately 4 cm long and approximately 2.5 cm wide.

Atcher: When you deposited the plutonium, was the column dry?

Glover: Yes. We put a drop, approximately 10 lambdas, of our plutonium solution in 1 g of soil, mixed it as best we could on a piece of foil, and then poured it onto the top of the soil column. So it was a dry soil column. We also packed it by a standard method. Then we put the glass beads on top, which turned out to be a mistake, because the glass beads sorbed the plutonium. So we then had to put another layer of uncontaminated soil on top of the contaminated soil and then the glass beads.

Atcher: The reason I asked was because those curves that you showed for the eluate looked a lot like the ones that we saw for the hydrolyzed fraction coming off instead of that one Idaho sample, where it looked like a pure ionic kind of a thing.

Glover: These were dry columns initially. We didn't want to add the plutonium standard to the water because it would have hydrolyzed immediately. We felt that by adding the plutonium to the soil initially and then passing the water through, you might prevent hydrolysis. We figured this would be a better way.

Rai: Your elution tests indicated that two out of three soils behaved alike. Did the soils differ in SAR and do you think the differences in SAR could explain the different elution behavior of the soils?

Glover: What is SAR?

Rai: SAR is sodium adsorption ratio and it relates the amount of sodium in solution to the amount of divalent cations. The colloid fractions of soils having high SAR would disperse easily and thus would be more prone to movement.

Glover: The pH's are 5.7 for CO-A, 7.8 for ID-A and 8.3 for ID-B. The pH's of those two were very close.

Rai: It's possible that high pH soils have high SAR. It would be worth looking into.

Wildung: I would like to make one more suggestion, or perhaps provide a bit of philosophy. You really have combined two goals in your study that shouldn't have been combined at all. I think you selected your soils on the basis of their proximity to sites of interest, and you then tried to relate the sorption to properties of the soil. Normally, when you want to look at the effect of soil properties on sorption or some other parameter, you make a careful effort to select your soils so that you will obtain something approaching a normal distribution of the various properties that you are concerned with. Usually this takes on the order of 40 to 75 soils. Most of the successful studies include on the order of 65 soils.

Glover: True. Once we started with the statistical analysis it was determined that first of all we had too many independent variables. And in order to get a good correlation with all those independent variables you would have to have had a long list of soils. We also found out that the variability of the soil has a tremendous effect on what could be done with the data statistically. Just in one soil, the Illinois soil, we got a wide range of sorptions with one plutonium concentration. With that one soil which we ran over and over again, there was nothing consistent at all about the sorption. We almost came to the conclusion that in order to get good data, where you can postulate a mechanism, you make up your own soil by adding a certain percent of sand, silt, and clay, and the whole bit.

Wildung: You don't want to do that.

Glover: You don't want to do that because it's very superficial. But after all the problems we've had it sounds good. Starting out on this study, we chose soils from all of the sites that presently had or would soon have some plutonium handling facilities. Once we characterized these soils, a lot of them looked a lot alike. We then went to the soil people to determine if there is a soil classification that you can use and found out that Rocky Flats soils had never been classified. I am not a soil person, so I don't know what the classifications are. Nobody had ever come in and mapped them so we couldn't even go that route.

Rai: Rocky Flats soil hadn't been classified and mapped?

Glover: No, it sure hadn't. We had three soils from Rocky Flats, so we did come to the conclusion that there was a better way to go at it. Since we had all this good data, we did the best we could with it.

Rai: Some of the properties you called independent variables are not so independent. For example, CEC is a function of clay, sand, and silt, and the kinds and amount of clay minerals; similarly clay is a function of sand and silt.

Glover: Well, we had to throw out the silt because of statistical problems.

PLUTONIUM AND AMERICIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT

II. THE EFFECT OF SELECTED CHEMICAL AND PHYSICAL CHARACTERISTICS OF AQUEOUS PLUTONIUM AND AMERICIUM ON THEIR SORPTION BY SOILS

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INTRODUCTION

The determination of the sorption of the "soluble" form of the actinides, plutonium and americium, by 17 soils and the various trends in sorption data are discussed in Part I of this paper. Sorption, as measured by distribution coefficients, varied by as much as 300 times between soils and by as much as 30 to 60 times for an individual soil at the three levels of plutonium concentrations used, 10^{-8}, 10^{-7}, and 10^{-6} M. Sorption of americium tended to be as great or greater than that of plutonium. However, its variation was generally much less between soils and for individual soils at the concentrations used, $10^{-9.4}$ and $10^{-7.4}$ M. The distribution coefficient, $(K_{d(m)})$, of the actinides in soils is defined as the ratio of actinides sorbed to the concentration in solution under equilibrium conditions. The actinide sorbed is expressed as amount per gram of soil and the concentration in solution as amount per ml of solution. Therefore, with an increase in the total quantity of the actinide in the system the amount of the actinide sorbed should be proportional to the concentration in solution, if the $K_{d(m)}$ is to remain constant. A decrease in the amount sorbed relative to that in solution results in a lower $K_{d(m)}$ and an increase results in a higher $K_{d(m)}$.

In order to explain changes in sorption relative to the concentration of the actinide in the system, observations are made with respect to selected chemical and physical characteristics of the actinide in solution and the sorption of the actinide by soils. More specifically, sorption is discussed in relation to: 1) the relative concentration of the various aqueous actinide species, 2) polymerization of aqueous actinides, and 3) the formation of complexes with other ions. Most experimental work on aqueous actinides has been conducted under conditions unlike those in a soil/water environment. Therefore, the evaluation necessarily involves theoretical as well as experimental considerations.

THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

AQUEOUS SPECIES

The "soluble" form of plutonium used in the experiments was present as Pu(IV). According to Polzer (1971) soluble plutonium should form a number of species having oxidation states of III, V, and VI as well as IV. Plutonium reacts with hydroxyl ions to form aqueous hydroxide complexes such as $PuOH^{2+}$, $PuOH^{3+}$, $PuOH_2OH^+$, and $Pu0_2(OH)_3^-$. Complexes with other ions may be formed also, provided the plutonium and the other ions are present in sufficient quantities.

The relative concentrations of the plutonium species vary with the pH and Eh of the soil solutions. In the experimental work the pH values ranged from 4.9 to 8.9 and the Eh from -0.54 to -0.40V. Using these Eh and pH values, and theoretical data used by Polzer (1971), the calculated relative concentrations of aqueous plutonium species indicate PuO_2^+ is the predominant species for all the soil solutions. These calculations also indicate that the PuO_2^+ concentration is approximately equal to the total plutonium concentration. However, the other species, Pu^{4+}, Pu^{3+}, PuO_2^{2+}, and their hydrolyzed counterparts are still present but at much lower concentrations. Costanzo and others (1973) found that the oxidation states of Pu(III), (V) and (VI) are all formed when Pu(IV) is placed in aqueous solution at high acidities (pH values less than 2). Lingren (1966) found that with a electrochromatographic technique the behavior of the migrating plutonium ion in seawater was independent of the oxidation state of the plutonium originally added. This was interpreted to mean that only one predominant aqueous state exists in seawater and that any different state added is immediately changed to the more stable one. The experimental data in these two reports suggests that only one predominant aqueous species (excluding polymeric species), possibly PuO_2^+, can exist in a soil/water environment.

Although Pu(V) is probably the most predominant of all the plutonium oxidation states in soil solutions, the least information is available on its sorption characteristics. Its sorption capabilities are expected to be low compared to the species in the other oxidation states. Cleveland (1970) and Metz and Waterbury (1964) indicate the relative order of sorption of plutonium species for the different oxidation states on organic cation exchange resins is $Pu^{4+} > Pu^{3+} > PuO_3^{2+} > PuO_2^{+}$. Because of its low sorption characteristics, other species, such as Pu^{3+}, could significantly affect sorption of plutonium at pH values of 5 or less, even though their relative amount is lower than the PuO_2^{+} species. Similarly, at pH values higher than about 8.5, sorption could be affected by other species such as those of the Pu(VI) oxidation state.

A soluble form of americium was also used in this study. However, the oxidation state was (III) instead of the oxidation state of (IV) used for plutonium. Literature data (Latimer, 1952) indicate similar oxidation states exist for both plutonium and americium (III, IV, V and VI). Table 1 lists species of americium, and their free energies of formation, that possibly exist under the pH and Eh conditions observed in our experimental studies and in the environment. The species of probable significance can be estimated from the data in Table 1 and the procedure used by Polzer (1971). Species of americium having an oxidation state of (III) are the only species likely to be of any importance. However, it should be noted that additional work is needed to evaluate their significance quantitatively.

TABLE 1. Standard Free Energies of Formation, $\Delta F_f°$, of Americium Species at 25°C

Species	State	$\Delta F_f°$ (kcal/mole)	Source
Am (metal)	Solid	0.0	Latimer (1952)
Am^{3+}	Aqueous	-142.2	Fuger, Spirlet & Muller (1972)
Am^{4+}	Aqueous	-88.2	Fuger, Spirlet, Muller (1972)
$Am\ O_2{}^+$	Aqueous	-176.7	Perlman & Street (1954)
$Am\ O_2{}^{2+}$	Aqueous	-138.9	Perlman & Street (1954)
$Am\ OH^{2+}$	Aqueous	-194.4	Shalinets & Stepanov (1972)
$Am\ (OH)_2{}^+$	Aqueous	-245.9	Shalinets & Stepanov (1972)
$Am\ (OH)_2{}^°$	Polymeric	?	Korotkin (1972)
$Am\ (OH)_3$	Solid	-281.7	Latimer (1952) Recalculated
$Am\ O_2$	Solid	-206.4	Fuger, Spirlet & Muller (1972) Latimer (1952)
$Am\ (OH)_4$	Solid	-315.0	Latimer (1952) Recalculated
$Am\ O_2OH$	Solid	-242.2	Latimer (1952) Recalculated
$Am\ O_2(OH)_2$	Solid	-273.5	Latimer (1952) Recalculated

Korotkin (1972) using an electromigration technique determined the charge of the species present in solution for pH values ranging from 1 to 11 at an americium concentration of 10^{-6} M. Figure 1 depicts in a general way the effective positive charge of americium in solution as determined from the data of Korotkin (1972) for 0.1 M Li ClO_4 solutions. The diagram indicates that over the pH range observed in the present study (5 to 9) the effective positive charge ranged from about 2 to approximately 0 with the greatest change in charge occurring at pH values greater than 8. The change in the effective charge is caused by the change in the relative concentrations of the species of americium (III). As the pH is increased a greater degree of hydrolysis takes place, thus reducing the overall effective positive charge. The low effective positive charge at pH values greater than 8 is attributed to the formation of polynuclear hydroxyl complexes which likely behave as aqueous species at the concentrations used in this study.

POLYMERIZATION

The initial concentrations of plutonium in the soil solutions at equilibrium were, for the most part, in excess of that calculated from the solubility of plutonium hydroxide based on the data of Polzer (1971). Therefore, polymerization might be expected to occur initially. However, in addition to polymerization, sorption takes place. This would decrease the concentration of the aqueous species below the solubility limits of

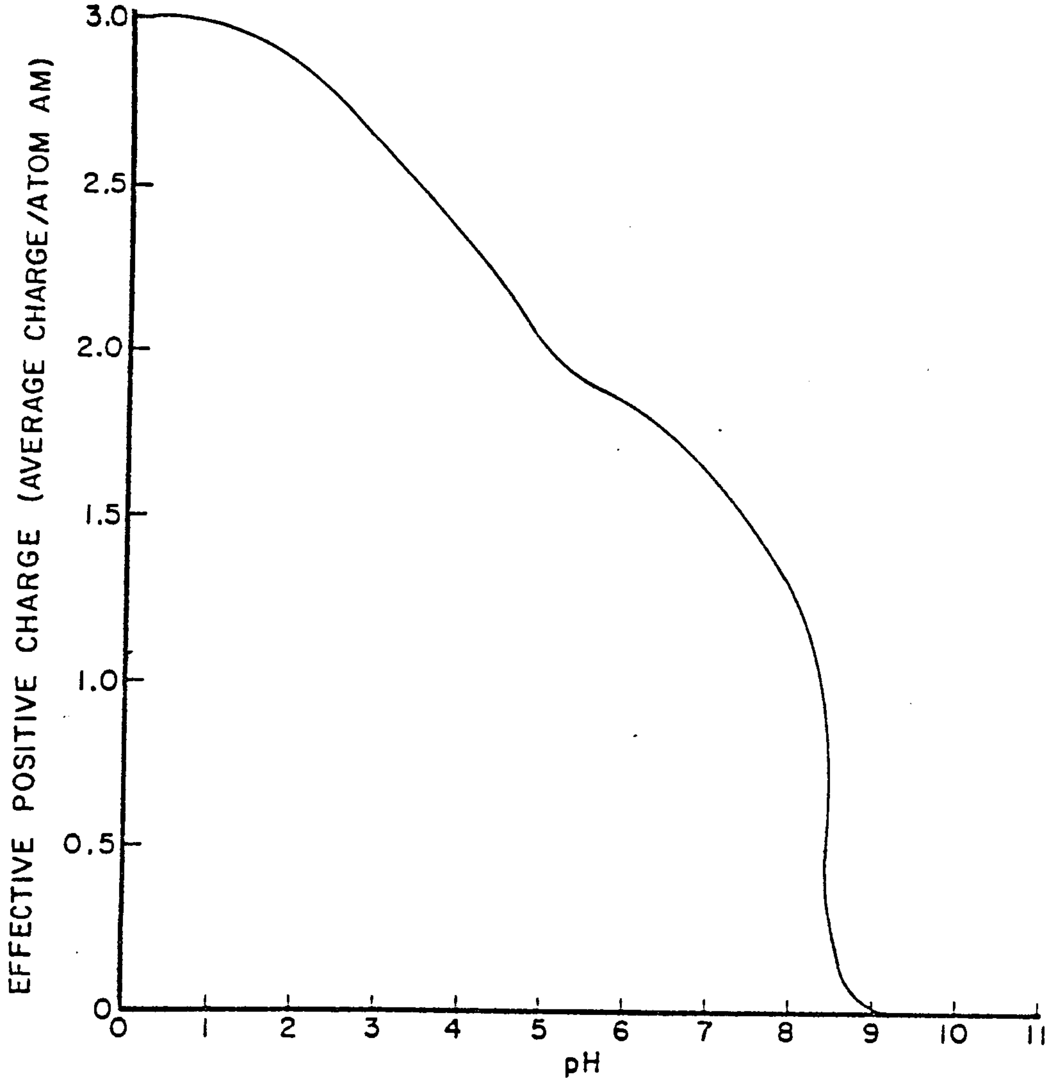

FIGURE 1. Effective Positive Charge of Americium as a Function of pH. Estimated from data of Korotkin (1972).

plutonium hydroxide for the specified Eh and pH. In an attempt to equilibrate, polymerized plutonium would tend to depolymerize. At equilibrium, then, the soil solution could contain plutonium in the form of monomeric or low molecular weight polymeric species or in an ionic form. The ionic form may either be complexed or uncomplexed, as will be discussed later.

Lloyd and Haire (1973) showed that plutonium, on polymerizing, behaves as very small discrete particles of an amorphous nature, probably hydrous PuO_2. Upon extensive aging or heating the polymers may form into small crystallites. With increased concentration they may combine with other similar particulates to increase the total size even though they still maintain their particulate behavior.

Polymers may have different characteristics depending on the pH region in which the polymer is formed. For example, two values for solubility products can be found in the literature for plutonium hydroxide. One value, $10^{-51.9}$, was calculated from estimated oxidation potentials for various plutonium reactions in basic solutions (Latimer, 1952) and the other, $10^{-55.2}$, was determined by noting the pH at which collodial $Pu(OH)_4$ forms in acid solutions (Kasha, 1949). It is conceivable that plutonium polymorphs can occur, one in acid solution and the other in basic solution, and each with its own particular solubility product. This would be analogous to the existence of polymorphs of aluminum hydroxide (each with a different solubility product) which is probably a result of the mode of stacking of successive layers of aluminum hydroxide (Schoen and Roberson, 1970).

Kepak (1971), in reviewing the sorption and collodial properties of radioactive elements in trace concentrations, discusses both adsorption by ion exchange and sorption by physical means. An increased concentration of electrolytes will depress sorption of trace cations. In the case of radiocolloid sorption, an increased concentration of electrolyte does not influence or increase sorption. An increase in sorption of colloids with an increase in electrolyte should be attributed to physical sorption, not ion exchange, with the process being irreversible. A trace element may also be incorporated into a solid phase of another compound, assuming the properties of the compound present in excess, and therefore lose its individual properties. This process is also irreversible in nature. Physical sorption of ionic species of microelements may also occur, but unlike colloids the process is likely to be reversible (Hingston et al., 1968). In general, however, the capacity of ion exchangers for physical adsorption of radiocolloids is lower than the capacity for ion exchange.

According to Rozzell (1969) low molecular weight plutonium polymers behave like ionic species whereas large polymers behave differently. For example, at high ionic strength, other ions compete for exchange sites, thus decreasing sorption of ionic plutonium species. High ionic strength solutions will also decrease the repulsion between large polymers thus allowing coagulation and an increase in the size of the polymer. Sheidina and Kovarskaya (1970) noted that a change in the charge of colloidal plutonium is dependent upon concentration and pH. For high concentrations of plutonium (10^{-6} M) the colloidal particles exhibit a net positive charge at low pH values and a net negative charge at a pH 7 or above. At low concentrations (10^{-8} M) a negative charge is exhibited by colloidal particles at a pH as low as 3.

In the soil solutions studied in these experiments, the ionic strength is low, probably on the order of 0.005 to 0.05 moles/liter. These values were estimated using the relationship between ionic strength and specific conductance of water as discussed by Griffin and Jurinak (1973). Based on this ionic strength and information from Rozzell and from Sheidina and Kovarskaya, low molecular weight polymeric hydrous plutonium oxides will behave as ionic species in solution. The charge of the polymers will be pH dependent, positive at low pH values and negative at high pH values.

The work of Korotkin (1972) suggests that hydrolysis of americium (III) occurs in solutions at pH values of approximately 3. As the pH is increased to approximately 6 to 7, nonionized molecules of americium are formed, but the relative amount does not become significant until a pH of about 8 or greater is reached. At the concentrations of americium used in this study, the polymerization probably would not occur to the extent that colloidal formation would be observed. Thus polymerized americium molecules would likely behave as nonionized aqueous species. As the pH is increased still further, for example pH 9 or above, these polymers may become negatively charged. Therefore for solutions having high pH values, greater than 8, sorption is reduced significantly as a result of a reduction in the net effective positive charge of americium.

FORMATION OF COMPLEXES

Plutonium has the ability to complex with most anions normally found in soil solutions. According to Gelman et al., (1962) doubly charged ions generally form stronger complexes with Pu (III, IV, V and VI) than do singly charged ones. The anions may be arranged in the following order with respect to their disposition to form complexes.

Singly charged anions: $F^- > NO_3^- > Cl^- > ClO_2^-$

Doubly charged anions: $CO_3^{2-} > C_2O_4^{2-} > SO_4$

Gelman et al. also concluded that the tendency of different plutonium ions to form complexes should fall in the following order: $Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$, i.e., in the order in which their ionic potential decreases. In some cases, however, this order may change, i.e., the PuO_2^{2+} ion may have a greater tendency to form complexes than the Pu^{3+} ion.

Plutonium forms strong complexes with organic anions. In this study, however, the anions were considered to be in a low enough concentration so that any complex formed would have an insignificant effect on plutonium sorption.

Of all the anions present in the soil, carbonate is the one most likely present in high enough concentrations to significantly complex plutonium. Moskvin and Gelman (1958) concluded from their work that Pu^{4+} reacts with carbonate to form the $PuCO^{2+}$ complex. Their determined stability constant seems much too high and therefore the value is suspect (Cleveland, 1970). Because of the low concentration of Pu^{4+} species, the $PuCO_3^{2+}$ complex is considered to be insignificant in this study.

Carbonate complexes can also be formed by Pu(VI) in solutions having a pH of 8 or higher. These complexes have been identified by Gelman et al. (1962) as $[PuO_2(CO_3)_2]^{2-}$, $[PuO_2(OH)(CO_3)]^-$ and $[PuO_2(OH)_2\ CO_3]^{2-}$. Stability constants are given as 1.1×10^{15}, 7.1×10^{23} and 1.0×10^{23}, respectively. In calculating the stability constants the authors used a value for the solubility product of $PuO_2(OH)_2$ that is different from the one used by Polzer (1971). For the data to be internally consistent with that used in this study, the respective stability constants were recalculated to be 2.5×10^9, 1.6×10^{18} and 2.2×10^{17}. Of the three complexes, the concentration of $[PuO_2(OH)(CO_3)]^-$ would be greatest for conditions found in soil/water environments. For a pH of 8.0, the CO_3^{2-} concentration would be on the order of $10^{-4.5}$ M. The PuO_2^{2+} concentration would be some fraction of the PuO_2^+ concentration (in the range of 10^{-8} to 10^{-6}, depending on the Eh of the solution). Using $10^{-7.7}$ times the PuO_2^+ concentration for that of PuO_2^{2+} and substituting the values given for CO_3^{2-} and OH^- concentrations into the following expression, $[PuO_2(OH)(CO_3)^-] = [PuO_2^{2+}][OH^-]\ [CO_3^{2-}]\ 10^{18.2}$, it is found that the concentration of the Pu(VI) complex is equal to that of the normally predominant species, PuO_2^+. Therefore, the complex with its negative charge would be expected to significantly decrease the sorption of plutonium compared to the sorption in the absence of the complex, assuming that the primary mechanism of sorption is one involving a charge.

Lingren (1966), in electromigration experiments with dissolved plutonium in seawater, obtained results which indicated that negatively charged carbonate complexed ions and a colloidal fraction are formed when soluble plutonium in any of its three oxidation states [Pu(III), Pu(IV), and Pu(VI)] is added to seawater or when plutonium metal is dissolved in seawater. The pH of the seawater was 8.0 and the original plutonium concentration was 70 μg/liter or 3 x 10^{-7} moles/liter. Rhodes (1957a, 1957b) observed a decrease in sorption of plutonium by a Hanford soil above a pH of 8 and attributed the decrease to a change in the characteristics of the polymer in alkaline solutions. In this pH range the existence of a plutonium carbonate complex also provides an explanation for his experimental results.

A review of the literature indicates that no apparent complexing of ions, such as carbonate, with americium is evident which would likely affect the sorption of americium by soils. However all possible complexing has not, at the same time, been thoroughly investigated.

METHODS AND PROCEDURES

Certain criteria, which are based primarily on the above discussion are used to explain the observed differences in sorption, as measured by distribution coefficients, at the different actinide concentrations. These criteria are as follows:

(1) Although physical sorption may occur in the soils studied, the primary mechanism for sorption is most likely that of exchange. A preliminary examination indicates that the sorption data does not conform to the Langmuir adsorption equation as given by

Syers et al. (1973) and thus implies primarily a nonspecific or exchange type mechanism. However, additional data points for the range in the initial concentrations of plutonium are needed to properly evaluate the type of sorption involved.

(2) The presence of monomeric or low molecular weight polymers of plutonium hydroxide in solution should decrease sorption because of their small size and low effective charge density. In the very low pH region the net positive charge density of the polymer may exceed that of the plutonium ions in solutions, thereby enhancing sorption. If the measured plutonium concentration at sorption equilibrium exceeds the concentration calculated to be in equilibrium with a hydroxide at the Eh and pH of the soil solution, then polymers are assumed to be present. Two different solubility products were assumed in calculating the concentration of plutonium in equilibrium with plutonium hydroxide. In basic solutions (pH 7 or greater) a solubility product of $10^{-51.9}$ was used, and in acid solutions (less than pH 7) a solubility product of $10^{-55.2}$ was used in the calculations.

(3) In acid solutions (pH less than 7) the net positive charge density of polymers should decrease with an

increase in pH. Therefore, the relative sorption of plutonium polymers for a given soil should also be less with an increase in pH. In basic solutions the net charge is assumed to be negative in character.

(4) For soil/water conditions in which the pH is 8 or higher the assumption is made that the concentration of a carbonate complex having a negative charge approaches or exceeds the concentration of the non-complexing species, thus decreasing the overall sorption of plutonium.

(5) The effective positive charge of americium in solution should decrease as a result of the hydrolysis of americium (III). However the change in the effective positive charge resulting from a small change in pH may not affect sorption of americium significantly except when the pH is greater than 8.

RESULTS AND DISCUSSION

The results of the determination of distribution coefficients of plutonium in 17 soils are listed in Table 2-A and 3-A. The pH, Eh, distribution coefficient ($K_{d(m)}$) and the ratio of measured plutonium concentration in the aqueous phase to the calculated concentration in equilibrium with plutonium hydroxide (Pu_m/Pu_c) are presented. The results for americium are listed in Tables 2-B and 3-B. Tables 2-A and 2-B list results in which the equilibrium pH is greater than 7 and Tables 3-A and 3-B list results in which the equilibrium pH is less than 7.

ACTINIDE SORPTION BY SOILS IN BASIC SOLUTIONS

A lower plutonium sorption is observed at an initial concentration of 10^{-6} M for soils WA-A, WB-B and ID-D than at the other initial concentrations (Table 2-A). This decrease is attributed to the presence of polymers as indicated by a Pu_m to Pu_c ratio of greater than 1. The data for soils ID-C and ID-A show a lower distribution coefficient at the initial plutonium concentration of 10^{-8} M than at the higher initial concentrations (Table 2-A). This lower sorption is attributed to the formation of a plutonium carbonate complex, having a negative charge, which should be significantly greater at pH 8.4 compared to the lower pH values observed at the higher initial plutonium concentrations.

The decrease in $K_{d(m)}$ for the ID-B soil may possibly be attributed to both the presence of low molecular polymers and carbonate complexing. In the ID-B soil, the pH is relatively high for all three initial concentrations. This suggests that a carbonate complex could be formed with PuO_2^{2+}. As noted

TABLE 2-A. Sorption of Plutonium in Soils. Distribution Coefficients for Soils in Basic Solutions.

Soil	Initial Pu Conc, M	$K_{d(m)}$ [a]	pH	-Eh,V	$\frac{Pu_m}{Pu_c}$*
WA-A	10^{-8}	100	7.9	0.41	0.4
	10^{-7}	98	7.9	0.42	3.2
	10^{-6}	35	7.9	0.44	40
WA-B	10^{-8}	430	7.8	0.50	0.004
	10^{-7}	590	7.8	0.46	0.2
	10^{-6}	110	7.8	0.41	7.9
ID-D	10^{-8}	2100 [d]	7.8	0.44	0.008
	10^{-7}	1500	8.0	0.41	0.4
	10^{-6}	310 [b]	7.9	0.41	5.0
ID-C	10^{-8}	690 [b]	8.4	0.44	0.03
	10^{-7}	4100	8.0	0.43	0.06
	10^{-6}	4000	8.0	0.44	0.3
ID-A	10^{-8}	1700	8.4	0.45	0.005
	10^{-7}	4300	8.0	0.44	0.03
	10^{-6}	5000	7.8	0.45	0.2
ID-B	10^{-8}	320	8.8	0.44	0.05
	10^{-7}	300	8.9	0.41	1.6
	10^{-6}	140	8.6	0.40	63
CO-C	10^{-8}	1900	8.0	0.49	0.001
	10^{-7}	1800	7.8	-	-
	10^{-6}	2000 [b]	8.2	0.44	1.0

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*Ratio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water phase were in equilibrium with $Pu(OH)_4$ (Pu_c). Pu_c is based on a solubility product for Pu(OH) of $10^{-51.9}$ in basic solutions.

The standard error of the mean [a] 8% or less unless indicated otherwise, [b] between 11% and 16%, [c] between 20% and 25%, and [d] 31%.

TABLE 2-B. Sorption of Americium in Soils. Distribution Coefficients for Soils in Basic Solutions.

Soil	Initial Am Conc, M	K_d(m)	pH	-Eh,V
WA-A	$10^{-9.4}$	120	8.0	0.43
	$10^{-7.4}$	200	7.8	0.46
WA-B	$10^{-9.4}$	230	8.0	0.44
	$10^{-7.4}$	430	7.9	0.44
ID-D	$10^{-9.4}$	10000 [b]	7.8	0.45
	$10^{-7.4}$	8500	7.9	0.44
ID-C	$10^{-9.4}$	820	8.4	0.47
	$10^{-7.4}$	1300	8.2	0.47
ID-A	$10^{-9.4}$	6200 [d]	8.1	0.44
	$10^{-7.4}$	514	8.4	0.46
ID-B	$10^{-9.4}$	300	8.7	0.43
	$10^{-7.4}$	610 [b]	8.5	0.42
CO-C	$10^{-9.4}$	5200	8.0	0.42
	$10^{-7.4}$	8100	8.0	0.44

The standard error of the mean is [a] 10% or less unless indicated otherwise, [b] between 12% and 20%, [c] 32%, and [d] 60%.

TABLE 3-A. Sorption of Plutonium in Soils. Distribution Coefficients for Soils in Acid Solutions.

Soil	Initial Pu Conc, M	$K_{d(m)}$[a]	pH	-Eh,V	$\frac{Pu_m}{Pu_c}$*
SC	10^{-8}	280	5.5	0.48	20
	10^{-7}	870	5.2	0.53	14
	10^{-6}	1000	5.2	0.53	100
NM	10^{-8}	100	6.9	0.48	20
	10^{-7}	200	6.0	0.47	600
	10^{-6}	220	6.2	0.51	1000
TN	10^{-8}	2600[c]	4.9	-	-
	10^{-7}	1200	4.9	-	-
	10^{-6}	14000[c]	5.0	0.53	8.0
AR-B	10^{-8}	80	5.6	0.58	1.0
	10^{-7}	230	5.3	0.55	9.0
	10^{-6}	260[b]	5.0	0.64	3.0
CO-A	10^{-8}	2200[c]	6.5	0.49	2
	10^{-7}	2700	6.2	-	-
	10^{-6}	1200[b]	6.8	0.43	16000
CO-B	10^{-8}	190[b]	5.8	0.53	6
	10^{-7}	130	5.8	0.54	60
	10^{-6}	40	5.8	0.53	3200
AR-C	10^{-8}	430	5.9	0.40	100
	10^{-7}	570	5.9	0.42	680
	10^{-6}	870	6.0	0.57	13
IL	10^{-8}	230	5.8	0.61	0.1
	10^{-7}	630[b]	5.4	0.65	0.06
	10^{-6}	27	5.7	0.64	26
AR-A	10^{-8}	710	6.7	0.51	1.6
	10^{-7}	660	6.5	0.54	5.8
	10^{-6}	760	7.0	0.50	200
NY	10^{-8}	810[b]	6.0	-	-
	10^{-7}	1100	6.0	0.54	6.0
	10^{-6}	870	6.1	0.49	600

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*Ratio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water phase were in equilibrium with $Pu(OH)_4$ (Pu_c). Pu_c is based on a solubility product for $Pu(OH)_4$ of $10^{-55.2}$ in acid solutions.

The standard error of the mean is [a] 8% or less unless indicated otherwise, [b] between 11% and 16%, [c] between 20% and 25%, and [d] 31%.

TABLE 3-B. Sorption of Americium in Soils. Distribution Coefficients for Soils in Acid Solutions.

Soil	Initial Am Conc, M	$K_{d(m)}$	pH	-Eh,V
SC	$10^{-9.4}$	82	6.1	0.54
	$10^{-7.4}$	190	5.9	0.55
NM	$10^{-9.4}$	400	6.9	0.49
	$10^{-7.4}$	420	7.3	0.48
TN	$10^{-9.4}$	2000 [b]	5.2	0.49
	$10^{-7.4}$	9700 [b]	5.1	0.49
AR-B	$10^{-9.4}$	390	6.6	0.57
	$10^{-7.4}$	760	6.5	0.56
CO-A	$10^{-9.4}$	2500	6.6	0.41
	$10^{-7.4}$	2600	6.4	0.43
CO-B	$10^{-9.4}$	600	6.4	0.52
	$10^{-7.4}$	840	6.4	0.43
AR-C	$10^{-9.4}$	1800	5.9	0.57
	$10^{-7.4}$	2300	6.0	0.60
IL	$10^{-9.4}$	1600 [b]	5.9	0.56
	$10^{-7.4}$	1900	5.8	0.56
AR-A	$10^{-9.4}$	820 [c]	6.6	0.57
	$10^{-7.4}$	3300	6.5	0.56
NY	$10^{-9.4}$	920	6.2	0.45
	$10^{-7.4}$	2300 [b]	6.0	0.50

The standard error of the mean is [a] 10% or less unless indicated otherwise, [b] between 12% and 20%, [c] 32%, and [d] 60%.

earlier, this complex would probably be negatively charged, thus causing a decrease in sorption. Complexing is probably significant at the 10^{-8} and 10^{-7} M initial concentrations. Based on Eh and pH values, it would be less significant at 10^{-6} M; therefore, the distribution coefficient should be higher. However, the ratio of measured to calculated plutonium is very large indicating that if complexing had been considered in calculating the plutonium concentration in equilibrium with $Pu(OH)_4$, the ratio could likely still exceed unity. Thus, a combination of complexing and polymerization could decrease the $K_{d(m)}$ at the 10^{-6} M concentration.

The data for the CO-C soil indicated no difference in plutonium sorption for the three initial concentrations. A difference (increase) in the relative sorption might be expected at a pH 7.8 (less carbonate complexing). However the Eh, not measured in this instance, could possibly have been high enough to offset the effect of a lower pH.

The americium sorption data presented in Table 2-B indicate little difference in the distribution coefficients for the two initial americium concentrations of $10^{-9.4}$ and $10^{-7.4}$ M, with the exception of the results for the ID-A soil. The difference in the distribution coefficients for the ID-A soil is a factor of approximately 12, whereas the differences for the other soils are a factor of 2 or less. In each case where a difference does occur a lower sorption is observed with the higher pH values. This trend is in agreement with the data presented in Figure 1, where a decrease in the effective positive charge of americium in solution is observed with an increase in pH. This decrease is attributed to an increase in hydrolysis. The increase in pH (7.8 to 8.0) may not be sufficient to account for the necessary decrease in the effective positive charge of americium which is needed to reduce the distribution coefficients of the WA-A and WA-B soils by a factor of 2. However, the decrease in sorption for the ID-A and ID-B soils can be attributed to an increase in pH (8.1 to 8.4 and 8.5 to 8.7, respectively) which could account for the necessary decrease in the effective positive charge of the americium in solution.

ACTINIDE SORPTION BY SOILS IN ACID SOLUTIONS

The results for the SC and NM soils (Table 3-A) indicate a lower distribution coefficient and a higher pH at the 10^{-8} M initial plutonium concentration compared to that for the higher initial concentrations. The ratio of Pu_m to Pu_c indicates the presence of polymers for all concentrations. The reduced sorption can be explained on the basis of a difference in charge density; the higher the pH, the lower the positive charge density. In the case of the TN soil lower distribution coefficients are observed at the two lower initial concentrations compared to that at the highest initial concentration. Although the ratio of Pu_m to Pu_c could not be calculated (Eh not measured) for the lower initial concentrations, polymers are most likely absent. At a pH of 5.0 the positive charge density of the polymers probably exceeds that for the nonpolymerized plutonium, thus resulting in a higher sorption in the presence of polymers. The difference in the distribution coefficients for the AR-B soil can be explained on the same basis as the difference in distribution coefficients for the TN soil.

The differences in the distribution coefficients at different initial plutonium concentrations for the CO-A, CO-B, and AR-C soils are attributed to a disproportionate amount of polymers in the solutions. For example, a disproportionately higher concentration of polymers should give a lower distribution coefficient based on a lower positive change density for polymers compared to nonpolymerized species. The decrease in the distribution coefficient for the IL soil at the 10^{-6} M initial concentration is attributed to the presence of polymers having a lower positive charge density than the nonpolymerized plutonium.

No significant difference is observed in the distribution coefficients for the AR-A and NY soils. A difference (decrease) might be expected at the 10^{-6} M initial concentration because of disproportionately higher concentrations of polymers as estimated by the ratio of Pu_m to Pu_c. Apparently the increase in polymers is not great enough to cause a significant decrease in the sorption of plutonium.

As in the case of americium sorption in basic solutions, a general trend is observed in acid solutions in which a decrease in sorption is observed with an increase in pH (Table 3-B). The largest decrease (approximately 4) was observed for the TN soil in which the pH differed from 5.1 to 5.2. The data in Figure 1 suggest that a factor of 4 reduction in sorption would not be expected from such a small change in pH. However, the data in Figure 1 and in Table 3-B cannot be considered as absolute quantities but only as indicators of a trend.

COMPARISON OF PLUTONIUM AND AMERICIUM SORPTION

A general trend becomes apparent when the distribution coefficients for plutonium are compared with the distribution coefficients for americium. Qualitatively, sorption of plutonium can be related to the sorption of americium for a soil on the basis of the expected effective positive charge of the actinides in solution. For example, based on the data in Figure 1, the effective positive charge of americium in solution (where americium has an oxidation state of III) probably varies from about 1.5 to 1.0 as the pH varies from 7 to 8. Also the effective charge of plutonium in solution should be about 1, assuming polymers are not present in the solution. Under these conditions the distribution coefficients for americium should be equal to or greater than that for plutonium. Examples of soils having distribution coefficients which follow this trend are WA-A, WA-B, ID-D and CO-C (Tables 2-A and 2-B). A direct proportionality between the effective positive charge and the distribution coefficients for these two actinides would not be expected because of other factors which could affect sorption. For example, the oxidation state and effective size of the molecules could influence sorption. This influence could either be minimized or maximized by the mineralogical composition of the soils.

The results for the ID-A soil also suggest a relationship between effective positive charge and sorption. The larger distribution coefficients for both plutonium and americium are observed under conditions when an effective positive charge of approximately 1 is expected. The smaller distribution coefficients are observed when an effective positive charge of less than 1 is expected.

The data in Tables 3-A and 3-B also indicate a qualitative relationship between the expected effective positive charge and the distribution coefficients. Again, based on data in Figure 1, the effective positive charge for americium [Am(III)] varies from about 2 to 1.5 as the pH varies from 5 to 7. Under acid conditions the nonpolymerized plutonium in solution should have an effective positive charge of about 1, PuO_2^+(PuV). Polymerized plutonium is likely to have an effective positive charge of less than 1 at the higher pH values under acid conditions and an effective positive charge of greater than 1 at the lower pH values (near 5.0).

Data for the NM, CO-B, and AR-C soils provide examples in which the effective positive charge of the polymerized plutonium is probably less than one and the effective positive charge of americium in solution is greater than one. The sorption of americium is also greater than the sorption of plutonium for each individual soil. The data for the SC and TN soils provide examples in which the charge of the polymerized plutonium is expected to be greater than 1 and possibly even greater than 2.

The data for the IL soil provide an example in which both the plutonium (10^{-8} and 10^{-7} M) and the americium in solution are expected to be nonpolymerized, but the effective positive charge of the americium is expected to be greater than that for plutonium. The sorption of americium is also greater than that for plutonium as indicated by their respective distribution coefficients.

SUMMARY AND CONCLUSIONS

Observations are made with respect to experimentally measured plutonium and americium sorption by soils. Sorption by most of the soils, as expressed by $K_{d(m)}$ values, is found to depend on the initial concentration of the actinides in the system. In general, however, the sorption of americium varied less for an individual soil than did the sorption of plutonium. Initial concentrations of 10^{-8}, 10^{-7} and 10^{-6} M were used for plutonium and $10^{-9.4}$ and $10^{-7.4}$ M were used for americium.

Several trends are observed with respect to the changes in sorption.

(1) A lower sorption generally occurs in solutions containing plutonium polymers compared to solutions containing only nonpolymerized plutonium. However, in solutions with pH values less than 5.5 a higher sorption occurs in the presence of polymers. The presence of polymers is postulated on the basis that more plutonium is found in the water phase than can be explained by the solubility of plutonium hydroxide. When the ratio of measured plutonium to that calculated to be in equilibrium with plutonium hydroxide exceeds unity, then polymers are assumed to be present in solution.

(2) In acid solutions where differences in pH occur for different initial plutonium concentrations and where polymers are present, a lower sorption usually occurs at the higher pH.

(3) A decrease in the sorption of plutonium occurs with an increase in pH when the pH values are approximately 8 or greater, even though polymers are not present in the solutions.

(4) A decrease in the sorption of americium occurs with an increase in pH. The largest decrease occurs when the pH is greater than 8.

(5) In general, for an individual soil, the sorption of americium tends to be as great or greater than the sorption of plutonium. However, exceptions do occur, but are limited to solutions in which the pH is less than 5.5 or greater than 8.0.

The above observations suggest an apparent qualitative relationship between sorption and the effective positive charge of the plutonium and americium in solution. The effective positive charge of plutonium in solution can be influenced by several factors. Normally, the positive charge of plutonium should be one in solutions in which the pH ranges from 5 to 8. This is due to the presence of PuO_2^+ (PuV) as the predominant species. When the pH of the solution becomes 8 or greater, another plutonium species may predominate. The PuO^{2+} (PuVI) species can react with hydroxyl and carbonate ions to form a negatively charged complex, probably $[PuO_2(OH)CO_3]^-$, in sufficient concentration to exceed the concentration of PuO_2^+; thus reducing the effective positive charge of plutonium in solution.

When the plutonium concentration exceeds the solubility of plutonium hydroxide, polymers are likely to be formed. The positive charge density will vary considerably over the pH range of interest (5.0 to 9.0). The positive charge density will be greater at a low pH and less at a high pH. Apparently, based on sorption data, the positive charge density of the polymers is likely to exceed the effective positive charge of PuO_2^+, the predominant aqueous species, at pH values less than 5.5. If the relative amount of the polymer is increased, an overall reduction in the effective positive charge should also occur when the effective positive charge of the polymer is less than the effective charge of the ions in solution.

The effective positive charge of americium is affected primarily by the hydrolysis of americium in solution. Americium is likely to be in an oxidation state of three, Pu(III), in solution. As the pH of americium solution increases from 1 to 9, stepwise hydrolysis is likely to occur, changing the effective positive charge of americium from 3 to near 0. In the pH range from 5 to 7, the charge should decrease from 2 to 1.5 and in the pH range of 7 to approximately 8.2 the charge should decrease to about 1. If a further increase in pH should occur, then the effective positive charge should decrease rapidly to near 0.

A comparison of the effective positive charge of americium and plutonium in solution suggests that between pH values of about 5.5 to 8.0, the effective positive charge of americium should be equal to or greater than the effective positive charge of plutonium. In solutions where the pH is less than about 5.5 and greater than 8 the effective positive charge of americium may either be greater, equal to, or less than the effective charge of plutonium.

LITERATURE CITED

1. Cleveland, J. M. 1970. The Chemistry of Plutonium. Gordon and Breach, Science Publishers, Inc. New York.

2. Constanzo, D. A., R. F. Biggars and J. T. Bell. 1973. Plutonium Polymerization-I. A spectrophotometric study of the polymerization of plutonium (IV). J. Inorg. Nucl. Chem. 35:609-622.

3. Fuger, J., J. C. Spirlet and W. Muller, 1972. A new determination of the heat of solution of americium metal and the heat of formation of various americium ions and compounds. Inorg. Nucl. Chem. Letters 8:709-723.

4. Gelman, A. D., A. T. Moskvin, L. M. Zaitsev, and M. P. Medfod'eva. 1962a. "Complex Compounds of Transuranic Elements", Translated by C. N. Turton and T. I. Turton, Consultants Bureau, New York, pp 65-66.

5. Gelman, A. D., A. I. Moskvin and V. P. Zaitseva. 1962b. Carbonate compounds of plutonyl. Soviet Radiochem. 4:138.

6. Griffin, R. A. and T. T. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci. 116:26-30.

7. Hingston, F. T., R. J. Atkinson, A. M. Posner, and J. P. Quirk. 1968. Specific adsorption of anions on goethite. Int. Cong. Soil Sci., Trans. 9th (Adelaide) III:669-677.

8. Kaska, M. 1949. Reactions between plutonium ions in perchloric acid solution: rates, mechanisms, and equilibria. p. 295-334. In G. T. Seaborg, J. J. Katz and W. M. Manning (ed). The Transuranium Elements. National Nuclear Energy Series, IV-14B, McGraw-Hill Book Co., New York.

9. Kepák, F. 1971. Adsorption and collodial properties of radioactive elements in trace concentrations. Chemical Reviews. 71:357-369.

10. Korotkin, Yu. S. 1972. Study of transplutonium element hydrolysis. II. Hydrolysis of americium (III) in the presence of ions with positive and negative hydration energy. Joint Institute for Nuclear Research. Report JIWR-P-6403 (preprint).

11. Latimer, W. M. 1952. Oxidation Potentials, Second Edition. Prentice-Hall, Inc. New York.

12. Lingren, W. E. 1966. The electrochromatography of sea-water containing dissolved plutonium. USNRDL-TRC-85:1-24.

13. Lloyd, M. H. and R. G. Haire. 1973. Studies on the chemical and collodial nature of Pu(IV) polymer. USAEC Report CONF 730927:1-9.

14. Metz, C. F. and G. R. Waterbury. 1964. Plutonium p. 260. In C. J. Rodden (ed). Analysis of Essential Nuclear Reactor Materials, USAEC.

15. Moskvin, A. I. and A. D. Gelman. 1958. Determination of the composition and instability constants of oxalate and carbonate complexes of plutonium (IV). Zhurnal Neorganischeskio Khimic (J. Inorg. Chem. USSR) III:4 P. 962-974.

16. Perlman, I. and K. Street, Jr. 1954. The chemistry of the transplutonium elements. p. 507-541. In G. T. Seaborg and J. J. Katz (ed.) The Actinide Elements. National Nuclear Energy Series, IV-14B, McGraw-Hill Book Co., Inc., New York.

17. Polzer, W. L. 1971. Solubility of plutonium in soil/water environments. p. 411-430. In Proceedings of the Rocky Flats Symposium on Safety in Plutonium Handling Facilities. USAEC Report CONF. 710401.

18. Rhodes, D. W. 1957a. Absorption of plutonium by soil. Soil Sci. 84:465.

19. Rhodes, D. W. 1957b. The effect of pH on the uptake of radioactive isotopes from solution by soil. Soil Sci. Soc. Amer. Proc. 21:389.

20. Rozzell, T. C. 1969. Sorption of Aqueous Plutonium on Silica Surfaces. Sc. D. Thesis, University of Pittsburgh.

21. Schoen, R. and C. E. Roberson. 1970. Structures of aluminum hydroxide and geochemical implications. The American Mineralogist. 55:43-77.

22. Shalinets, A. B. and A. V. Stepanov. 1972. Investigation of complex formation of the trivalent actinide and lanthanide elements by the method of electromigration. XVII. Hydrolysis. Translated from Radiokhimiga 14:280-282.

23. Sheidina, L. D. and E. N. Kovarskaya. 1970. Colloidal State of Pu(IV) in aqueous solutions. Soviet Radiochem. 12:229-233.

24. Syers, J. K., M. G. Browman, G. W. Smillie, and R. B. Corey. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Sci. Soc. Amer. Proc. 37:358-363.

FOLLOWING W. L. POLZER'S PRESENTATION

QUESTIONS AND ANSWERS

Garland: During the workup of your data, did you ever look at the total content of plutonium in solution at the three different concentrations? The reason I ask is that looking at the value of two or three of the ratios you showed, ratios were primarily changed by the change in the soil Pu concentration, indicating that maybe what you're seeing is a constant total concentration of "soluble plutonium" passing your 0.1 micron filter. Have you looked at your data in that manner to see whether that holds true with all the soils?

Polzer: If I understand what you're saying, the solubility of plutonium hydroxide may control the concentration of plutonium in aqueous solution. Even though the overall concentration of plutonium is increased, the aqueous form of plutonium remains constant while the excess forms a hydroxide.

Rai: Were you referring to the K_d values?

Garland: No, the ratio of the calculated to the . . . .

Polzer: Are you saying that it is just fortuitous that the ratios turned out the way they did and that some other phenomenon controls the $K_{d(m)}$ values?

Garland: What it might be, you may be in the range at which the hydrolysis, the rate of hydrolysis and so forth, or even equilibrium time in the three concentrations are giving you effectively the same concentration of plutonium in solution. Or you may have some organic soil component or something like that you've saturated.

Polzer: It's possible. We had hoped to have only one variable, that of the plutonium concentration. However, other changes did occur. I have tried to explain the trends in the data. Other mechanisms could account for these differences, but it appears that these postulates do hold.

Nyhan: Do you have any idea what possible iron and carbonate equilibria would do to the whole system? Lower pH's would probably have a lot better chance of iron-plutonium complexation.

Polzer: No. The interpretation given our data suggests several mechanisms which can explain the differences in sorption. Future work can be directed towards the evaluation of these mechanisms.

BEHAVIOR OF PLUTONIUM-238 SOLUTIONS IN THE SOIL AND HYDROLOGY SYSTEM AT MOUND LABORATORY

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INTRODUCTION

Mound Laboratory is operated by Monsanto Research Corporation for the Energy Research and Development Administration The laboratory, constructed in 1947, is located in Miamisburg, Ohio, overlooking the old abandoned Miami-Erie Canal and the Great Miami River, as shown in Figure 1. Since 1959 the Laboratory has been the major research and development site for fabrication of radioisotopic heat sources used for peaceful space and terrestrial applications.

Radioisotopic Thermoelectric Generators (RTG) powered by Mound Laboratory ^{238}Pu heat sources have been used to provide electrical energy for many space satellites from the SNAP-3 RTG in 1961 to the SNAP-19 RTG in the Nimbus Weather Satellite in 1969 and the Transit Navigational Satellite in 1972.

Heat sources provided heat and electrical power for the scientific experimental packages left on the moon during the Apollo missions as shown in Figure 2. Recently, Mound-prepared ^{238}Pu heat sources were used to provide electrical energy for the Pioneer-Jupiter Missions and was used for the Viking Mars Lander.

Experimental ^{238}Pu sources also have been developed to supply energy for experimental heart pacemakers shown in Figure 3,

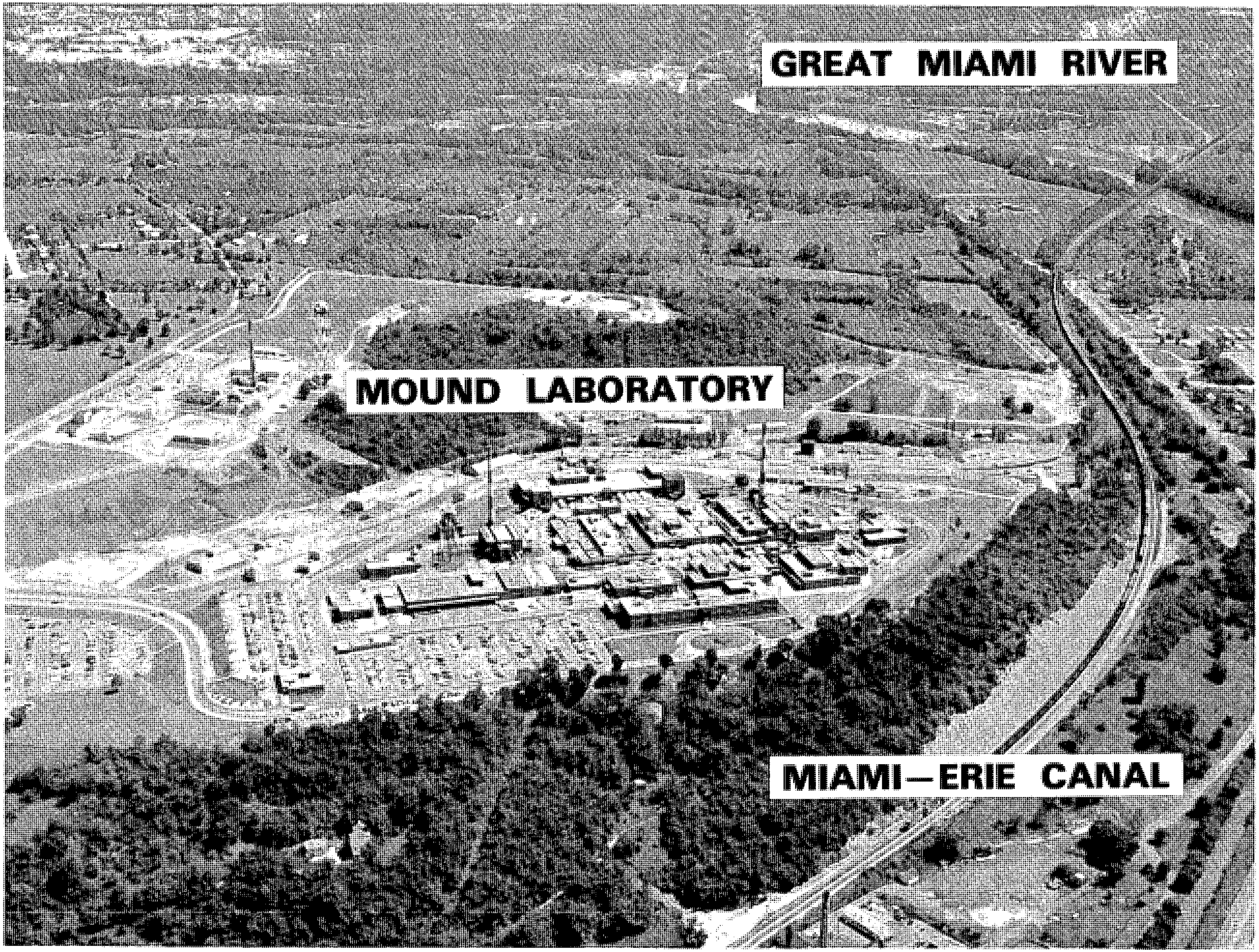


FIGURE 1. Aerial View of Mound Laboratory Looking South

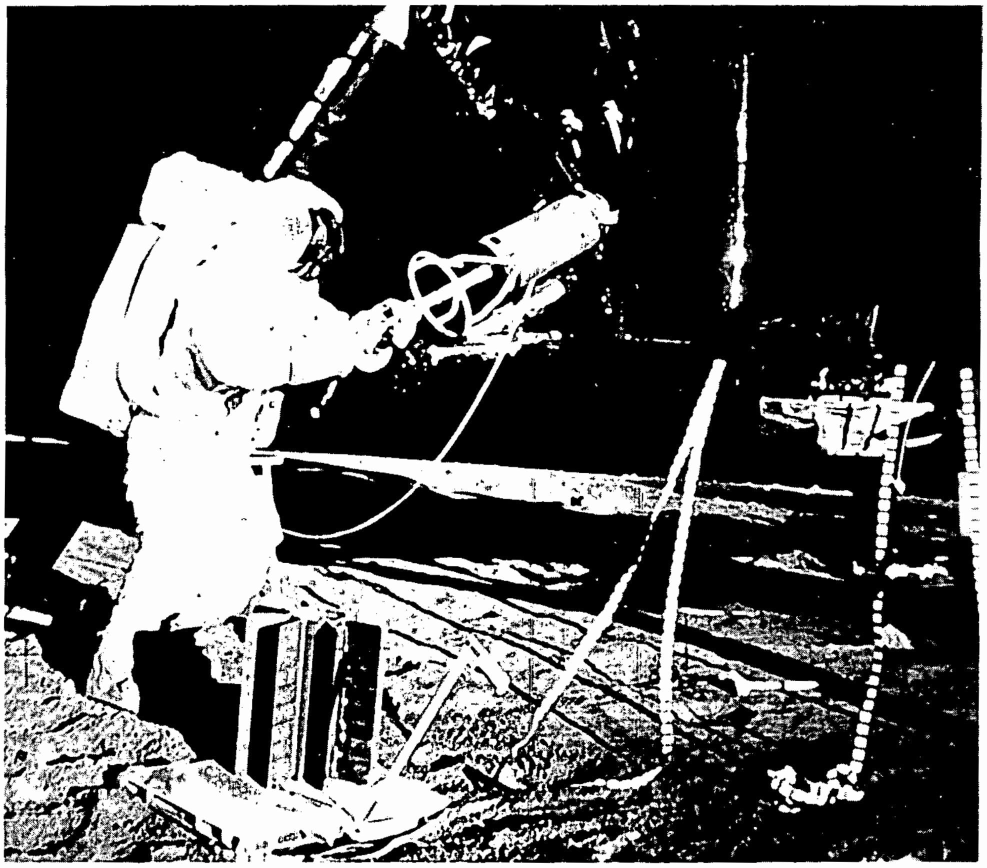


FIGURE 2. ^{238}Pu SNAP-27 Heat Source Being Removed from the LEM on the Lunar Surface on the Applo-12 Mission in 1969

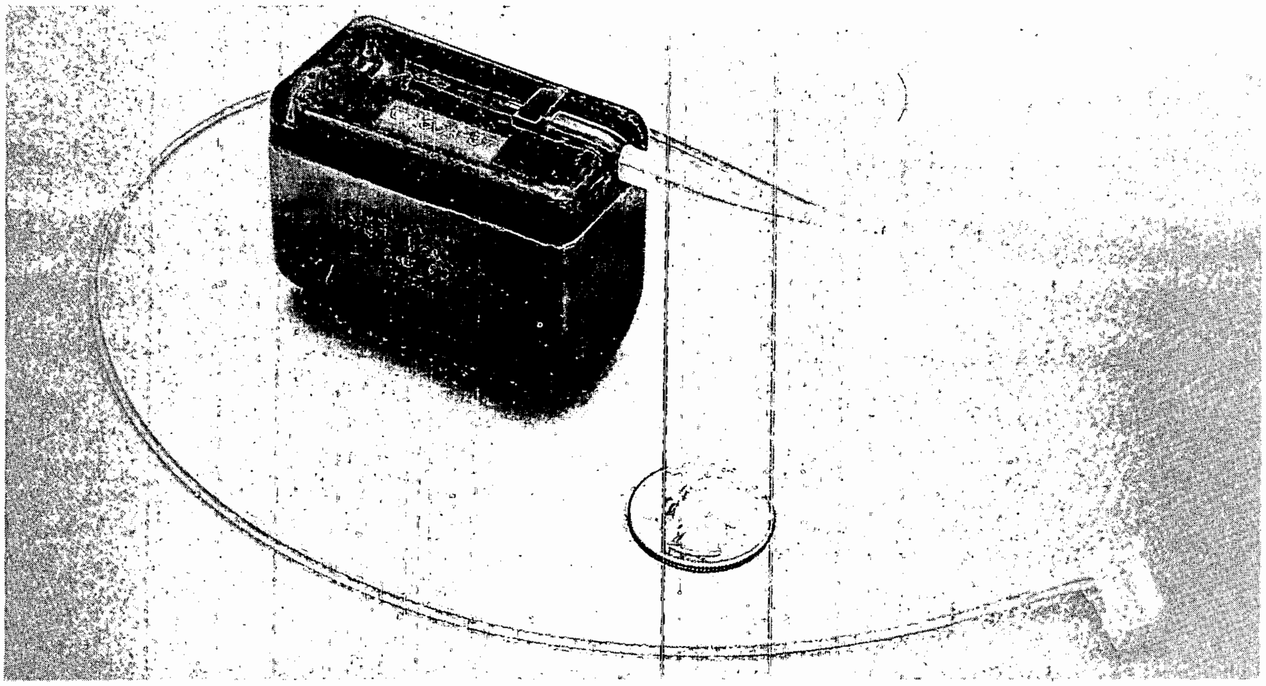


FIGURE 3. ^{238}Pu Powered Experimental Model Cardiac Pacemaker

and experimental artificial hearts. Miniature experimental ^{238}Pu X-ray sources were used to rapidly determine minute amounts of lead in the blood of children by a micro X-ray fluorescence technique.

Because plutonium is a potentially hazardous material, extensive precautions have been exercised since plutonium operations began at Mound Laboratory to carefully maintain strict control of the plutonium and to prevent significant amounts from entering the environment. These precautions include elaborate facility and equipment design criteria, scientific expertise, experience, personnel training, management and operational control systems, and environmental monitoring.

In spite of these precautions, in early 1974, core samples collected and analyzed by the Mound Laboratory Environmental Monitoring Group as a part of an upgrading program, established that ^{238}Pu concentrations in the sediment of certain waterways adjacent to the site were above the baseline levels expected (<0.0004 nCi/g). These ^{238}Pu deposits presented no immediate hazard to the general population in the area as indicated by the air and water concentrations which were well within accepted Radioactivity Concentration Guides (RCG) for ^{238}Pu. These preliminary findings were reported to ERDA, to local, state and federal government representatives and agencies and to the public through the news media.

Mound Laboratory launched the Mound Laboratory Environmental Plutonium Study to fully investigate the extent of the contamination, the source of plutonium, how it was transported and deposited in these waterways and what potential hazards these deposits might present to the general public now and in the future. A special scientific and management team was organized to participate and direct this study. The members of this team and their primary responsibilities are listed in Table 1.

A Monsanto Research Corporation advisory group, consisting of Mound Laboratory department directors, also reviewed plans, goals, schedules, and accomplishments during the programs.

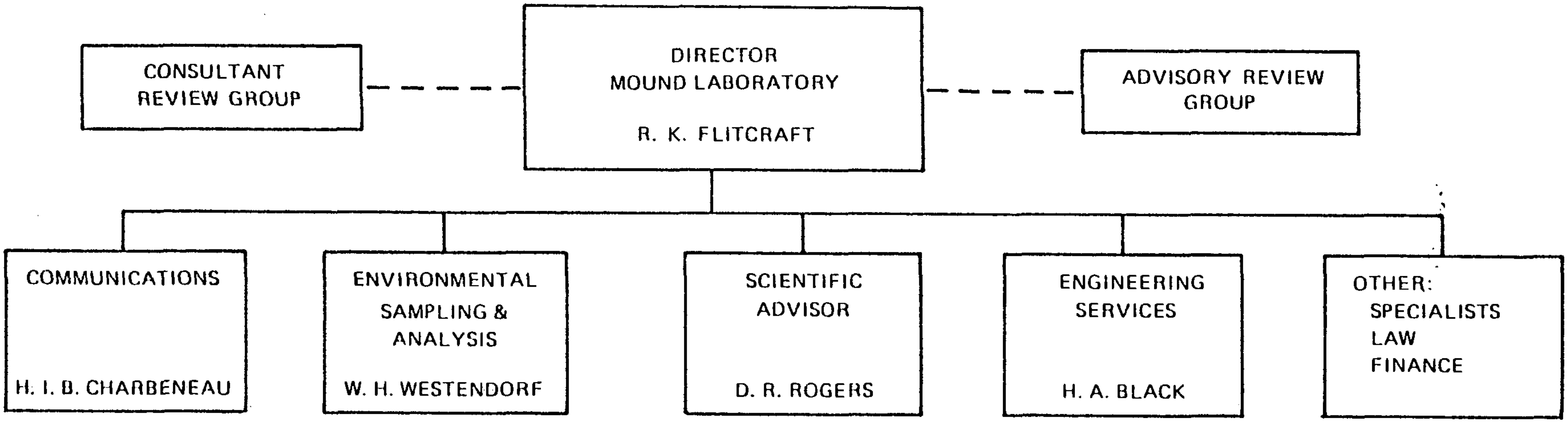
A number of outside consultants were used to augment and review plans and help interpret the data obtained. The consultants' specialties are:

- Hydrology
- Sedimentation
- Soil Chemistry
- Geology
- Ecology
- Biology

The consulting organizations are:

- Georgia Institute of Technology
- Emory University
- Wright State University
- Dames and Moore Company

TABLE 1. Mound Laboratory Environmental Plutonium Study Team and Responsibilities



COMMUNICATIONS	ENVIRONMENTAL SAMPLING & ANALYSIS	SCIENTIFIC ADVISOR	ENGINEERING SERVICES	OTHER
● PROVIDE, MAINTAIN AND COORDINATE COMMUNICATION CHANNELS TO THE PUBLIC, MEDIA, HEALTH AGENCIES, GOVERNMENTAL AGENCIES, MOUND EMPLOYEES AND OTHER INTERESTED GROUPS	● MANAGE ALL OPERATIONS ● DEVELOP SAMPLING PLAN FOR ON-SITE AND OFF-SITE AREAS	● REVIEW SCIENTIFIC VALIDITY OF ALL OPERATIONS & PLANS ● IDENTIFY CAUSE ● DETERMINE MECHANISMS ● PERFORM HEALTH AND SAFETY EVALUATIONS	● DEVELOP ENGINEERING PLANS FOR ELIMINATION OF HEALTH AND SAFETY PROBLEMS ● DEVELOP ENGINEERING PLANS TO PREVENT RECURRENCE ● PROVIDE ENGINEERING SERVICES & DATA	● SERVICES AS REQUIRED

- United States Geological Survey
- Miami Conservancy District
- United States Department of Agriculture.

The overall objectives of the Mound Laboratory Environmental Plutonium Study were to:

- Perform a comprehensive ^{238}Pu Environmental Survey of the entire affected area to define the spatial extent, distribution, concentrations, and total inventory of the plutonium in and around these waterways;
- Perform an intensive and thorough Investigation and Cause Analysis to determine the source of the plutonium, the cause of the release, and the mechanisms of transport and deposit in the waterways;
- Perform a comprehensive Health and Safety Analysis to evaluate credible potential health hazards to the general public.

During the course of this program, interim reports were periodically submitted and reviewed with health, environmental and governmental agencies to keep them informed as the environmental results became available.

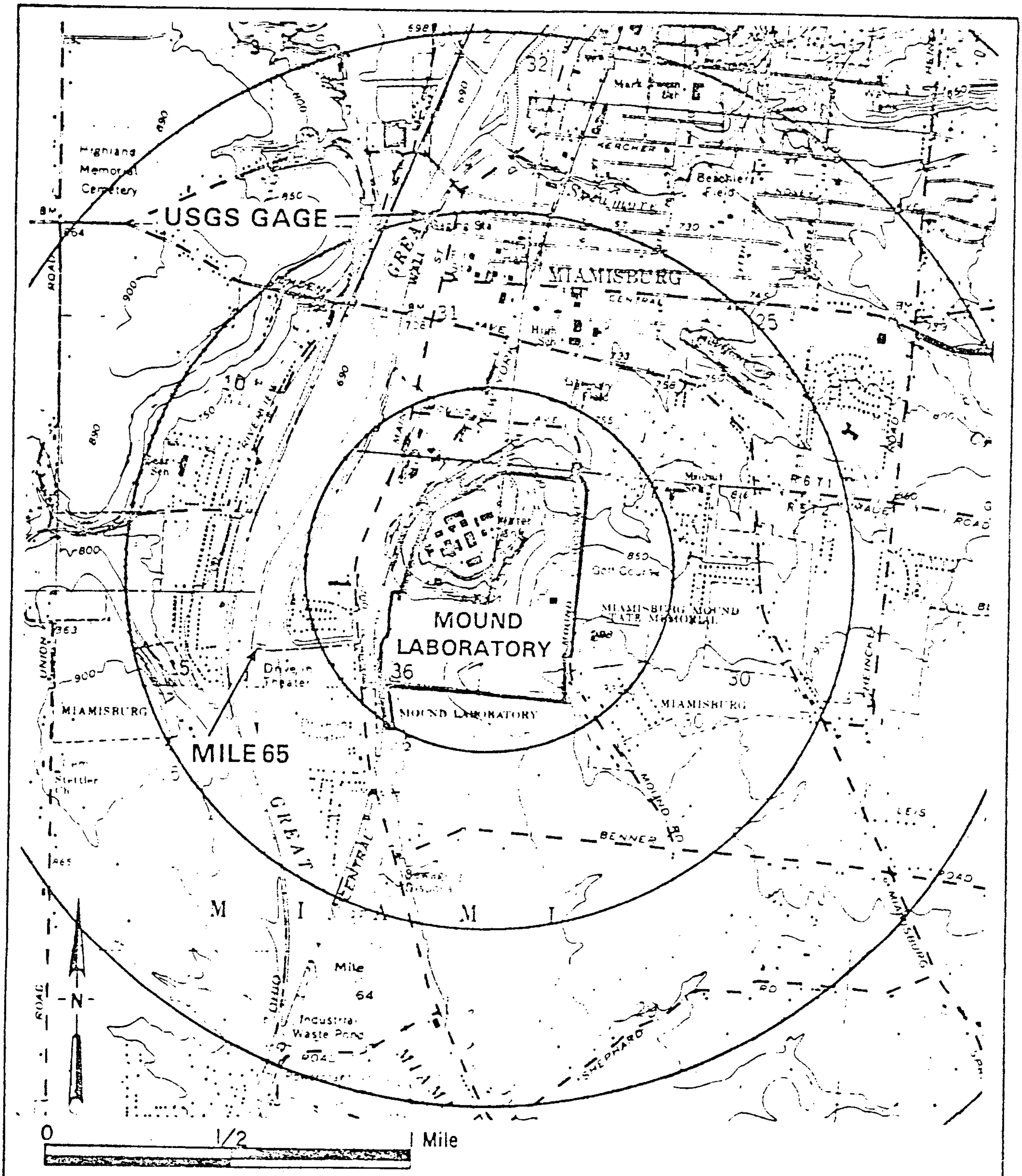
The findings of the Mound Laboratory Environmental Study, essentially completed in September 1974, were orally presented to interested local, state and federal government officials, and health and environmental agencies prior to a press conference held at Mound Laboratory on October 2, 1974.

The purpose of this report is to summarize the results and conclusions of the Mound Laboratory Environmental Plutonium Study, concentrating on the details of the health and safety analyses which were performed.

TOPOGRAPHY, HYDROLOGY AND DESCRIPTION OF THE AREA

Mound Laboratory is situated on a topographically high area overlooking Miamisburg, the Great Miami River, and the river plain area to the west. Figure 4 shows the topography in the general area.

The 180-acre laboratory site is basically located on two hills of about 880 ft elevation and a valley between with an elevation of about 705 ft. The site topography and facilities are shown in Figure 5. The Plutonium Processing Facility (SM-PP) is on the southeast hill while the Plutonium Research Facility (R Building) and the Waste Disposal (WD) and Sewage Disposal (SD) facilities are on the northwest hill.



Circles on ½-mile radii from center of site.

FIGURE 4. Topology of Mound Laboratory and Neighboring Areas

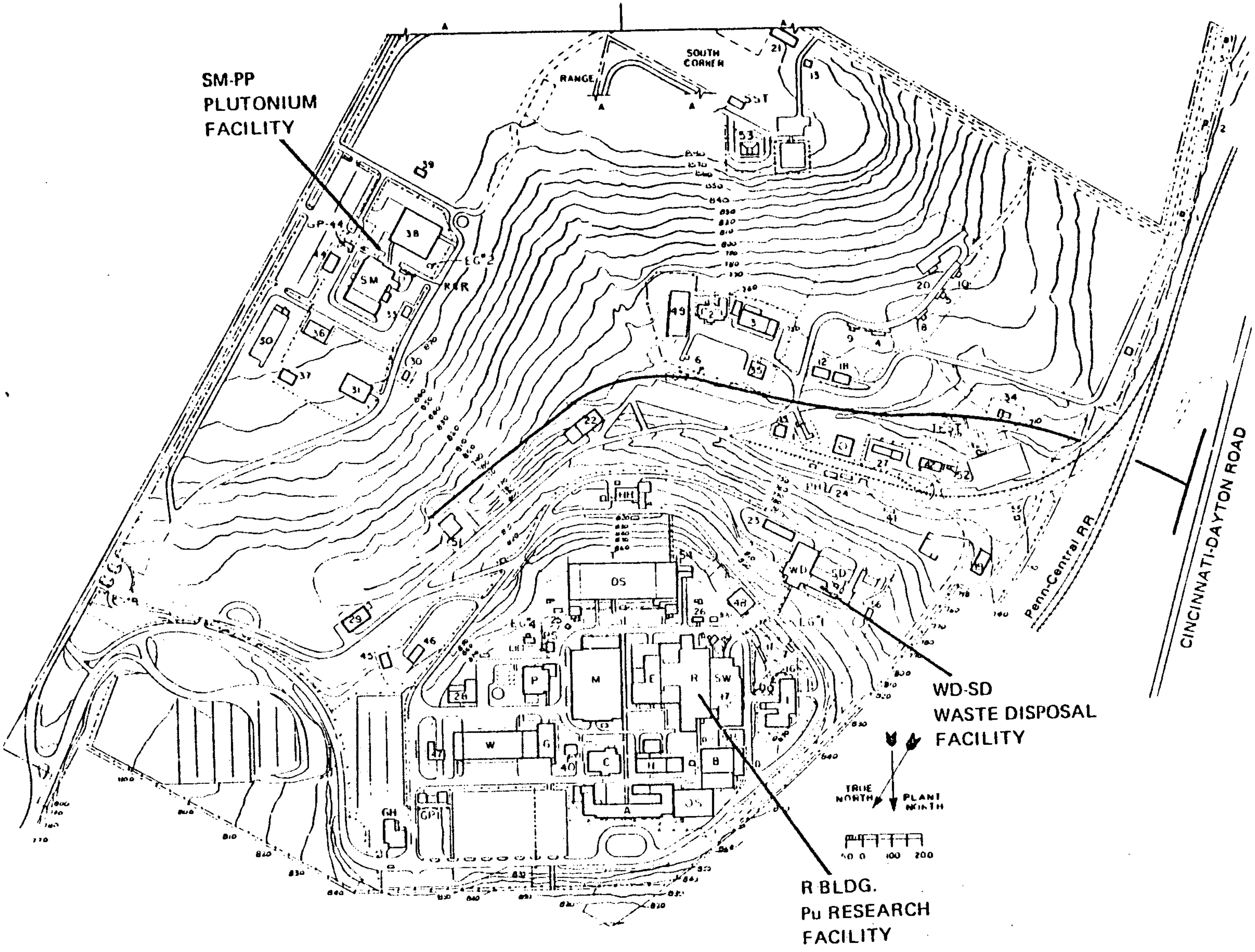


FIGURE 5. Topology of Mound Laboratory Site

A drainage ditch flows continuously through the onsite valley generally from east to west and is the major surface hydrological artery for carrying surface runoff water from the site (Figure 6). This drainage ditch flows off the site on the western side through a culvert under a raised railroad grade which runs generally north-south along the western boundary of the laboratory. Since 1971, Mound Laboratory has had an automatic flow measurement weir and an environmental sampling station on the drainage ditch just before it flows offsite (Figure 7). After the drainage ditch passes under the railroad grade, it flows to an abandoned section of the old Miami-Erie Canal. Part of the water is diverted north through pipes under an earthen dam into the North Canal while the remainder of the water flows around a make-shift dam into the South Canal (Figures 8, 9, and 10). These two sections of the old Miami-Erie Canal extend north and south (2500 ft north and 2700 ft south) of the drainage ditch/canal confluence as shown in Figure 11. The canal bed is approximately 40 ft wide and 5 to 10 ft deep relative to the bank height. It was constructed in the 19th Century as a commercial transportation barge canal and abandoned in 1913.

The North Canal, immediately north of the earthen dam, is a high sedimentation area and contains 5 ft or more of sediment. Turbulent water, heavily laden with erosion products from the

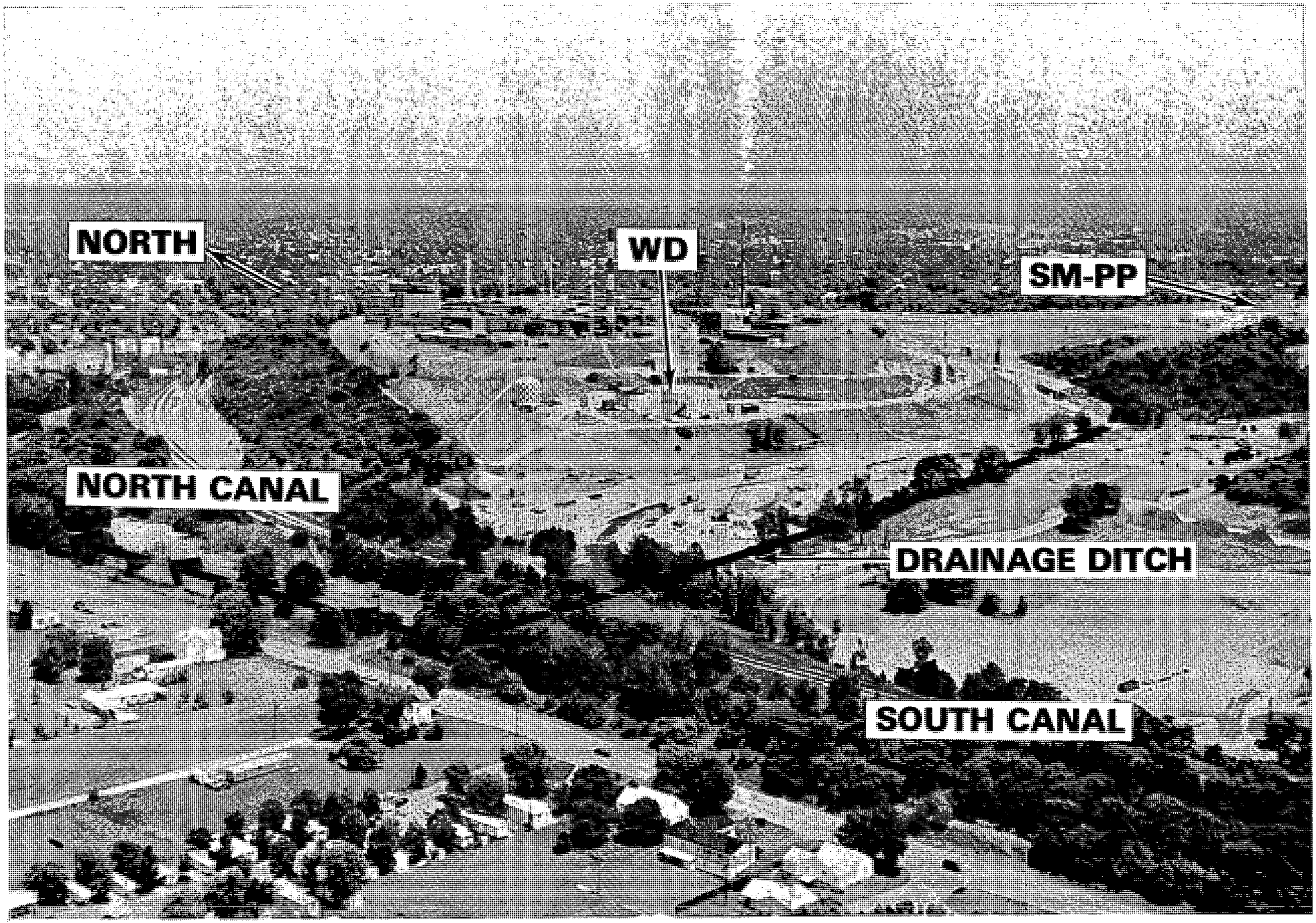


FIGURE 6. Aerial View (from the west) of Mound Laboratory Showing Major Surface Hydrological Arteries

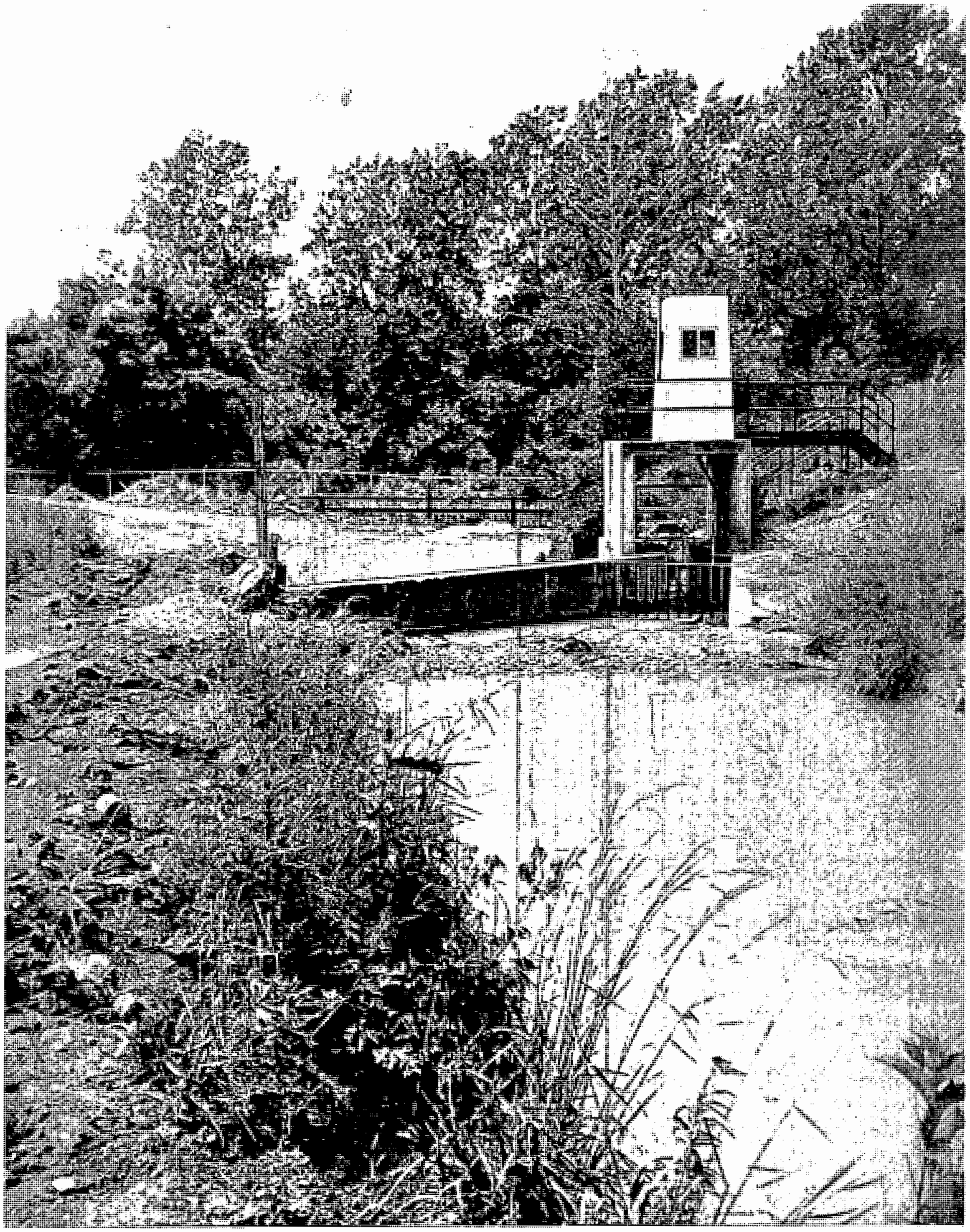


FIGURE 7. Environmental Monitoring Station and Automatic Flow Measurement Weir on the Drainage Ditch

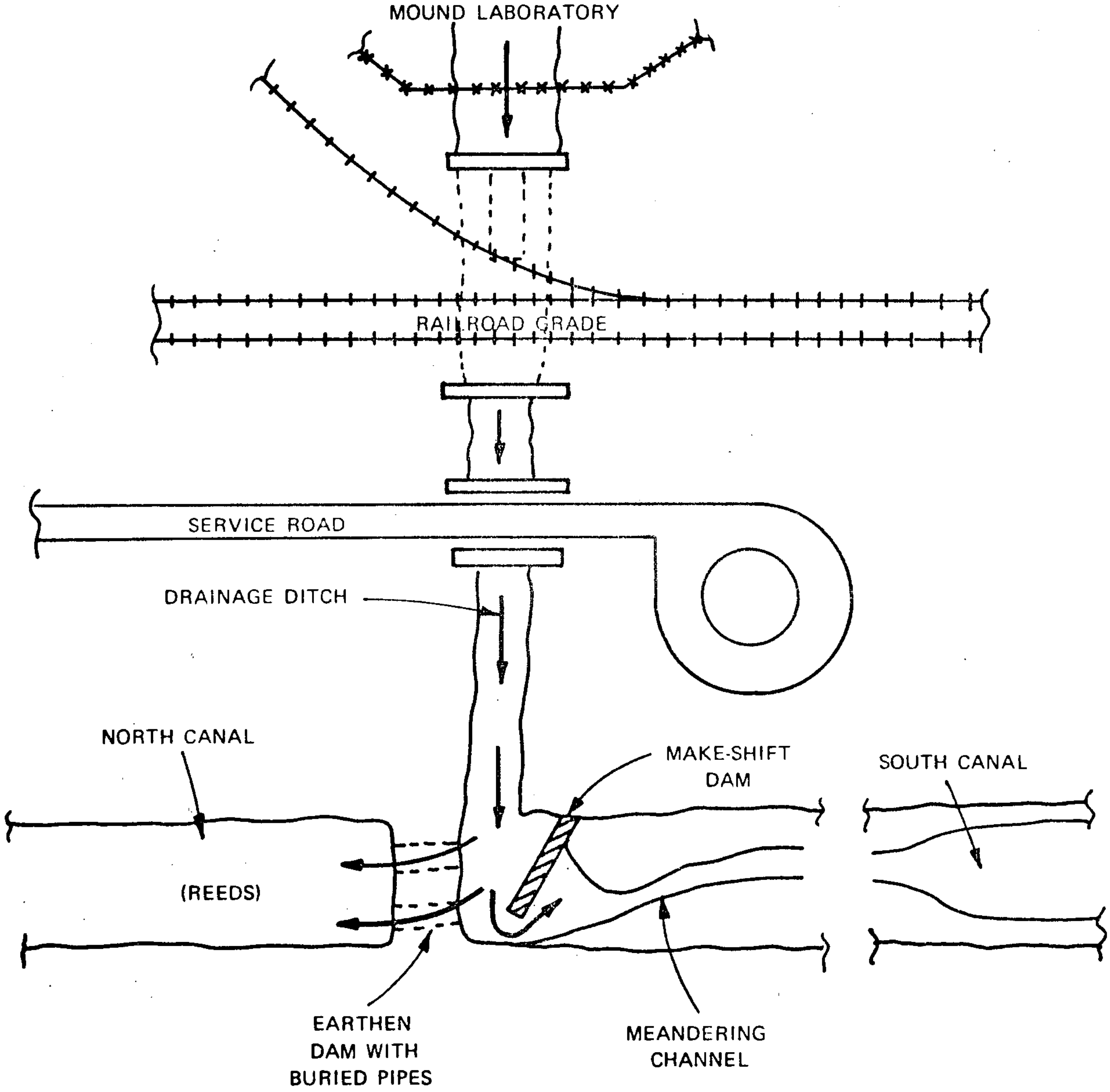


FIGURE 8. Schematic Diagram of the Drainage Ditch/Miami-Erie Canal Confluence Area

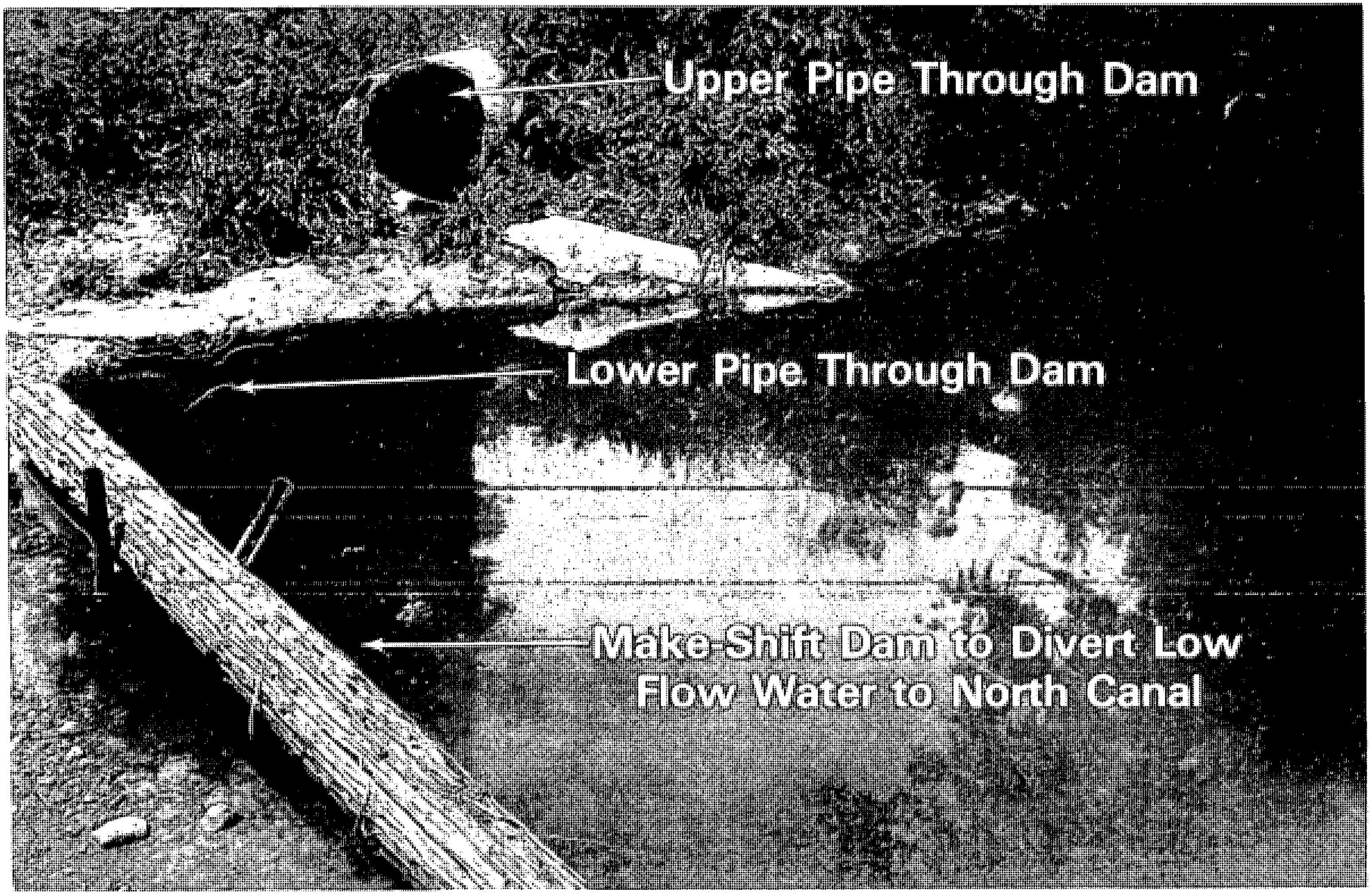


FIGURE 9. Earthen Dam Separating the North and South Canals

FIGURE 10. South Canal Viewed from the Top of the Earthen Dam

FIGURE 11. Aerial View (from the north) of Off-Site Waterways

drainage ditch, passes through the pipes in the earthen dam and encounters calm water and a heavy growth of cattail reeds which tends to cause laminar flow (Figure 12). Under the less turbulent flow condition, a large percentage of the erosion products settle out and deposit. In a short distance, ∿100 to 200 ft, the canal gets wider and deeper. At the northern end of the North Canal (Figure 13), the water is again diverted by an earthen dam and an underground pipe into the South Pond (Figure 14). The water flows north from the South Pond (which consists of a north and south basin) and into the North Pond (Figure 15) where the excess is carried off through a standpipe drain into the underground Mound Street storm sewer which carries the water directly to the river.

Under very high flow conditions, water in the North Canal flows through a notch in the earthen weir and can be released to the Mound Street storm sewer directly by opening a sewer gate at the north end of the canal (Figure 13). The North Canal and ponds remain under water at all times.

The South Canal is essentially overgrown with vegetation except for a meandering channel within the old canal bed (Figure 10). Under normal flow conditions, only a small amount of water flows past the make-shift dam into the South Canal and this water is carried by the meandering channel. Under high flow conditions, the entire South Canal channel fills and contains the water flow. There is a high sedimentation

FIGURE 12. North Canal, Viewed from the Top of the Earthen Dam, Showing Growth of Cattail Reeds

FIGURE 13. North Canal Viewed from the Extreme Northern End

FIGURE 14. South Pond Viewed from the South

FIGURE 15. North Pond Viewed from the Northeast

area which extends from approximately 600 to 1500 ft south of the earthen dam. This area is wide and also has a heavy stand of cattail reeds which impedes the water flow and induces laminar flow conditions. At the extreme south end of the South Canal, the water flows under a railroad bridge, then over a concrete weir spillway (Figure 16) to a culvert under the Cincinnati-Dayton Road, then to an overflow creek which carries the water to the river (Figure 17).

The banks of the North and South Canals are high and quite definite except at the extreme southern end. In the section adjacent to the overflow weir, the bank to the east is lower. Water flows north to this area from a drainage ditch that extends to the south. During periods of heavy flow, water backs up and overflows the eastern bank and floods an area about 400 ft long and 30 ft wide. The grade of the land beyond this prevents further flooding. The area immediately behind the overflow creek spillway is considered only a moderate sedimentation area since it is already nearly full of sediment.

The overflow creek was used, when the canal was in operation, to carry the excess water from the canal during periods of high accumulation. This cannel is 15 to 25 ft wide and is quite rocky. Its outfall on the river is immediately south of the railroad river bridge.

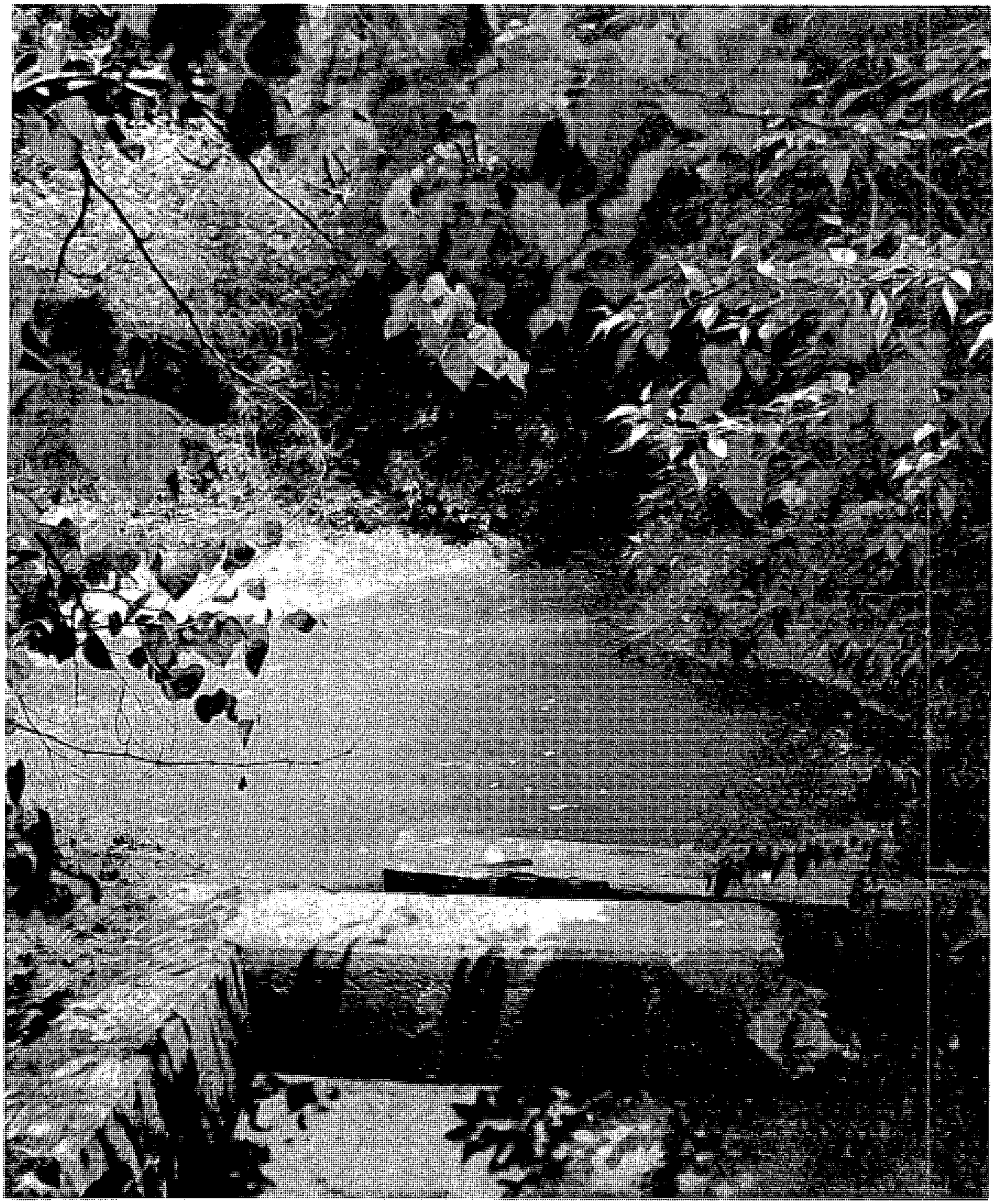


FIGURE 16. - Water in the South Canal as it enters the overflow creek as viewed from the Cincinnati Dayton Road.

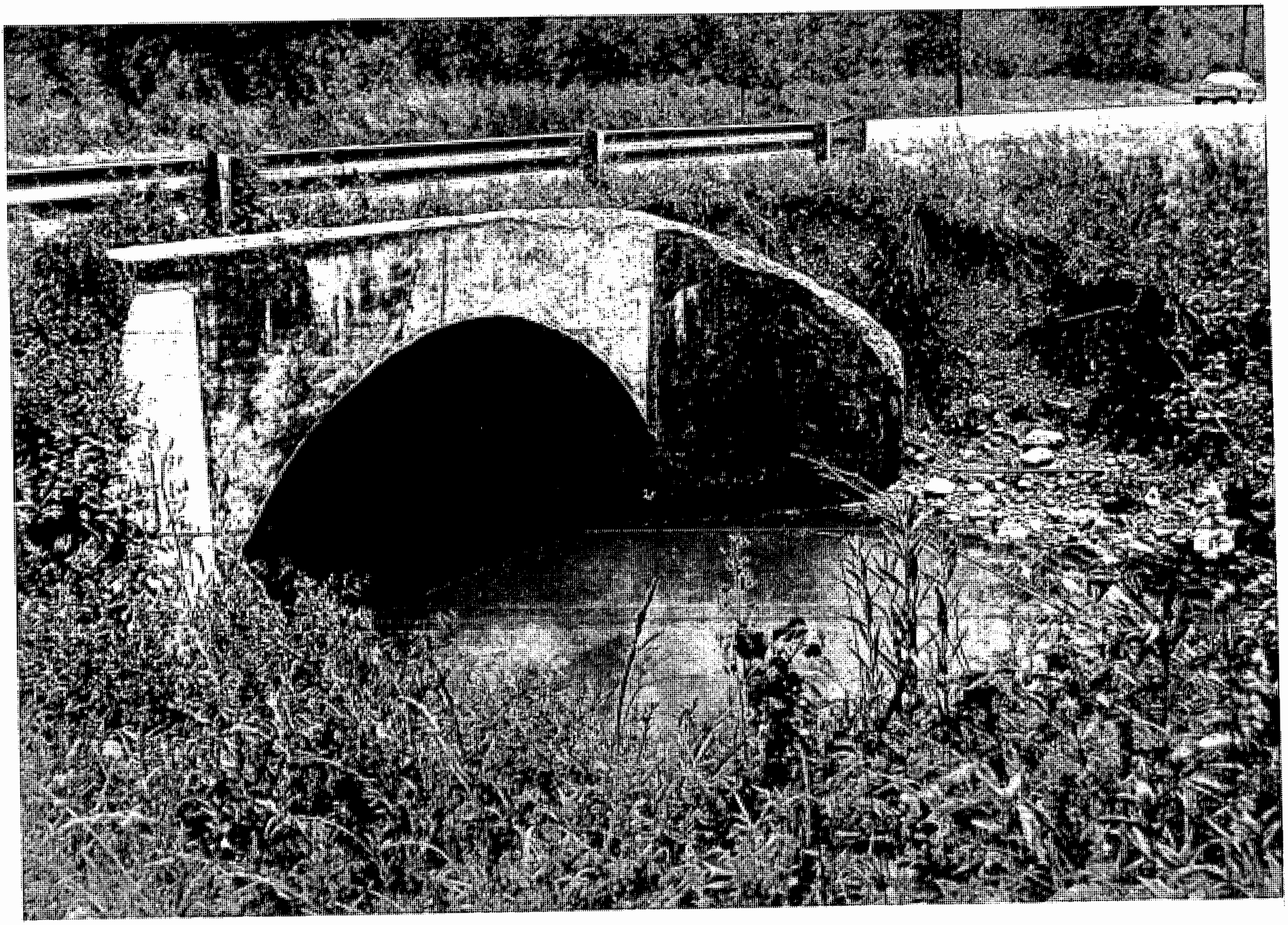


FIGURE 17. Overflow Creek on the West Side of the Highway

The area to the east of the North Canal, west of the raised railroad bed, and north of the drainage ditch, is a grassy area owned by the City of Miamisburg. Its present use is as a utility area for storage of street maintenance supplies. North of the canal pond area is a municipal swimming pool and an abandoned (Miamisburg) power plant. It is anticipated that this area will be improved to become a city park. The run-off hollow, a very narrow strip of land between the railroad grade and the Mound Laboratory site, is the Penn Central Railroad right-of-way.

The area south of the drainage ditch, east of the South Canal and west of the railroad grade, is an undeveloped strip of land that is heavily overgrown with vegetation. The area adjacent to the canal is owned by the Miami Conservancy District; the land further to the east is the Penn Central Railroad right-of-way. It is anticipated that this land will ultimately be improved and utilized as a park. All of the area from the drainage ditch to and beyond the overflow weir with contamination greater than 0.001 nCi/g is owned by the Miami Conservancy District.

The overflow creek flows across the Miamisburg Sewage Treatment Plant property. To the southeast is a large grass field used by the city for sanitary sewage sludge disposal. To the northwest is the raised railroad grade (Penn Central Railroad). It is anticipated that the treatment plant property will maintain its present use for a considerable time, but will be ultimately used as a park.

The Cincinnati-Dayton Road parallels the North and South Canals, approximately 50 to 75 ft to the west of these waterways. This is a two-lane paved road which essentially follows the river to Franklin, Ohio, and on to Cincinnati. The area between Cincinnati-Dayton Road and the river is relatively flat and grassy and is used presently as a commercial and residential section of the city. The area immediately adjacent to the river is owned by the Miami Conservancy District and includes grassy flood dikes and the flood plain between the dikes and the river.

ENVIRONMENTAL PLUTONIUM STUDY

SAMPLING AND ANALYSIS

Based on fragmentary information obtained by preliminary sampling, a comprehensive ^{238}Pu environmental sampling plan was developed for the waterways and adjacent areas to determine the full extent of the contamination. This proposed sampling plan was reviewed by the Monsanto Company, ERDA the Montgomery County Health Department, the Miami Conservancy District, the Ohio Department of Health, the Ohio EPA, the U.S. EPA, and the consultants from the USDA, universities and private companies. The plan called for ^{238}Pu analysis of over 1340 samples of the following materials:

- Soil (core, plug and scoop samples)
- Sediment (core samples)
- Water (both canal and well water)
- Solids suspended in water
- Vegetation
- Fish
- Air

As was expected at the outset, the plan was modified subsequently as the data or other information became available and on the advice of expert consultants. In all, about 1750 samples were taken and analyzed for ^{238}Pu. These analytical results(1) have been reported previously to governmental, health and environmental agencies.

Figures 18, 19 and 20 show the major sediment core sampling locations in and around the drainage ditch, runoff hollow, North Canal, ponds, South Canal and overflow creek. At most of the sampling locations, multiple core samples were taken as shown in Figures 21 and 22. These multiple samples were taken to establish the distribution of concentration across the

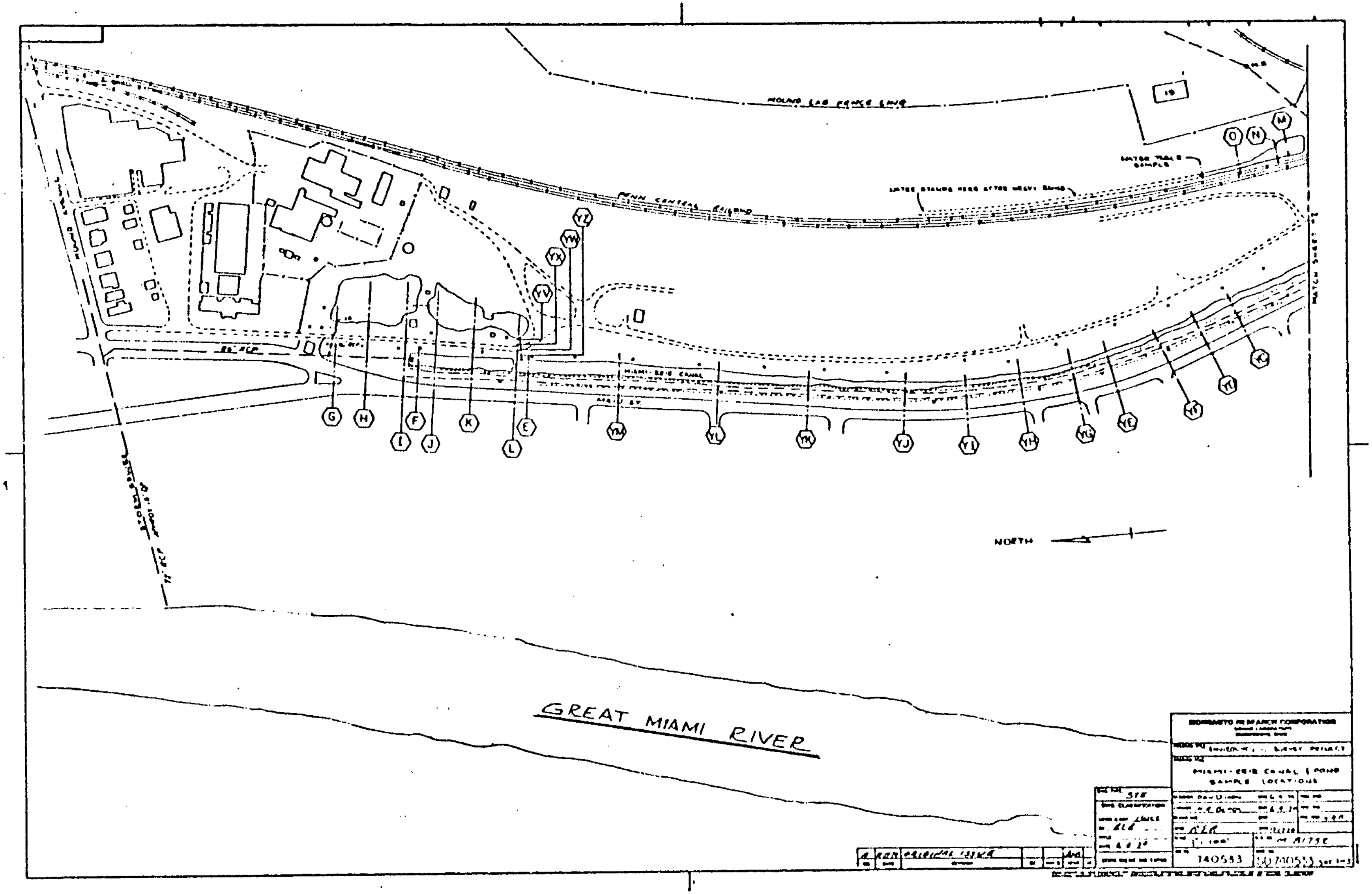


FIGURE 18. Core Sampling Locations: North Canal and Pond Area

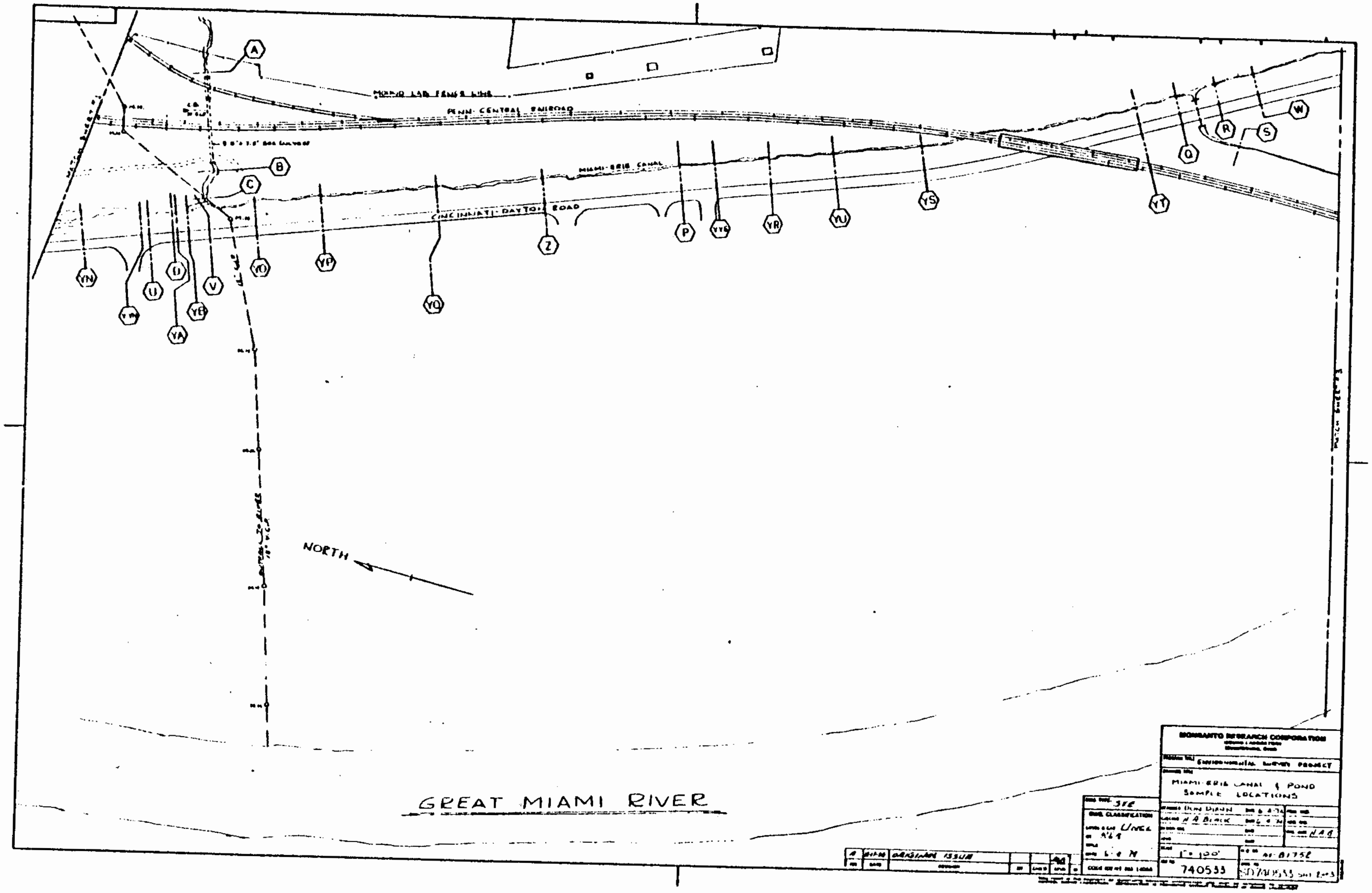


FIGURE 19. Core Sampling Locations: Drainage Ditch and South Canal Area

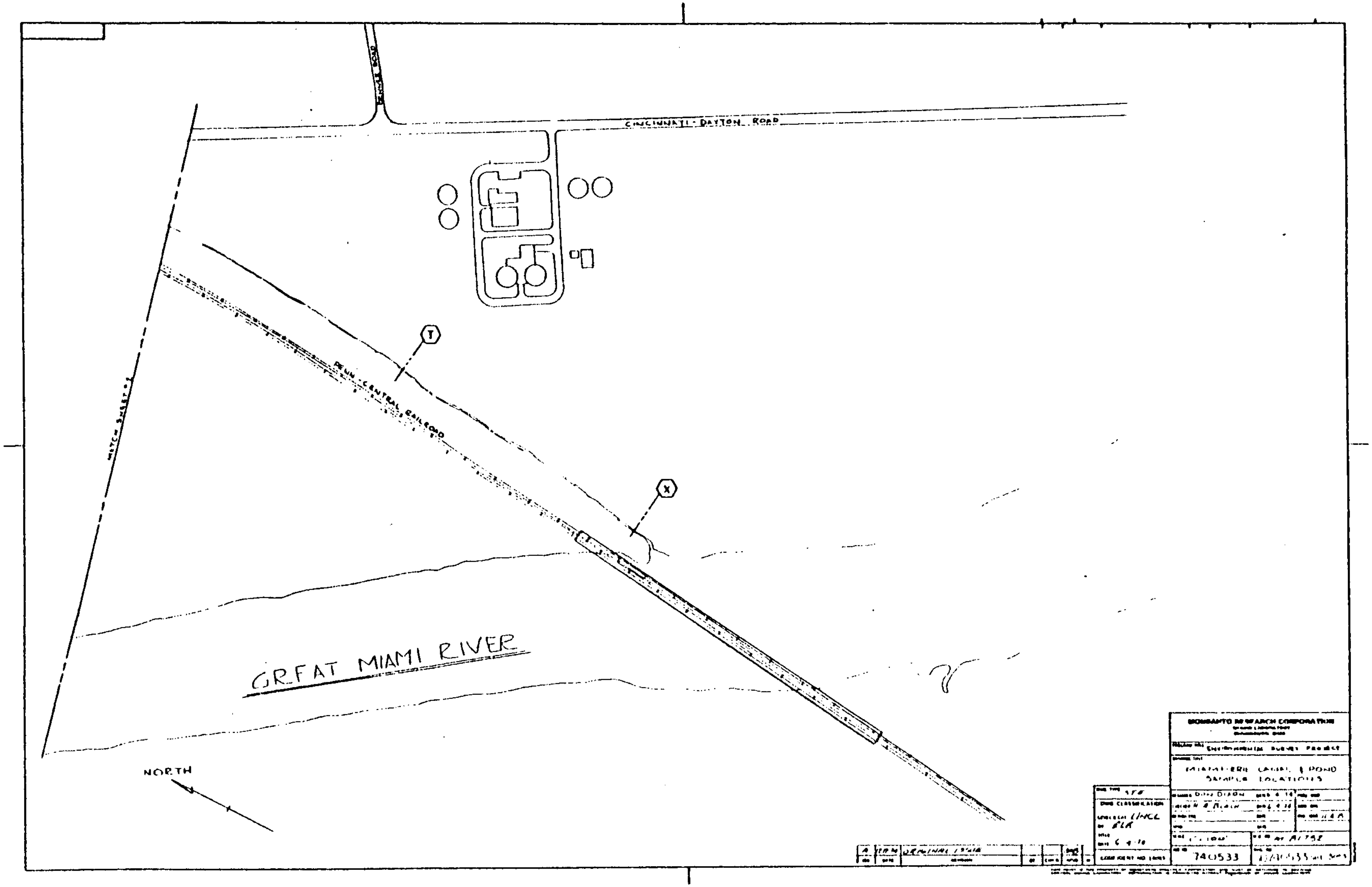


FIGURE 20. Core Sampling Locations: Overflow Creek Area

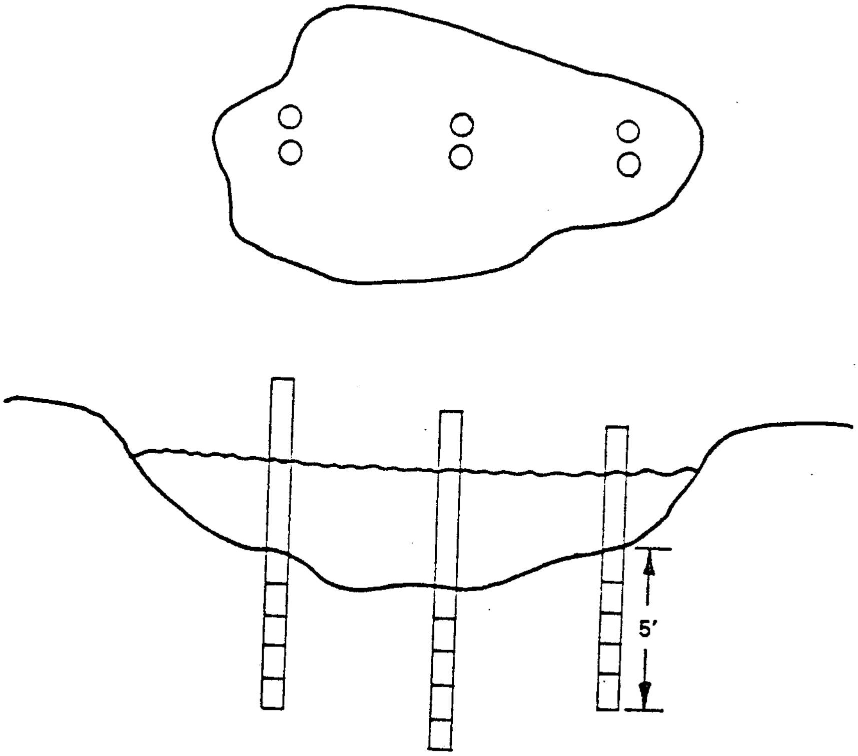


FIGURE 21. Typical Distribution of Samples Taken at Pond Location

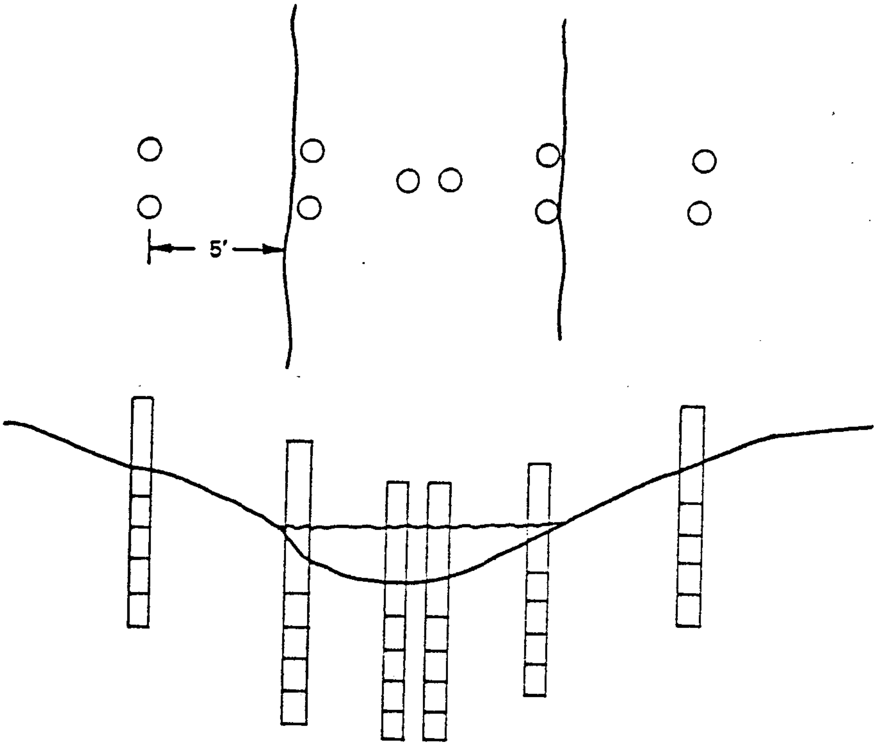


FIGURE 22. Typical Distribution of Samples Taken at Canal Locations

waterways and on the banks, and to establish local variability. The cores were generally 5 ft deep and were divided into five equal sections to determine concentration as a function of depth. Typical sampling techniques are shown in Figures 23 and 24. Additional scoop and 2-inch plug samples were taken at frequent distance intervals in the land areas near the waterways to determine the level of ^{238}Pu contamination on the surface.

The Great Miami River sediment was core-sampled upstream from the laboratory and at several locations downstream for a distance of 10 miles. Core samples were collected near the Mound Avenue storm sewer (pond) outfall, near the outfall of the closed pipeline carrying effluent from the laboratory sewage and waste disposal operations to the river and near the overflow creek outfall. These sampling locations are shown in Figure 25. Typical spatial distribution of samples taken at a particular location are presented in Figures 26 and 27. The river core samples were collected by an independent company, Bowser Morner Testing Laboratory, Dayton, Ohio, utilizing a sampling rig shown in Figure 28.

Considerable care was exercised during sampling, analyses, and data evaluation to ensure the reliability of the results. Figure 29 shows a schematic flow sheet of the analytical and

FIGURE 23. Sampling Tube Being Carried to North Canal Sampling Site

FIGURE 24. Typical Sampling Techniques

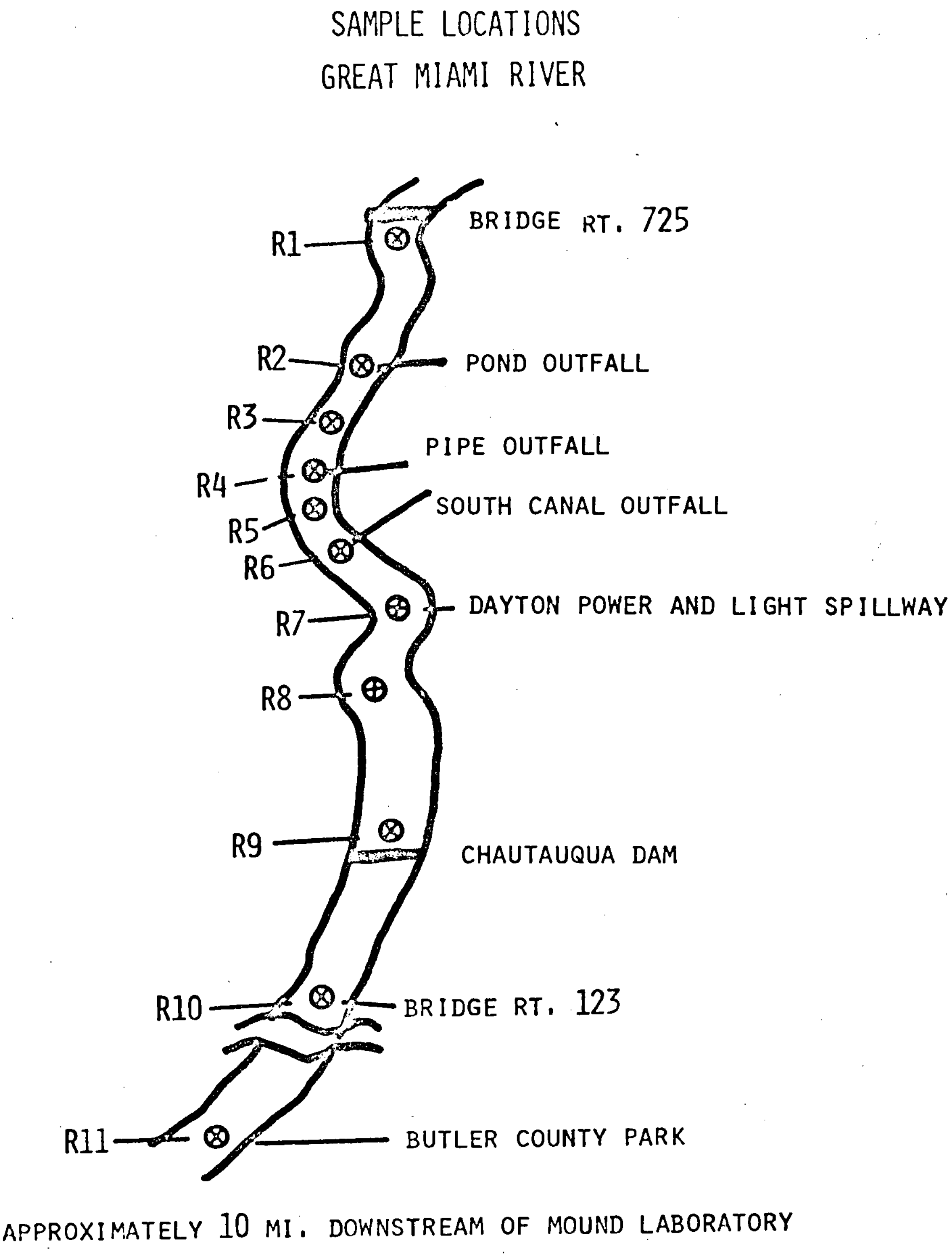


FIGURE 25. Great Miami River Core Sampling Sites

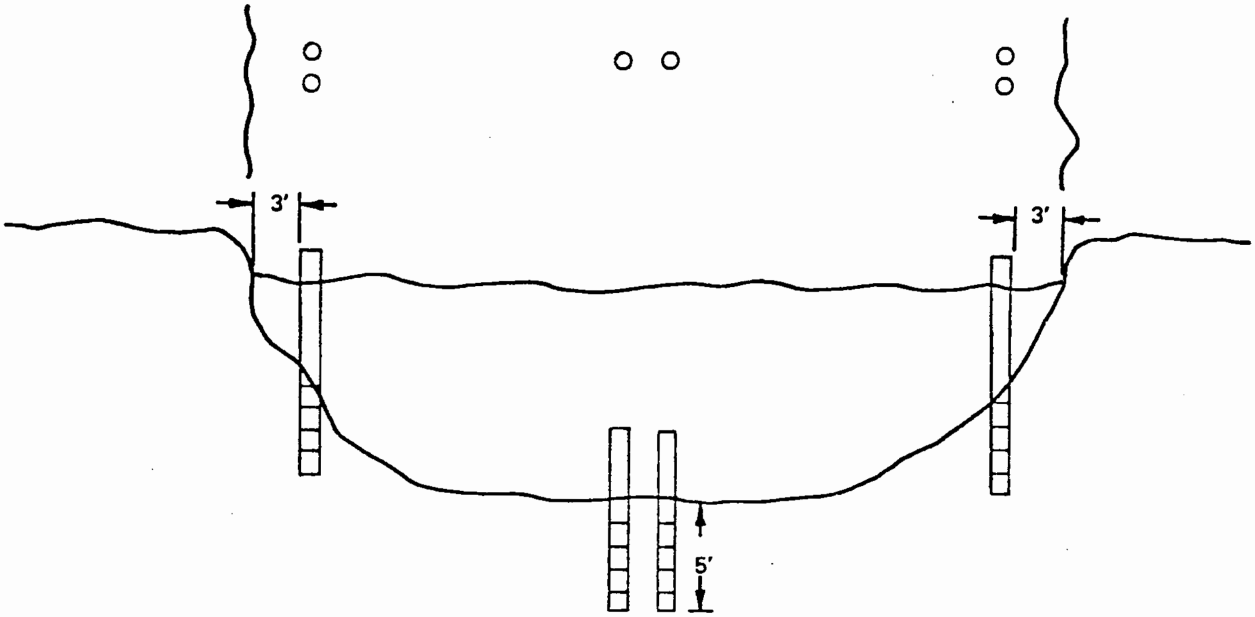


FIGURE 26. Typical Distribution of Samples Taken at River Locations

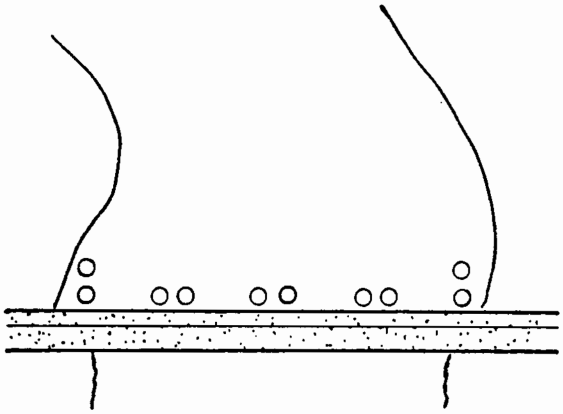


FIGURE 27. Typical Distribution of Samples Taken Behind Dams in the River

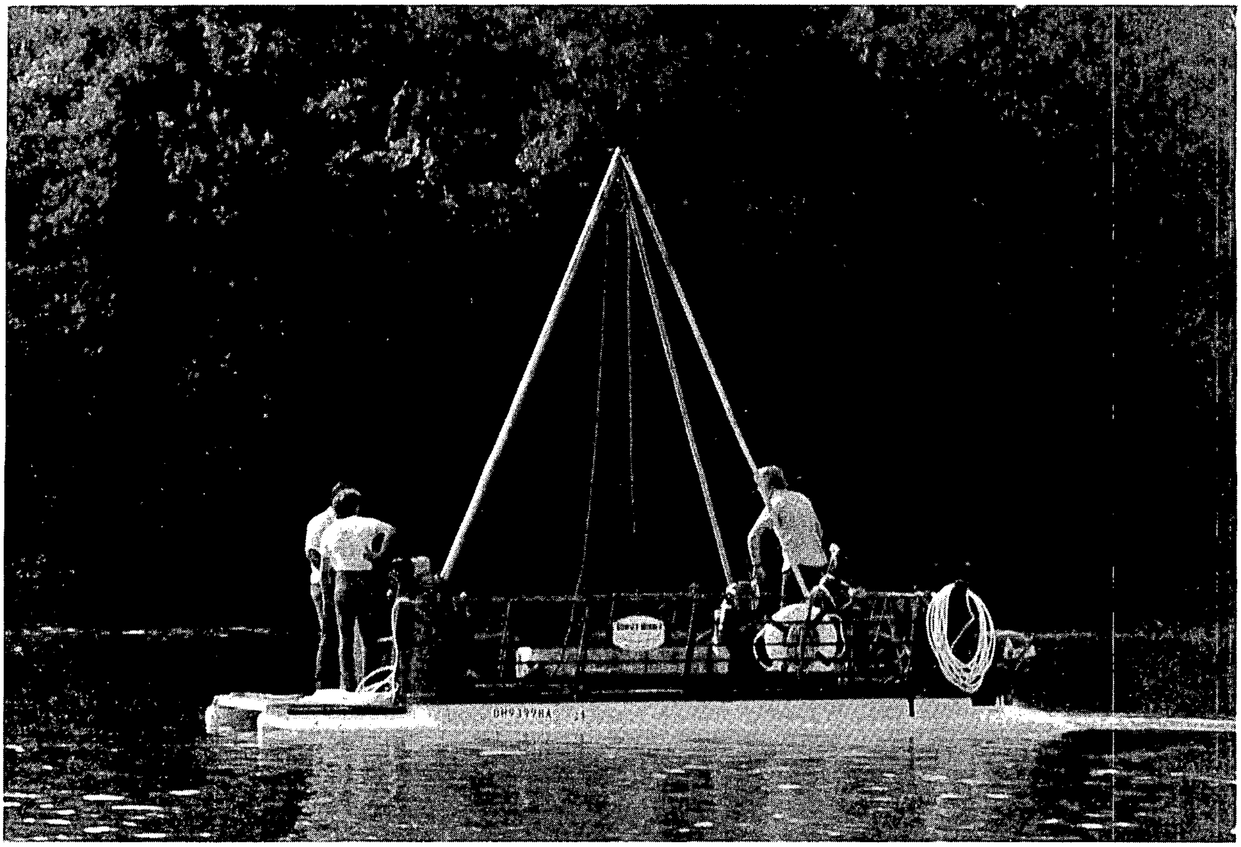


FIGURE 28. Rig Used for River Sampling by Bowser Morner

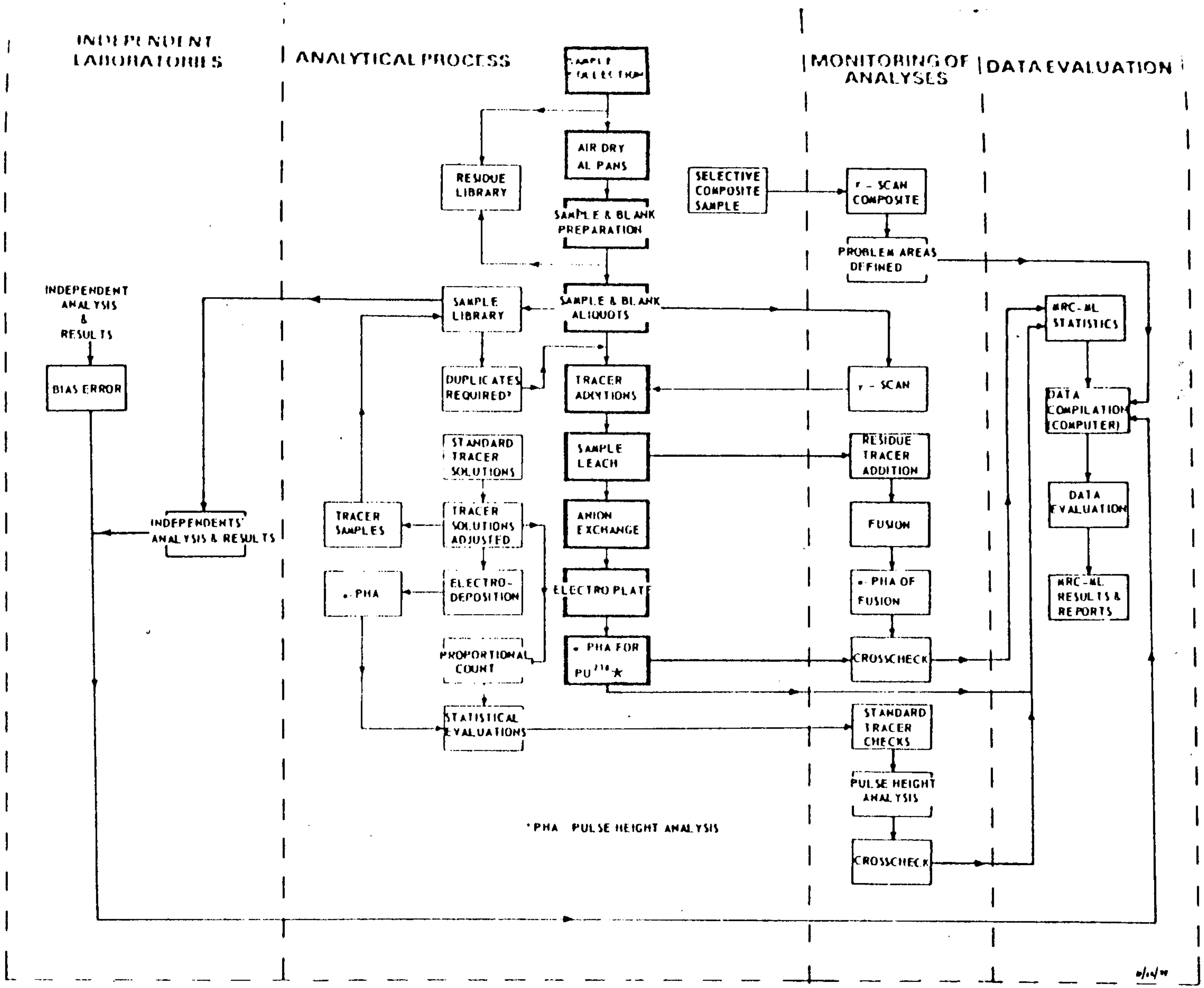


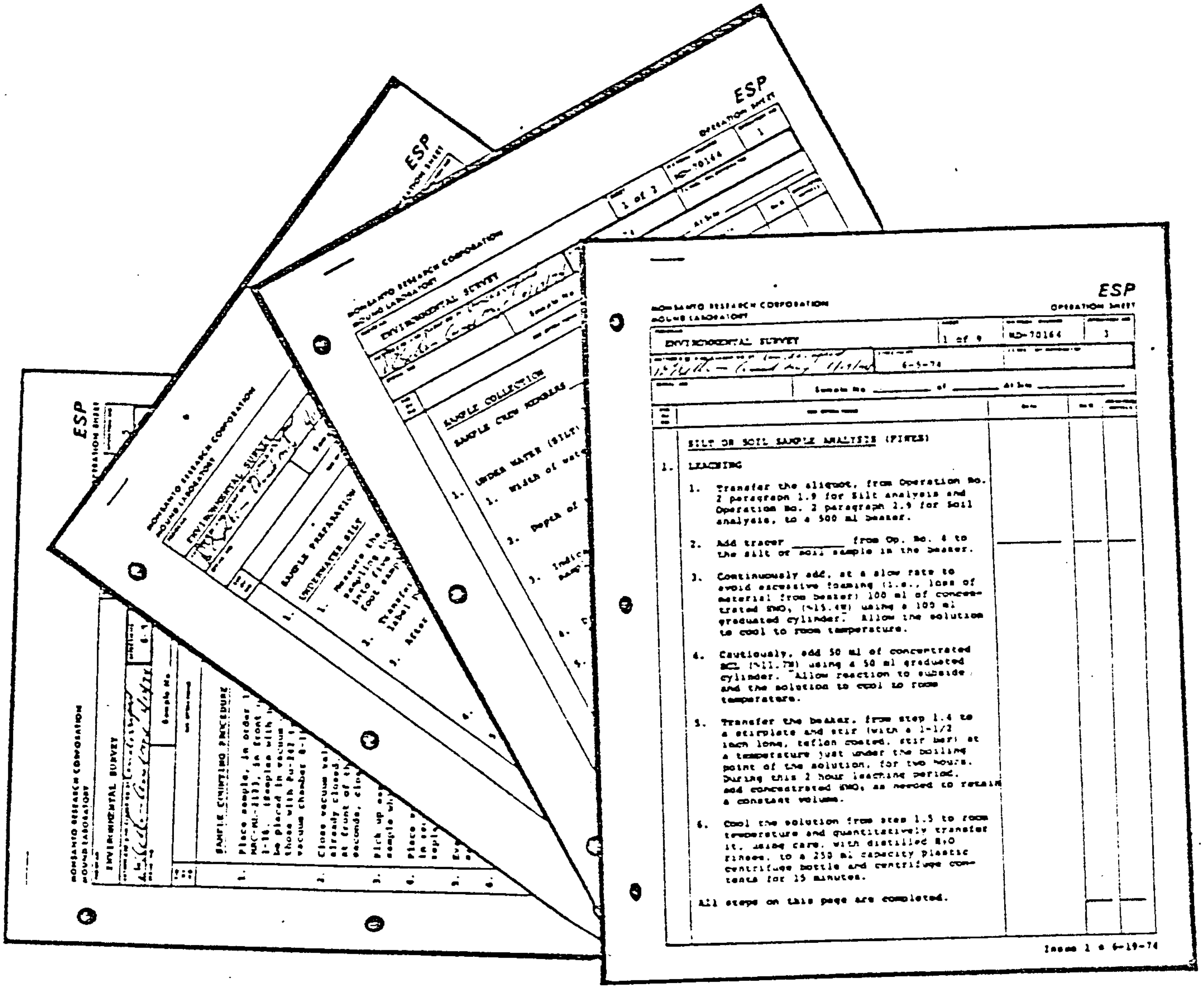
FIGURE 29. Schematic Flow Sheet of Analytical and Data Cotrol Methods

data control methods. Quality control methods routinely applied for Mound Laboratory products for space applications were implemented on this program to ensure sampling and analytical process control, personal accountability, data processing and review, and record keeping.

Operation sheets, shown in Figure 30, which described the sampling and analytical procedures in step-by-step detail were used for each sample. These operation sheets required the sampling team and analytical chemists to record data and verify strict adherence to procedure by initialing each step as it was completed. A permanent operation sheet record package was then maintained on each sample taken and analyzed. Quality control inspectors made unannounced inspections in the field and in the laboratories to further check for adherence to procedures and good analytical practices.

Blank soil or sediment samples were processed with each group of samples to indicate laboratory sample contamination levels. The blank results were never subtracted from the sample results, but were used for reliability reference.

Approximately 135 replicate analyses on samples containing a wide range of plutonium were performed periodically during the program and used to develop statistics for the analytical operations. Figure 31 shows the relationship established between the precision of the analytical determination (standard deviation) and the plutonium concentration in the soil or sediment.



MONSANTO RESEARCH CORPORATION
MOUND LABORATORY

ESP
OPERATION SHEET

ENVIRONMENTAL SURVEY	1 of 9	MD-70164	1
	6-5-74		
	Sample No ________ of ________ At hrs ________		

SILT OR SOIL SAMPLE ANALYSIS (FINES)

1\. LEACHING

1. Transfer the aliquot, from Operation No. 2 paragraph 1.9 for Silt analysis and Operation No. 2 paragraph 1.9 for Soil analysis, to a 500 ml beaker.
2. Add tracer ________ from Op. No. 4 to the silt or soil sample in the beaker.
3. Continuously add, at a slow rate to avoid excessive foaming (i.e., loss of material from beaker) 100 ml of concentrated HNO_3 (~15.4N) using a 100 ml graduated cylinder. Allow the solution to cool to room temperature.
4. Cautiously, add 50 ml of concentrated HCl (~11.7N) using a 50 ml graduated cylinder. Allow reaction to subside and the solution to cool to room temperature.
5. Transfer the beaker, from step 1.4 to a stirplate and stir (with a 1-1/2 inch long, teflon coated, stir bar) at a temperature just under the boiling point of the solution, for two hours. During this 2 hour leaching period, add concentrated HNO_3 as needed to retain a constant volume.
6. Cool the solution from step 1.5 to room temperature and quantitatively transfer it, using care, with distilled H_2O rinses, to a 250 ml capacity plastic centrifuge bottle and centrifuge contents for 15 minutes.

All steps on this page are completed.

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FIGURE 30. Operation Sheets for Analytical Quality Control

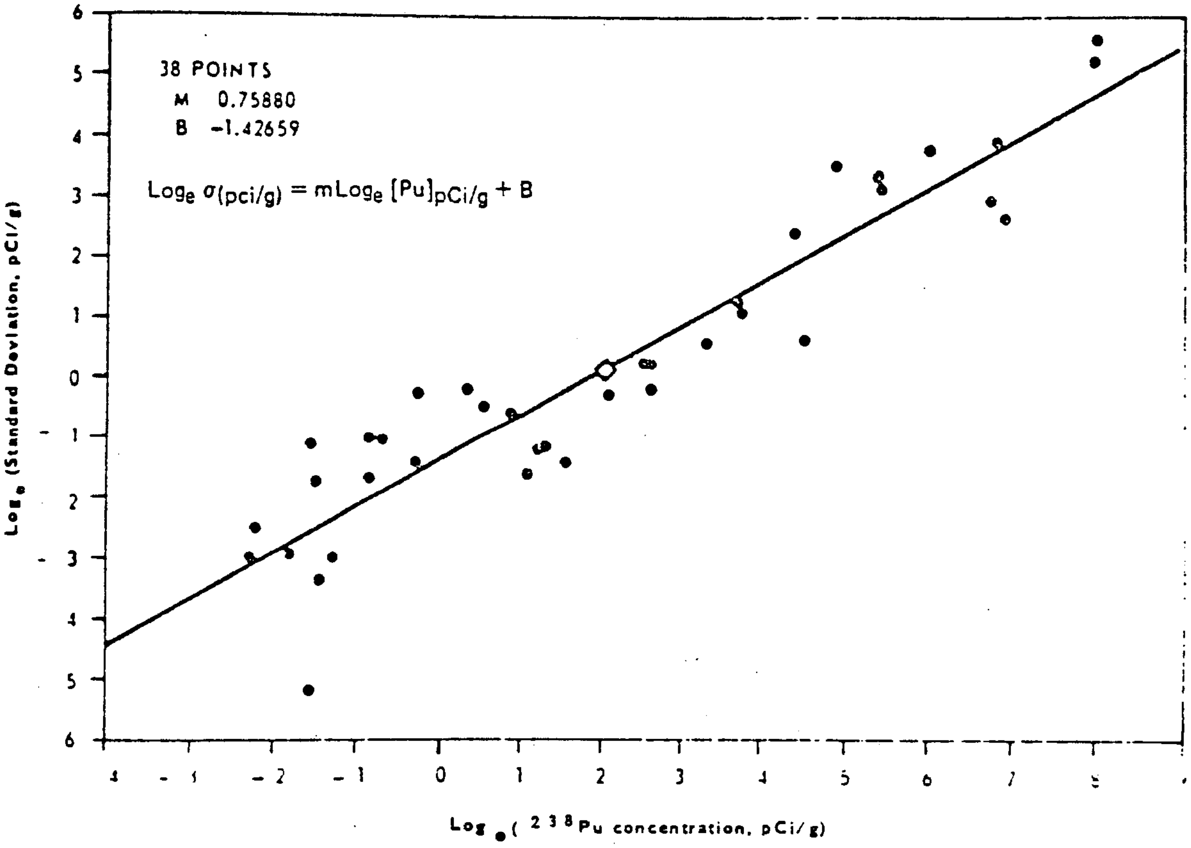

FIGURE 31. Standard Deviation as a Function of the ^{238}Pu Concentration in Soil and Sediment Samples

After exhaustive evaluation, several data rejection criteria were established to remove data which have a high potential for systematic error. These criteria were applied systematically to all data without regard for plutonium concentration or sample location. The rejected samples were generally reanalyzed and valid data reported.

In order to verify that the measured plutonium concentrations were valid, many samples were sent to independent laboratories for analysis. These independent laboratories were: the ERDA Health and Safety Laboratory (HASL), in New York, New York the U.S. Environmental Protection Agency Laboratory (EPA), in Atlanta, Georgia and the LFE Environmental Analysis Laboratory in Richmond, California.

The samples were collected by Mound Laboratory, Bowser Morner Testing Laboratory, and U.S. EPA, then dried and ground to less than 20-mesh particle size. The samples were homogenized and aliquots from these samples were riffled and sent to the independent laboratories for analysis.

Interlaboratory analytical agreement was generally good at all concentration levels.(1) EPA results tended to be slightly higher than the Mound values while LFE results tended to be slightly lower. The Mound and HASL results were almost identical except at very low concentrations where HASL values tended to be lower.

In addition to the analytical variance, the variance due to the actual distribution of plutonium in and around these waterways was estimated by taking duplicate local variability samples 1 to 3 ft apart in many of the sampling locations.

The plutonium deposition in the areas, based on the local variability samples, exhibited log-normal distribution characteristics. The geometric standard deviation of the 5-ft composite samples representing variation of total deposition within a local area was found to be 1.77. This value did not vary significantly with plutonium concentration or location.

The local variability on individual 1-ft sections of the cores representing the local variability with respect to depth was considerably higher ($\sigma_g \simeq 10$). These variances are believed to arise from the way in which the plutonium is deposited rather than to sampling or analytical techniques.

Samples, independently collected in and around these waterways and analyzed by HASL, U.S. EPA, Ohio EPA, and ORNL showed agreement with Mound samples taken nearby.(1)

SUMMARY OF RESULTS

The individual analytical values of each of the samples taken have been reported previously(1) to governmental, health and environmental agencies. In this summary, the data are ordered and presented on the basis of plutonium availability to man in order to permit their use later in the report to evaluate the potential health and safety hazards to the public. The data are divided into three categories:

1. ^{238}Pu concentration available to man
2. ^{238}Pu concentration potentially available to man
3. Inventory of plutonium deposited in waterways

1. The ^{238}Pu available to man in this case is that which is deposited on the "very surface" of the soil or sediment, is dissolved in water, or is present in biota used for food. The dry land "very surface" contamination is available to be suspended in air under certain conditions where it might be inhaled or is available to be ingested directly. The "very surface" of sediment, which is under water, is subject to easy suspension in water or if the sediment dries, then it could be subject to suspension in air.

a. "Very Surface" ^{238}Pu concentration in sediment and soil. The "very surface" concentrations of ^{238}Pu in the sediment were measured in most cases by collecting and analyzing the solids suspended in the natural water by in situ vigorous agitation of the water near the sediment interface. These solids were usually found to be in the particle size range less than 50 μm (silt and clay), although some samples contain small amounts of fine sand. These concentrations should approximate the ^{238}Pu concentration of the air suspendible dust should the sediment dry.

The maximum sediment "very surface" values found in each of the waterways is presented in Table 2. As can be seen, the values vary from 0.02 to 0.45 nCi/g depending on the location. This range of values was found to be in agreement with shallow surface scoop samples taken by Mound Laboratory, U.S. EPA, and HASL in sediment areas not covered with water.

TABLE 2. Maximum "Very Surface" ^{238}Pu Concentrations of Sediment in Waterways Near Mound Laboratory

Waterway	Maximum "Very Surface" Concentration (nCi/g ± 2σ)
Runoff Hollow	0.0286 ± 0.0061
North Pond	0.0223 ± 0.0051
South Pond	
North Basin	0.0653 ± 0.0114
South Basin	0.208 ± 0.028
North Canal	0.267 ± 0.033
Drainage Ditch	0.450 ± 0.050
South Canal	0.395 ± 0.045
Overflow Creek	0.270 ± 0.034

The maximum "very surface" concentrations along the immediate banks of the waterways which are subject to occasional flooding are presented in Table 3 for each of the waterways. The values were taken from shallow surface soil samples and tended to range from 0.002 to 0.06 nCi/g.

TABLE 3. Maximum ^{238}Pu "Very Surface" Concentrations in Soil Along the Immediate Banks of the Waterways Which Are Occasionally Flooded

Waterways	Maximum "Very Surface" Concentration (nCi/g ± 2σ)
Ponds (Composite)	0.0017 ± 0.0007
North Canal	
East Bank	0.0446 ± 0.0086
West Bank	0.0540 ± 0.0099
Earthen Dam/Ditch Area	0.0542 ± 0.0099
South Canal	
East Bank	0.0609 ± 0.0109
West Bank	0.0540 ± 0.0099
Overflow Creek	
East Bank	0.0116 ± 0.0031
West Bank	0.0021 ± 0.0008

The "very surface" values in the land areas (Table 4) adjacent to the waterways, which for physical reasons are not likely to be exposed to flooding from the waterways, were found to be in the 0.0002 to 0.001 nCi/g concentration range.

TABLE 4. "Very Surface" ^{238}Pu Concentration in Areas Adjacent to the Waterways Which Are Not Subject to Flooding

Land Area	"Very Surface" Concentrations (nCi/g ± 2σ)
North Canal - Pond Area (Composite)	0.00023 ± 0.00005
South Canal - Overflow Creek Area (Composite)	0.00075 ± 0.00020

TABLE 5. Concentration of ^{238}Pu in Water Taken from the Waterways

Waterway	Water Concentration (nCi/ml ± 2σ)
Runoff Hollow	<0.000001
North Pond	<0.000001
South Pond	
North Basin	<0.000001
South Basin	<0.000001
North Canal	0.000005 ± 0.000003
Off-Site Ditch	0.000006 ± 0.000003
South Canal	0.000014 ± 0.000006
Overflow Creek	0.000003 ± 0.000002
River (at Outfall)	0.000001 ± 0.000001

b. ^{238}Pu concentrations in water. The maximum soluble ^{238}Pu concentration in water samples taken in each of the waterways is presented in Table 5. The value varied from less than 0.000001 to 0.000014 nCi/ml.

c. Distribution of ^{238}Pu between water and sediment. Water samples which were allowed to remain in contact with suspendible soilds tend to attain a constant relationship between the water and solid ^{238}Pu concentration. When the two phases were separated, the ratio of the ^{238}Pu concentration between the natural water and sediment samples (distribution ratio, $D_{w/s}$) was found to approach 1 x 10^{-5}. This distribution ratio was reasonably constant for all waterways.

d. Concentrations of ^{238}Pu in biota samples. There is very little biota in or near the affected contamination area which is normally consumed directly by man (except for the fish in the waterways). It is assumed that the biota samples taken, however, provide an index for worst case consumable biota contamination considering the nature of the area.

The ^{238}Pu concentrations found in grass, algae and fish samples collected in or near the waterways are listed in Table 6.

TABLE 6. Concentration of ^{238}Pu in Biota Samples Taken in or near the Waterways

Biota	^{238}Pu Concentration (nCi/g ± 2σ)
Grass taken along banks in areas not subject to frequent flooding	0.000018 ± 0.000020
Grass taken along banks subject to frequent flooding (Areas A and R)	0.000874 ± 0.00305
Green algae (samples from North Canal and Pond water)	0.00239 to 0.111
Fish (edible portion)	
Bottom feeders (carp)	0.00000512
Other (blue gill)	0.00000079

Grass samples, taken along the immediate bank where flooding is unlikely for physical reasons averaged 0.000018 ± 0.000020 nCi/g (dry weight). Some of these values are higher than might be expected from systemic absorption into the grass and might indicate some surface contamination from light tracking. Samples of grass taken in two localized areas, where frequent flooding is observed, were higher and indicated definite external surface contamination from deposited sediment.

Algae samples taken from the surface of the ponds and the North Canal indicated that, as expected,(2) these algae tend to concentrate plutonium probably directly from the water. Two species of fish, blue gills and carp, were obtained from the waterways. Although only a few samples could be collected, the bottom feeding carp showed a higher concentration than the blue gills, as would be expected.(2)

2. ^{238}Pu Concentration Potentially Available to Man

Plutonium-238 in soil or sediment that is below the surface is normally not available to enter the "pathway to man" except for an extremely small fraction taken systemically into subsurface biota consumed by man. In order to become significantly available, it must be carried to the surface by physical actions of man or nature. The probability of this occurring decreases with the depth of the deposit.

The ^{238}Pu concentration in the first foot is considered potentially available since it could be brought to the surface without extreme measures. The concentrations which are deposited deeper than 1 ft are much less likely to be exposed and are, therefore, only to be considered as worst cases.

The concentrations reported here are taken on 1-ft core sections. Although higher concentrations may exist in thinner stratified layers, the physical action required to bring them to the surface would also tend to mix and dilute the more concentrated zones with the lesser concentrated strata which lie above and below.

The first foot of ^{238}Pu concentrations on the banks of the waterways and the adjacent land areas are lower than the "very surface" values reported previously and so will not cause a future potential increase in the surface contamination.

The maximum ^{238}Pu concentrations in the first foot of sediment in each waterway are listed in Table 7, and vary from 0.0003 to 3.80 nCi/g. The maximum concentrations in the waterways and the depth at which they occur are listed in Table 8.

TABLE 7. Maximum First-Foot ^{238}Pu Concentrations of Sediment in Waterways

Waterway	Maximum First-Foot Concentration (nCi/g ± 2σ
Runoff Hollow	0.0314 ± 0.0066
North Pond	0.0062 ± 0.0019
South Pond	
North Basin	0.0309 ± 0.0065
South Basin	0.0096 ± 0.0027
North Canal	1.14 ± 0.10
Drainage Ditch	0.749 ± 0.013
South Canal	3.80 ± 0.25
Overflow Creek	0.0744 ± 0.0126
River	
East Bank Near Canal Outfall	0.0367 ± 0.0074
East Bank Downstream	0.0016 ± 0.0007
Away from East Bank	0.0003 ± 0.0002

TABLE 8. Maximum Any-Depth ^{238}Pu Concentrations of Sediment in Waterways

Waterway	Depth (ft)	Maximum Any-Depth Concentration (nCi/g ± 2σ)
Runoff Hollow	1	0.0314 ± 0.0066
North Pond	0	0.0223 ± 0.0051
South Pond		
North Basin	0	0.0653 ± 0.0114
South Basin	0	0.208 ± 0.028
North Canal	3	4.56 ± 0.20
Drainage Ditch	1	0.749 ± 0.013
South Canal	1	3.80 ± 0.025
Overflow Creek	0	0.270 ± 0.034
River		
East Bank Near Canal Outfall	2	0.0415 ± 0.0081
East Bank Downstream	7	0.0037 ± 0.0013
Away from East Bank	4	0.0006 ± 0.0002

Unlike "very surface" concentrations that tended to be reasonably uniform within a given area, the plutonium deposited below the surface tends to be much more localized. These localized deposition patterns result from the nature of the transport and deposition mechanisms, which will be discussed in more detail later in this report.

The first-foot concentrations found in the North and South Canals, which vary greatly as a function of length and width, are shown in Figure 32. The concentration profiles across the canal that are presented are typical of many others measured. The highest concentrations are very localized near the middle of the South Canal.

Figure 33 shows the maximum concentrations (worst case) at any depth along or across the North and South Canals. The maximum levels occur just north of the earthen dam and midway down the South Canal.

The data confirm that the significant contamination is confined to the waterways. The difference between the shape of the width-concentration profiles in the North and South Canals results from the nature of these waterways. The water level in the North Canal remains reasonably constant for nearly all flow conditions, while the water level in the South Canal can vary from near zero to more than 4 ft. At low flow conditions, the South Canal maintains a narrow meandering channel, while at high flow, the entire canal channel is utilized. This meandering channel tends to contain less plutonium due to less original deposition or subsequent erosion.

Figure 34 shows typical depth concentration profiles. The solid-lined curves indicate the depth distribution at the locations of the highest any-depth concentrations in the

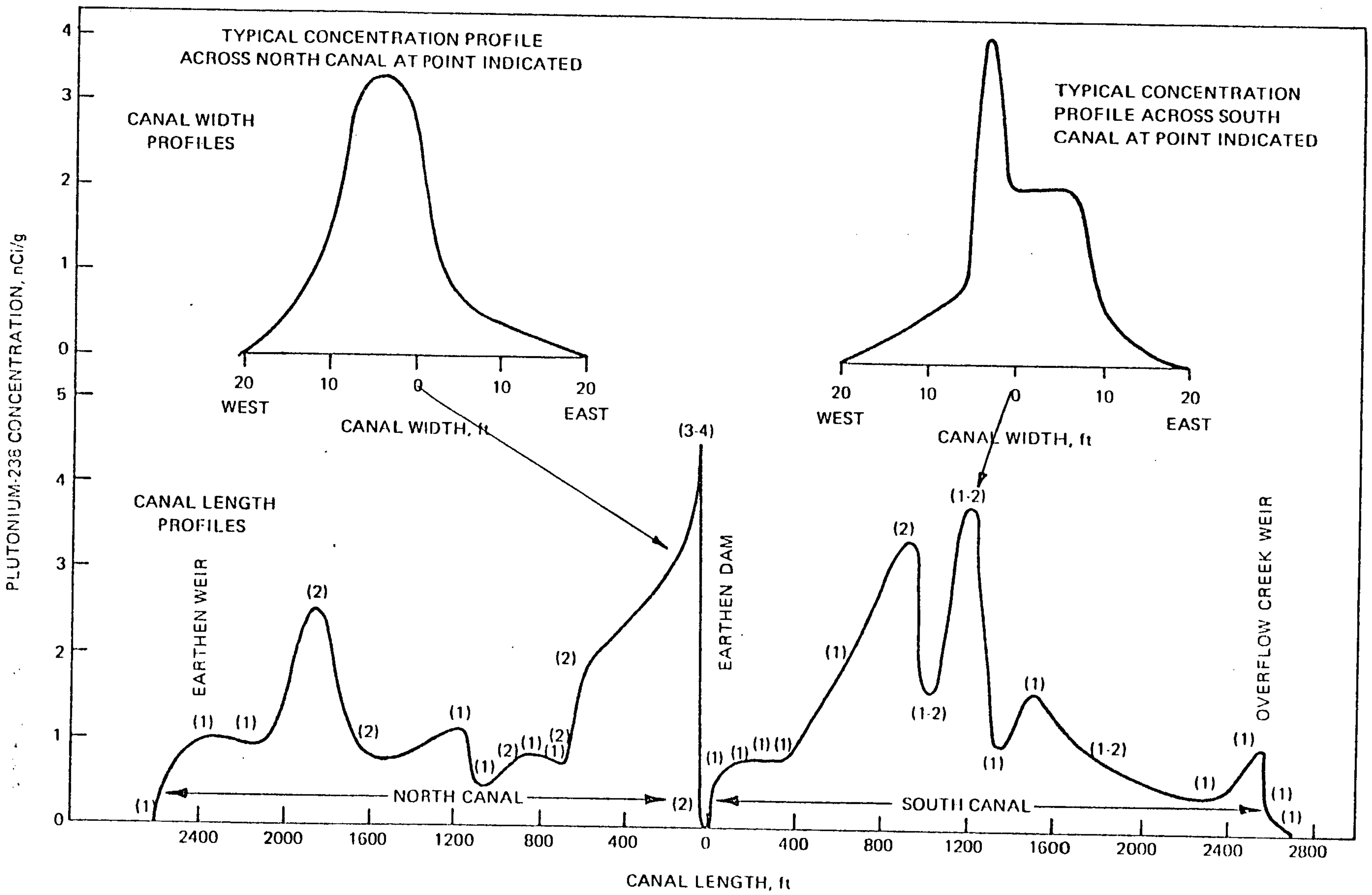

FIGURE 33. Maximum ^{238}Pu Concentration at any Depth Along the Miami-Erie Canal
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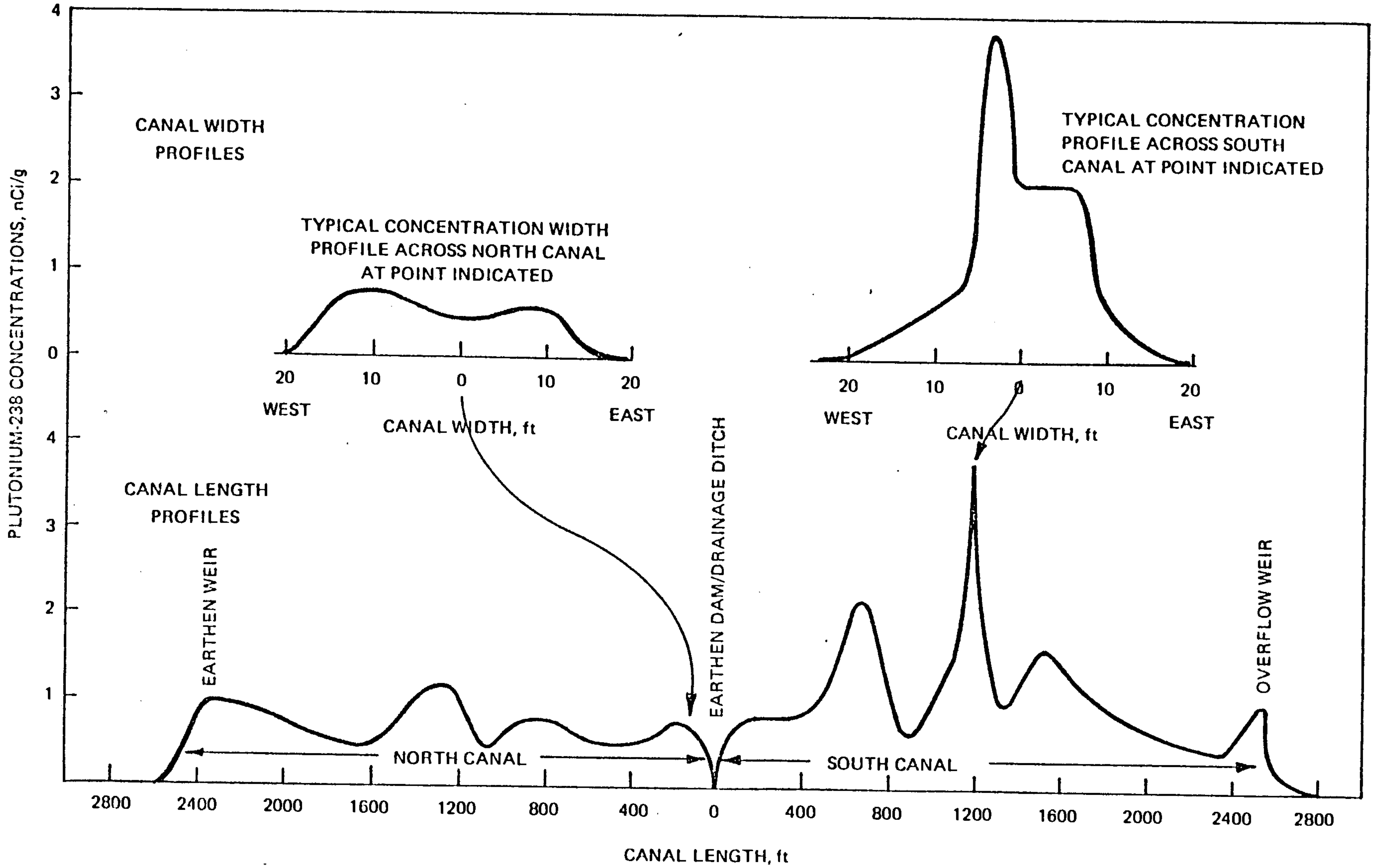


FIGURE 32. Maximum First-Foot ^{238}Pu Concentration Along the Miami-Erie Canal as a Function of Canal Length and Width

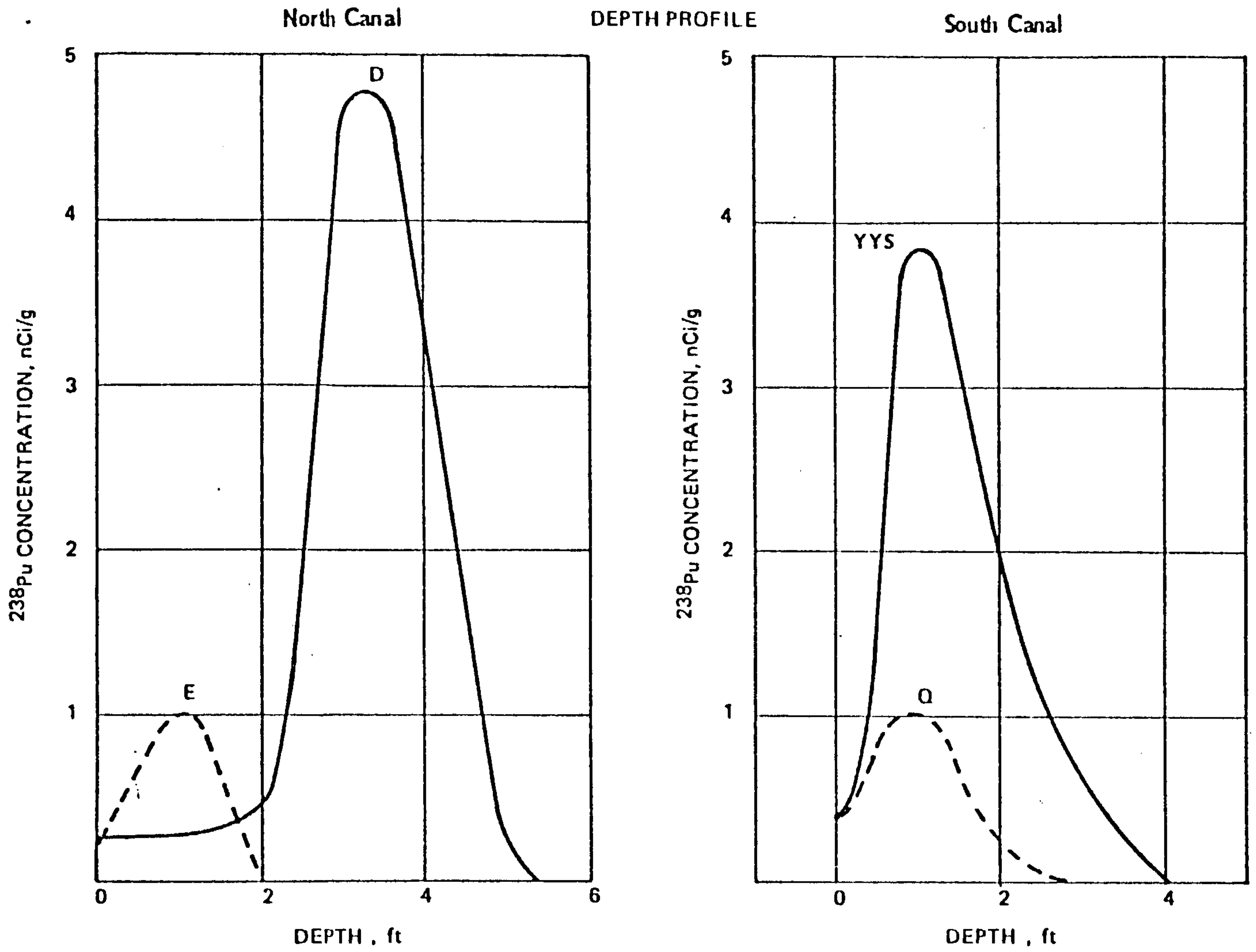


FIGURE 34. ^{238}Pu Concentration as a Function of Sediment Depth at Locations Indicated (see Figures 18 and 19). Solid Curve is Distribution at Location of Maximum Concentration; Broken Line is Distribution at the Extreme Ends of the North and South Canals Downstream

North and South Canals. The broken-lined curves show depth distribution at the extreme north and south ends of the North and South Canals, respectively.

3. Inventory of Plutonium Deposited in Waterways

The total ^{238}Pu inventory deposited in the waterways near Mound Laboratory was estimated by numerical integration of the plutonium concentration and dry sample weight data collected on the 261 cores taken with respect to depth, length, and width. The inventory of ^{238}Pu in each waterway is presented in Table 9. The total ^{238}Pu inventory in the offsite waterways was found to be 5.2 Ci.

TABLE 9. Inventory of ^{238}Pu in the Waterways

Location	Plutonium Inventory (Ci)
Run-off Hollow	0.0018
Drainage Ditch	0.082
North Canal	1.65
South Pond	0.0058
North Pond	0.0020
South Canal	3.17
Overflow Creek	0.076
Overflow Creek Outfall	0.260
TOTAL	5.2

From the data presented in the previous sections, most of the plutonium inventory is under the surface and, therefore, is not readily available to man.

CAUSE INVESTIGATIONS AND MECHANISMS

CAUSE INVESTIGATIONS

Intensive investigations were performed concurrently by a Mound Laboratory Investigation Team(a) and an ERDA Task Group(b) to find the source and cause of these plutonium deposits in the waterways.

The Mound Laboratory team pursued their investigation using a systematic-analytical-investigative technique. These activities included:

- A complete and detailed review of all environmental data related to the possible release of plutonium to these waterways.

- A detailed examination of all appropriate laboratory records.

(a) D. R. Rogers, Mound Laboratory, Chairman
(b) W. B. Johnston, ERDA/ALO, Chairman

- Private interviews and group discussions with knowledgeable Mound Laboratory personnel.

- Examination of all appropriate engineering drawings, data, and information.

Additional information was collected from field and laboratory investigations. Among these were:

- A radiological surface survey of the Laboratory site using the Field Instrument for Detection of Low-Energy Radiation (FIDLER).

- Onsite ^{238}Pu soil sampling and analysis program to supplement available data routinely collected.

- Other field observations, physical inspections and tests.

- Laboratory tests on the waterway sediments and onsite soil found to be contaminated with ^{238}Pu.

- Laboratory studies on the reactions of plutonium solutions with soil and sediment.

From this investigation and these scientific studies, the source of the plutonium, the place and nature of the release, the behavior of the plutonium and the transport and deposition mechanisms of the plutonium were identified and confirmed. The ERDA investigation task group concurred with these findings.

Source and Nature of Plutonium Released

During the processing of ^{238}Pu at Mound Laboratory, plutonium solutions that are too dilute for recovery operations are solidified and/or immobilized, drummed for burial, and shipped to ERDA-approved burial sites in the United States. Prior to 1967, this drumming operation was performed in the plutonium processing facilities (SM Building).

In 1967, an underground pipeline was installed between the SM Building, located on the southeast hill across the valley, to a waste drumming facility in the Waste Disposal (WD) Building, located on the side of the northwest hill (Figure 35). A pumping station (Building 41), located in the valley just south of the WD Building, was constructed to lift the solution up the final leg of the pipeline to hold tanks in the WD drumming facility.

This specifically-designed 1-1/2 inch pipeline was placed in operation in 1968, and both acidic and caustic solutions containing residual plutonium were thereafter routinely transferred from the plutonium processing hold tanks to hold tanks in the WD drumming facility.

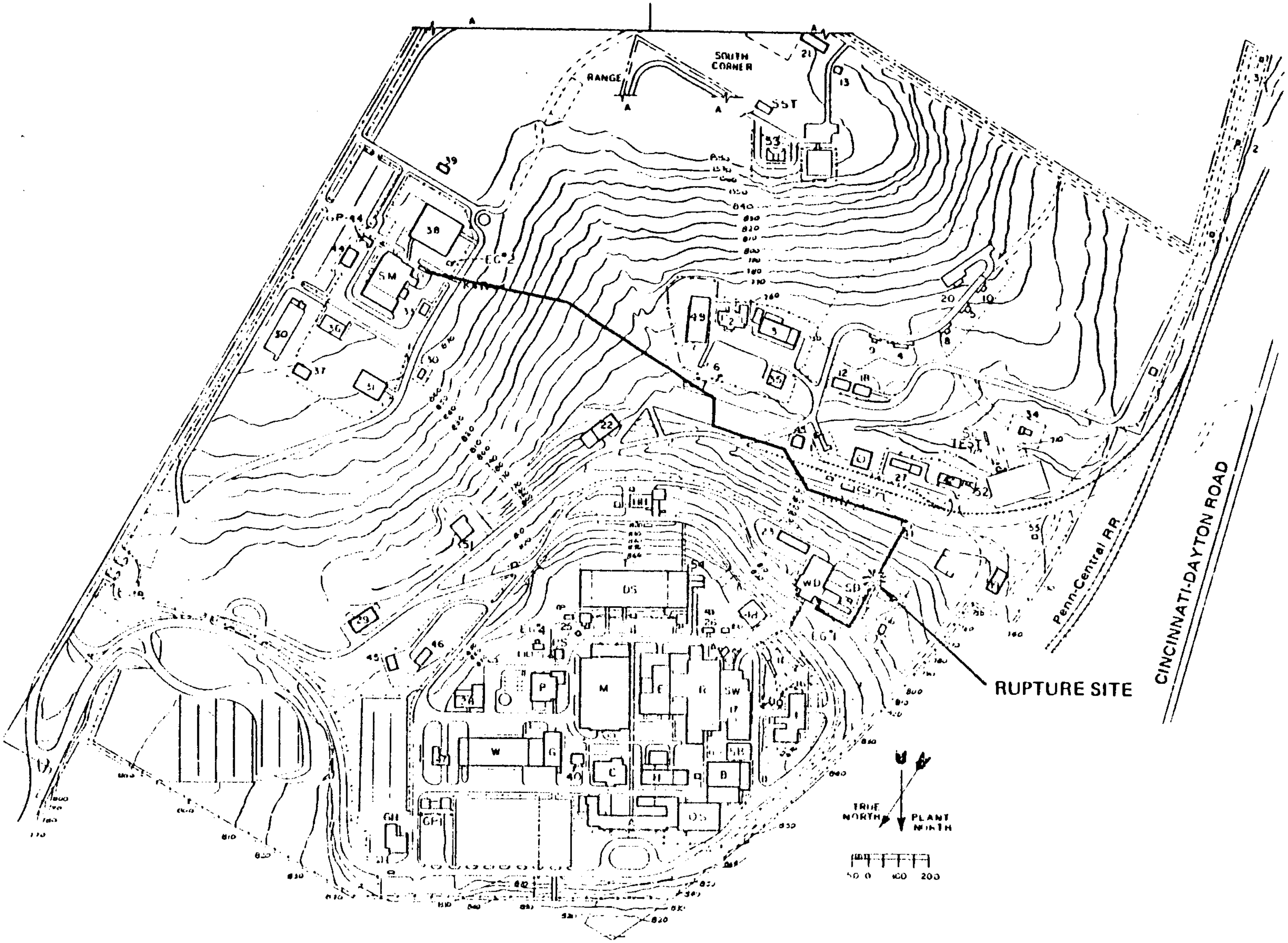


FIGURE 35. Underground Process Waste Solution Transfer Pipeline from PP to WD

In 1969, during such a routine transfer of an acidic process waste solution, the underground pipeline ruptured between Building 41 (pumping station) and WD Building, releasing the solution to the soil around the pipeline. This plutonium solution and the event were identified as the source of the plutonium found in the waterways offsite.

From the records available and from its observed behavior, the process waste solution was acidic ($>1\underline{M}$ HNO_3) and contained approximately 4.6 ppm $^{238}Pu(NO_3)_4$.

Description of the Rupture Site

The rupture occurred between Building 41 and the WD Building. The ruptured area was located about 4 ft underground on the edge of a roadway running east-west by the WD Facility. Immediately to the south of the rupture site, the land slopes sharply downward (∿19° slope) toward Building 41, as shown in Figure 36. An open concrete flume runs downward and across this hillside. This flume carries surface water from the WD street to an underground storm drain at the edge of the Building 41 road, west of Building 41. An underground storm sewer carries the water south under the road and the railroad tracks to an open tributary drainage ditch which flows to the main drainage ditch.

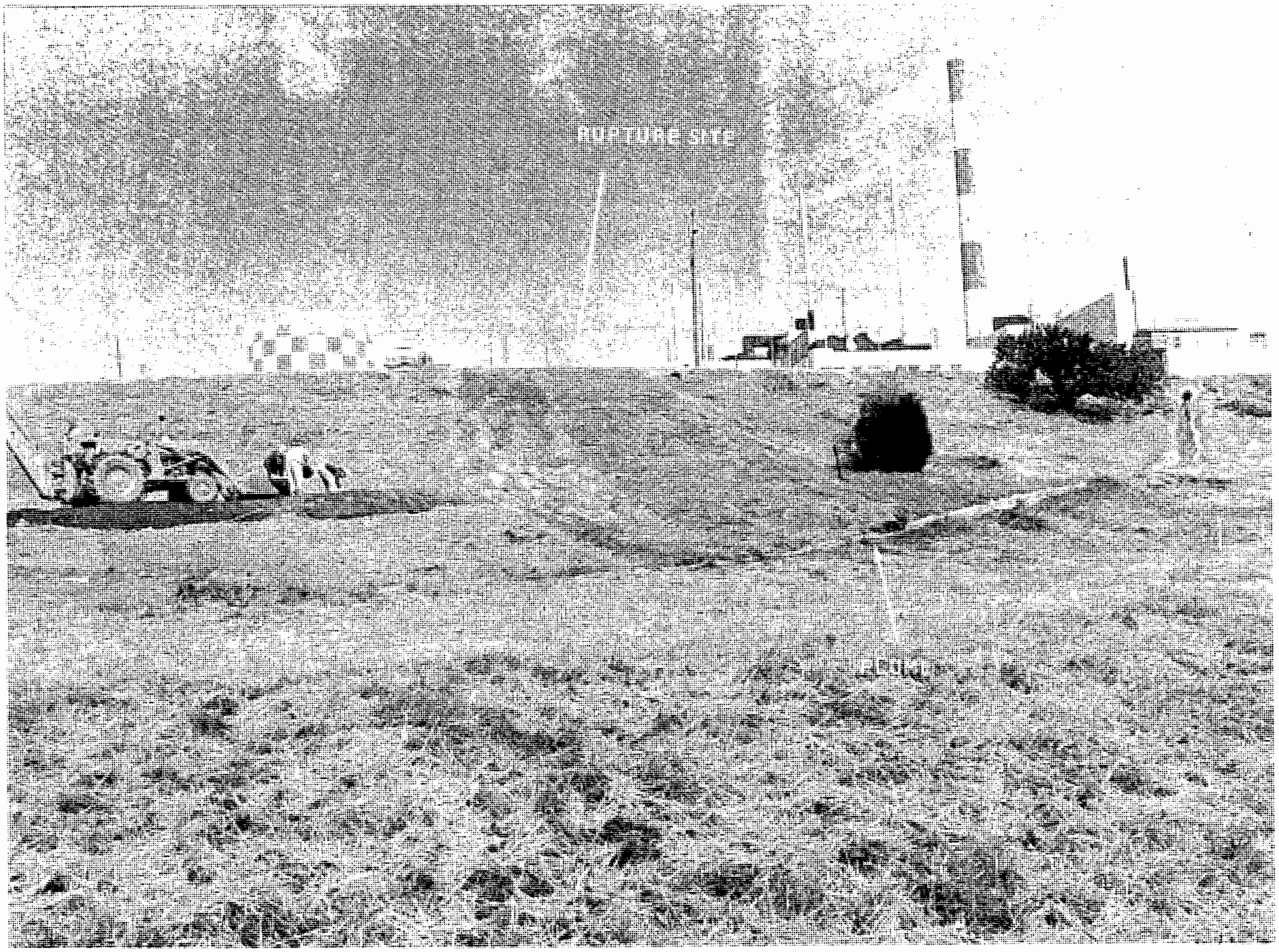


FIGURE 36. Hillside Below Pipeline Rupture Site Near the Waste Disposal Building

Description of the Event

On January 23, 1969, while an acid plutonium(IV) nitrate solution was being transferred to the WD Drumming Facility, the pipeline ruptured at a corroded joint. The plutonium solution was discharged to the soil surrounding the pipeline. A small amount of the solution came to the surface and soaked into the soil at the rupture site and on the hillside.

The operators observed the solution at the surface and shutdown the transfer. They noted that the solution was giving off brown fumes and there was a vigorous effervescent reaction with the soil.

Health Physics survey teams found that the contamination was confined to the immediate area of the rupture site and on a small area of the hillside below. According to their survey data and observations, it appears the plutonium did not reach the drainage flume.

The weather was cold with intermittent light snow flurries when excavation and repair operations were initiated. The contaminated soil removed during excavation was placed in 55-gallon drums for subsequent disposal. These drums were stored at the west end of the WD street. Excavation and drumming operations resulted in the contamination of the work area and street, and these areas were restricted by Health Physics.

Before excavation and repair operations were completed, the weather warmed and three days (January 28-30) of intense rainfall occurred.(3) The street became extremely muddy and the excavation filled with water. Water samples, taken in the drainage system below by the Environmental and Health Physics personnel, gave no indication (less than RCG for water) that significant concentrations of plutonium were moving offsite. The size of the contaminated area increased, but the situation appeared to be under control.

Following the rainstorms, repair operations were completed and the area was cleaned up. The area was surveyed with portable alpha counters and the pipeline was tested and placed back in operation.

The drums containing the contaminated soil were cleaned and shipped to an approved burial site.

Cause Conclusions

Although it was concluded at the time of this occurrence that no significant amounts of plutonium were released offsite; the 1974 investigations clearly indicated this event as the source of the offsite plutonium. The major evidence is briefly summarized:

- Using more sensitive survey instruments (FIDLER), a trail from the rupture area to the main drainage ditch and the runoff hollow was located in 1974.

- ^{236}Pu dating of the plutonium in the offsite areas were consistent with the time of the rupture. The ^{236}Pu content of the plutonium in the waterways matched the plutonium found on the hillside near the rupture site.

- The magnitude of the plutonium release to the soil during the January 23, 1969 pipeline rupture was consistent with the amount of plutonium found offsite considering the mechanisms of transport and deposit.

- The distribution of the plutonium inventory in onsite and offsite areas was consistent with the location of the rupture and the mechanisms of transport and deposit.

- The magnitude of the plutonium concentration in the offsite sediment was consistent with the concentration of plutonium in the soil near the rupture site considering dilution during transport and deposit.

Actions Taken to Prevent Recurrence

Several actions were planned, initiated or implemented in 1974 to further reduce or eliminate the potential for release of plutonium, especially to offsite areas.

- The surface soil contamination trail, found on the WD hillside, was excavated and removed in 1974 to eliminate the potential for additional erosion of contaminated soil. This soil was drummed and shipped to the ERDA burial site in Idaho.

- A process waste drumming facility was constructed in the plutonium processing facility (SM-PP) and the use of the process waste solution transfer pipeline was discontinued in 1974.

- A comprehensive soil erosion control program has been initiated to reduce the erosion potential of all onsite soil. This program includes the use of ground cover and improvement of the site surface water drainage system.

- Several temporary small dams were installed on the main drainage ditch in early 1974 to settle out the erosion products and reduce the amount of suspended solids leaving the site in the water.

- Construction projects have been initiated or planned to install large permanent settling basins, ponds and a reservoir to reduce the suspended solids in the water flowing to offsite areas to the lowest practical level.

- A routine sediment and suspended solids sampling plan was implemented by the Environmental Monitoring Group.

MECHANISMS OF RELEASE OF ^{238}PU TO OFFSITE AREAS FROM THE PIPELINE RUPTURE SITE

Mechanistic Model of the Release, Transport, and Deposition

The mechanisms that permitted the plutonium to move from the rupture site to offsite areas is of considerable interest since none of the information taken at the time of the rupture in 1969 indicated a significant release to offsite areas.

From laboratory studies, field tests, and observations, a general mechanistic model has been developed, consistent with all of the available information.

A flow diagram of the release mechanism is summarized in Figure 37. Using this model, the sequence of events leading to the deposition of plutonium in the offsite waterway can be summarized as:

- Acidic plutonium solution released to the soil (mainly underground) on January 23, 1969.

- The acid was neutralized by the calcareous soil.

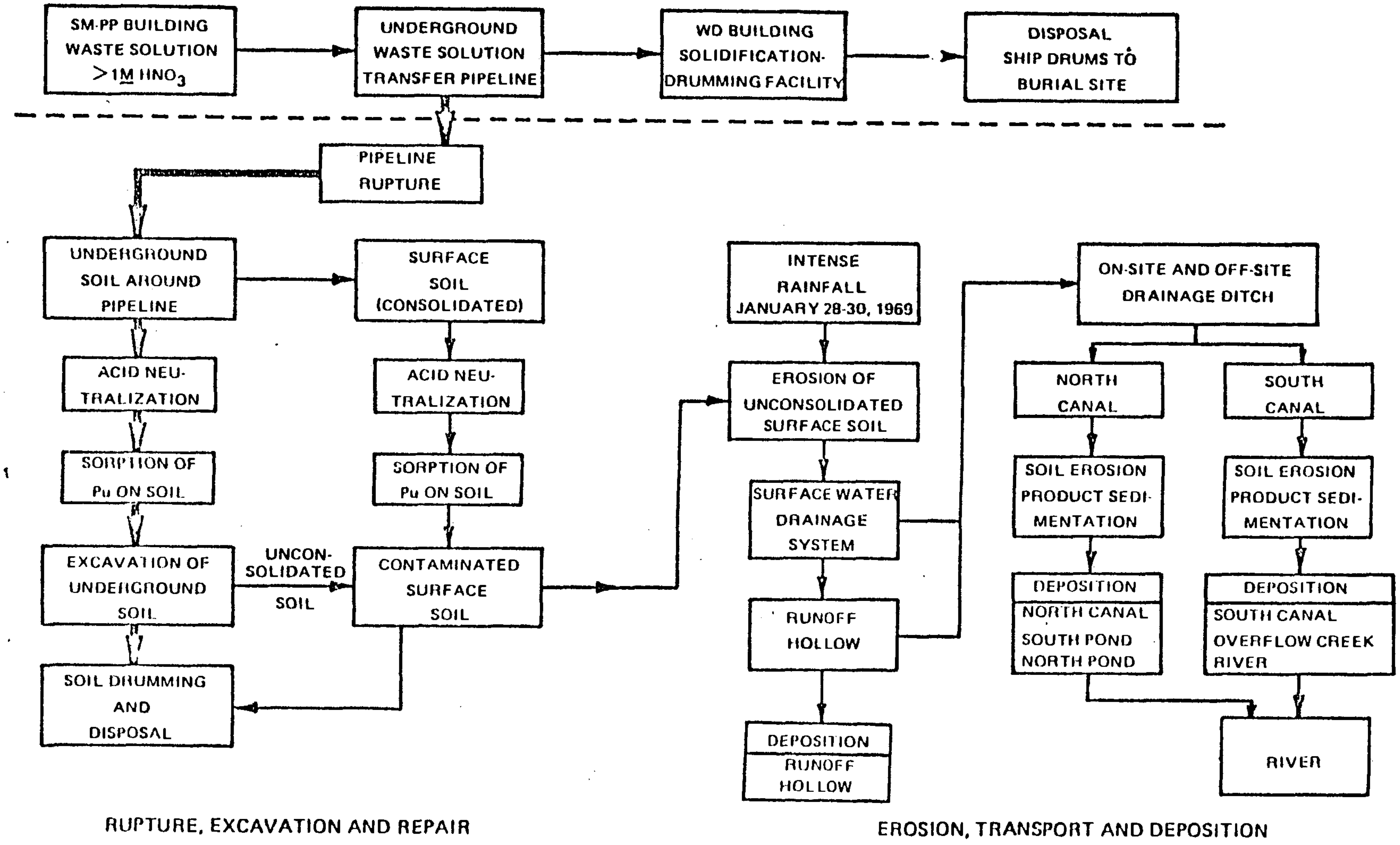


FIGURE 37. Flow Diagram of Release Transport and Deposit of ^{238}Pu in Off-Site Waterways

- The plutonium was strongly sorbed and fixed on the soil and was immobilized.
- The soil onto which plutonium was sorbed was brought to the surface and/or loosened by the excavation and repair operations.
- The heavy rainfall on January 28-30 eroded the soil loosened by excavation and the soil dropped on WD street, into the surface water system.
- The erosion products were carried by stream action to the main drainage ditch, then offsite to the water ways.
- The erosion products settled in the waterway locations most favorable for particle sedimentation.
- Subsequently, erosion of noncontaminated soil tended to result in sedimentation in the same locations and to cover the plutonium-contaminated sediment.

The key elements of this model are:

- Acid neutralization by the soil,
- Plutonium sorption on the soil,
- Erosion of contaminated soil,

- Transport of soil erosion products by steam action, and

- Deposition of the soil erosion products in offsite waterways by sedimentation processes.

Perhaps the most important mechanism examined in this case is the interaction of plutonium solutions and Mound Laboratory soil. From the time the pipe ruptured to the deposit of plutonium in the offsite waterways, the behavior of plutonium was controlled by the plutonium/soil chemical interactions and the physical properties of the Mound Laboratory soil.

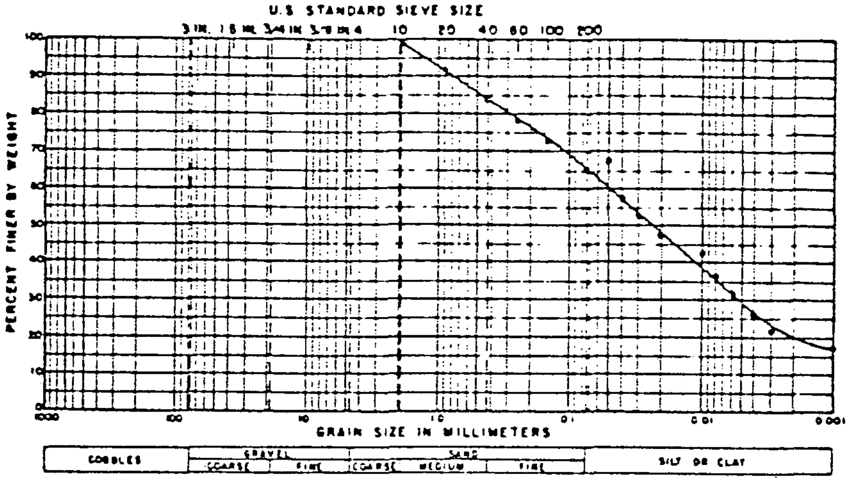
Interactions of Plutonium Solutions With Soil

Soil properties. The soil indigenous to Mound Laboratory is glacial till, a heterogeneous mixture of gravel, sand, silt, and clay.(4) A typical fully dispersed glacial till particle size distribution is presented in Figure 38.(4) The clay and silt fraction in glacial till which accounts for most of the surface area averages about 40 to 50%. The major chemical constituents of the soil are:

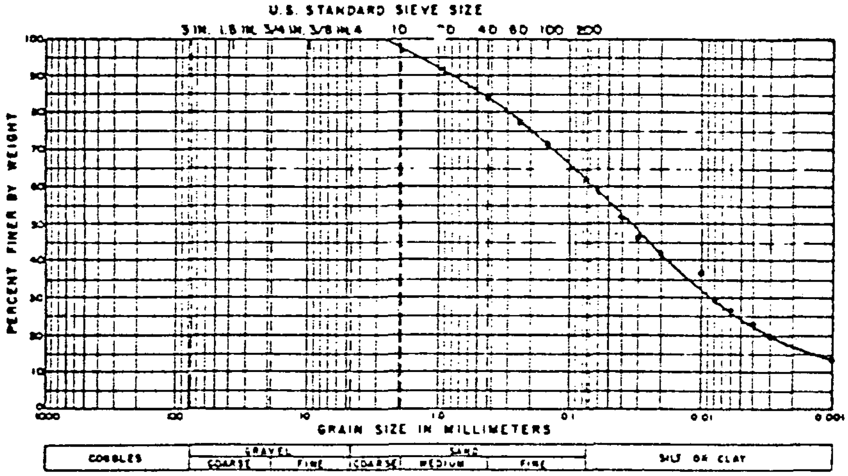
- Clay (hydromicas and other clays)

- Calcite ($CaCO_3$)

Depth 5 ft.



Depth 12.5 ft.



Depth 22 ft.

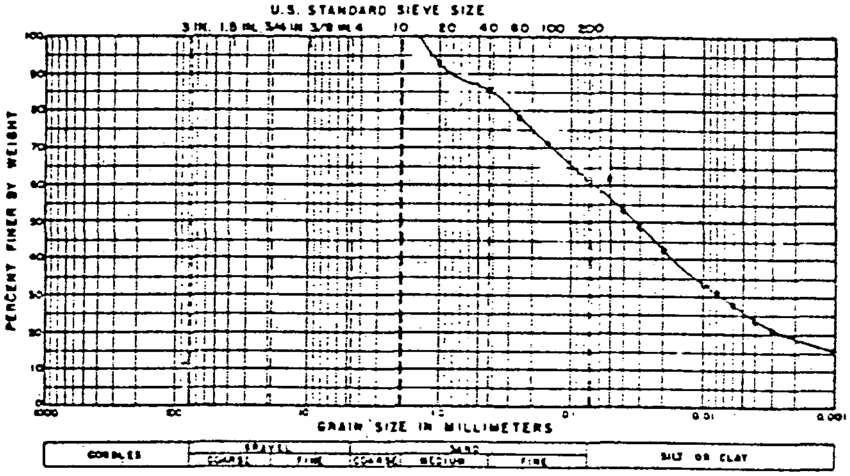


FIGURE 38. Fully Dispersed Particle Size Distribution of Glacial Till

- Dolomite [$MgCa(CO_3)_2$]
- Quartz (SiO_2)
- Limestone and Shale Rocks
- Organic Materials
- Water

The calcite, limestone, and dolomite gives the soil its buffer (acid neutralizing) capacity while the silt and clay fraction is responsible for most of its sorption or ion exchange capacity. Table 10 lists these important chemical properties for both whole soil, and the silt and clay fraction. The pH of water in equlibrium with the soil is typical of calcareous soils.

TABLE 10. Chemical Properties of Glacial Till at Mound Laboratory

	Whole Soil	<50 μm Fraction
Ion Exchange Capacity(a)	5-20 meq/100 g	20 meq/100 g
Buffer Capacity (pH = 7)(b)	400-1100 meq/100 g	400 meq/100 g
pH of Equilibrium Water	7.5-8.3	7.5-8.3

(a) Varies with particle size distribution
(b) Varies with amount of soil carbonates (minerals and rocks)

Acid neutralization by the soil. When acidic solutions are placed in contact with the soil, a violent effervescent reaction takes place liberating large amounts of carbon dioxide gas and reducing the acidity of the solution:

$$2HNO_3 + CaCo_3 \rightleftarrows CO_2 \uparrow + Ca(NO_3)_2 + H_2O$$

(calcite)

$$4HNO_3 + MgCa(CO_3)_2 \rightleftarrows 2CO_2 \uparrow + Ca(NO_3)_2 + Mg(NO_3)_2 + 2H_2O$$

(dolomite)

The rate of acidity neutralization, shown in Figure 39, is rapid. After contact with the soil, the pH increases rapidly to about pH 5 or 6, then more slowly to pH 7.5 to 8.3 as the dissolved CO_2 is expelled from the solution.

The capacity of the soil near the rupture site to neutralize the acidic plutonium solution released is about 4 to 11 milliequivalents of acid per gram of soil depending on the size, distribution, and composition of the soil. This capacity is large enough to have consumed all of the acid released at the rupture site.

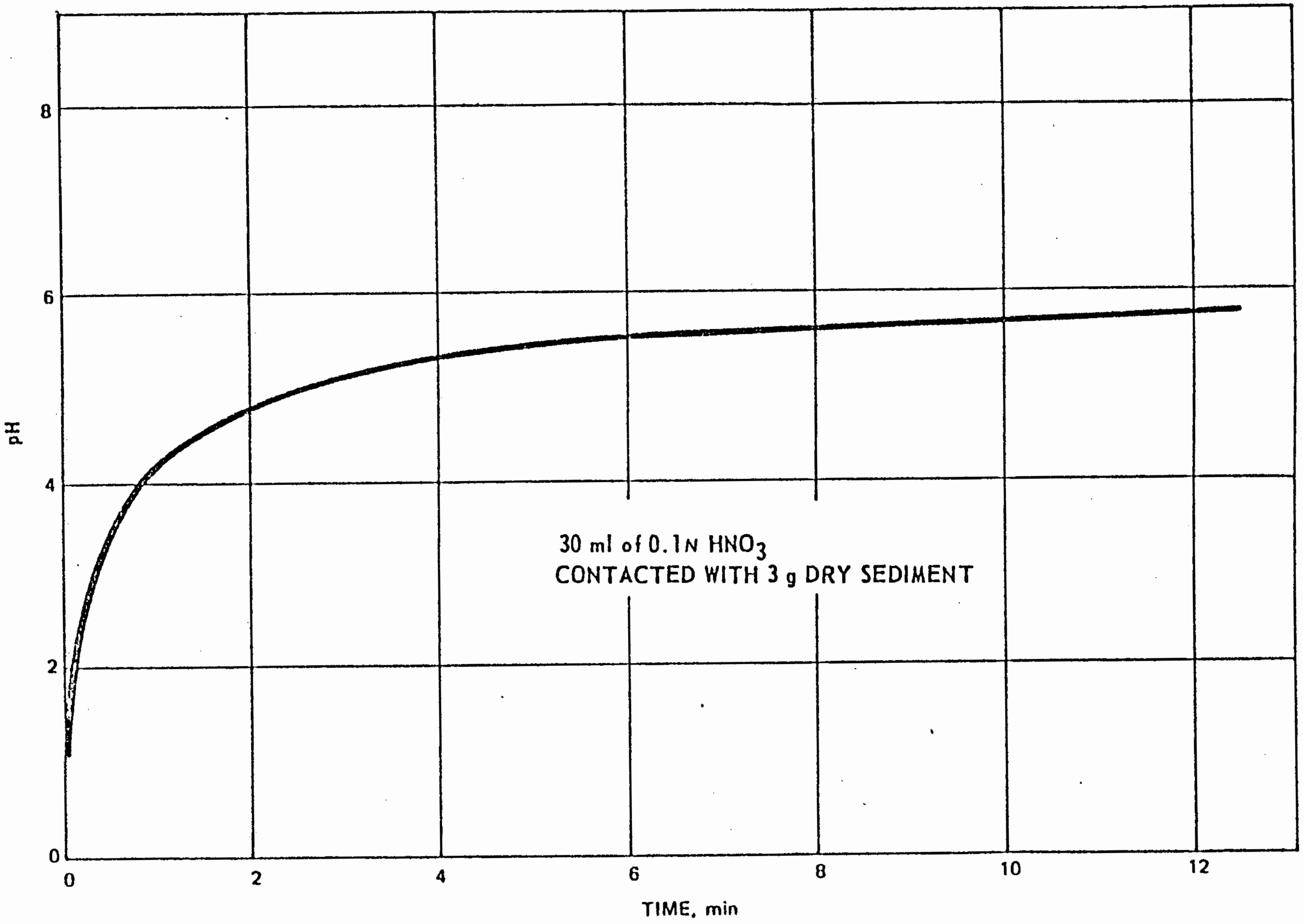


FIGURE 39. Rate of Acid Neutralization by Glacial Till

Sorption of ^{238}Pu onto the soil. The plutonium/soil sorption studies were performed with the clay and silt fraction of the soil and ^{238}Pu nitrate [$Pu(NO_3)_4$] solutions prepared and diluted in the laboratory to avoid nonequilibrium hydrolysis or "polymerization". The sorption studies involved contacting 20 ml of the plutonium solution with 2 g of air-dried soil. These samples were equilibrated with agitation at room temperature for 7 to 14 days. Separation of the two phases was performed using centrifugation and filtration.

1. pH dependence: The equlibrium distribution, $D_{w/s}$ defined as:

$$D_{w/s} = \frac{\text{Concentration of Pu in the water (nCi/g)}}{\text{Concentration of Pu in the soil (nCi/g)}}$$

was found to vary greatly with the equilibrium (final) pH of the solution as shown in Figure 40. (For a perspective of the percent of plutonium sorbed versus pH, see Figure 41.) It is noteworthy that the plutonium is extensively sorbed ($D_{w/s} \simeq 2 \times 10^{-2}$) onto the soil even when the final acidity is about 1 $\underline{M}$ HNO_3. The distribution ratio decreases (sorption increases) as the pH is increased and reaches a minimum value of 6×10^{-6} at about pH 5.5, then appears to increase again.

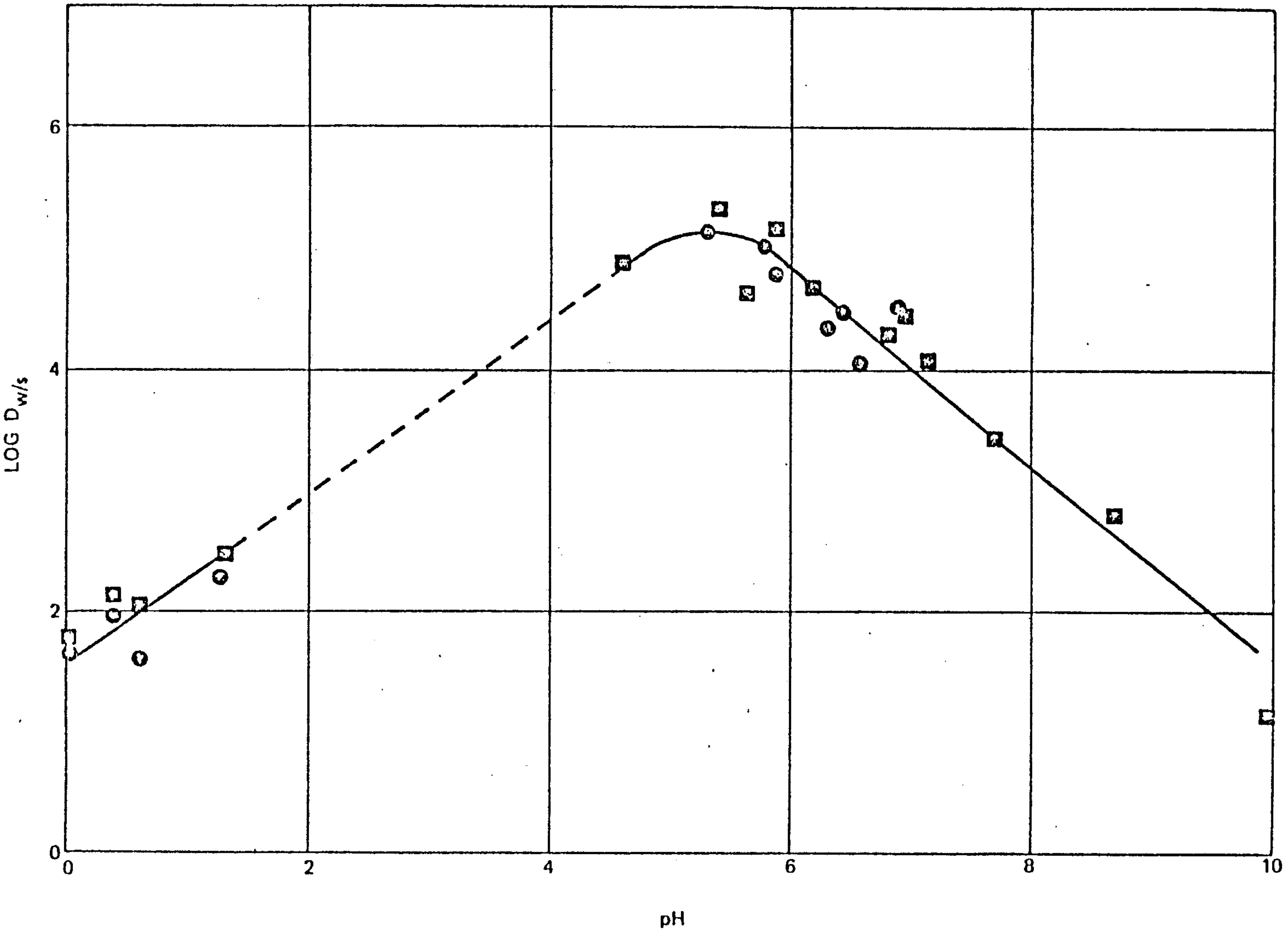


FIGURE 40. Distribution Ratio ($D_{w/s}$) of ^{238}Pu between Water and Soil as a Function of pH

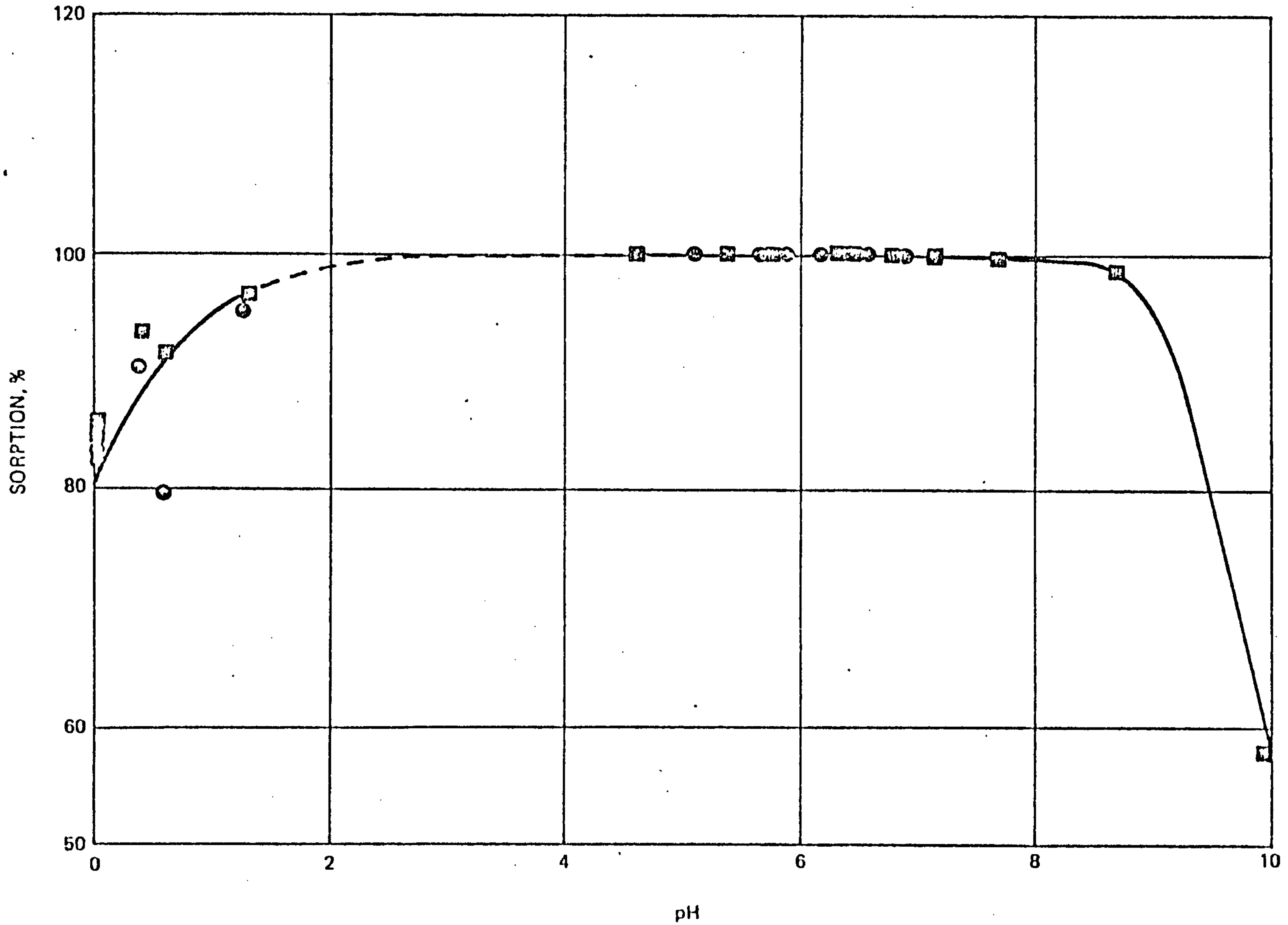


FIGURE 41. Percent Sorption of ^{238}Pu (20 ml Solution) Onto Two Grams of Soil as a Function of pH

The increasing distribution ratio with increasing pH in the alkaline region may be due, in part, to the formation of plutonium hydrolytic species and, in part, to clay dispersion. The clay tends to disperse in alkaline solutions and form colloidal suspensions which are difficult to remove by centrifugation and filtration. Some of the measured plutonium in the solution is undoubtedly sorbed onto these colloidal clay particles. The minimum distribution ratio (maximum sorption) found in these laboratory tests (6×10^{-6}) agrees fairly well with the distribution ratio measured on the contaminated sediment offsite (1×10^{-5}). This agreement tends to support the proposed mechanistic model.

2. Sorption as a function of plutonium solution concentration: At near neutral pH, the sorption of plutonium did not vary significantly using plutonium solution concentrations from 7×10^{-15} M to 2×10^{-7} M. This is not surprising since the soil exchange capacity (0.2 meq/g) is not challenged significantly ($<1 \times 10^{-2}$ %) using this concentration range. In an additional test, the filtrate solution from the sorption of the

2×10^{-7} M was equlibrated again with fresh soil and yielded approximately the same distribution ratio the second time. This indicates that essentially none of the plutonium would remain in solution after moving an extremely short distance through or on fresh soil.

3. Sorption rate: Some preliminary rate studies were performed and the reaction was found to be about 98% complete in less than 5 min. As expected, the sorption reaction appears to be a half-time of less than 1 min. The rate of reaction tends to decrease with increasing pH, but does not appear to vary much with solution concentration.

The importance of these findings is that the plutonium would have been almost immediately sorbed onto the soil after being released through the pipe rupture.

4. Distribution of plutonium as a function of soil particle size: In order to determine how the plutonium is sorbed onto the soil, a joint study was performed by Mound Laboratory and LFE.(5) Samples of soil were treated with plutonium solutions, as described previously, and air

dried. Each sample was dispersed and separated by sedimentation techniques into six particle-size ranges. Each of these fractions were then analyzed for plutonium. As is shown in Figure 42, the amount of plutonium sorbed on the soil increases with decreasing mean Stokes diameter. The solid line in this plot is the theoretical slope relationship between ^{238}Pu concentration and sorption capacity. The points shown are the values determined experimentally during this study.

As can be seen, the experimental data are in reasonable agreement with a plutonium concentration dependence on surface area and/or ion exchange capacity. The fact that the small particles tend to provide better general agreement may indicate that there is a change in chemical composition with size.

Also in Figure 42, the plutonium concentration versus particle size data for the synthetic samples are compared with similar data collected on contaminated sediment from the canal. Except for a displacement in the two functions, there appears to be agreement that the plutonium sorbs

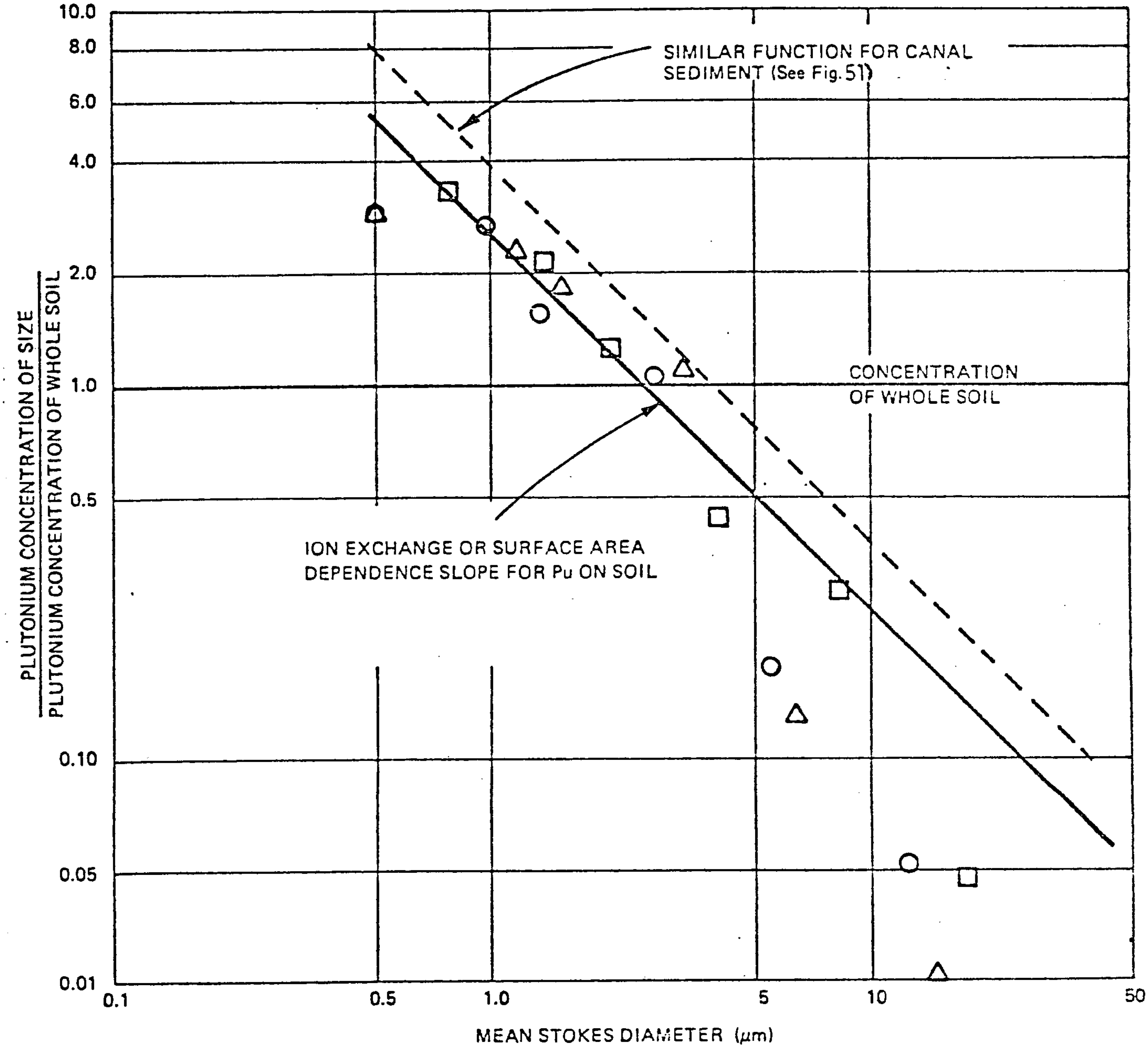


FIGURE 42. Variation of ^{238}Pu Concentrations in Soil as a Function of Fully Dispersed Particle Size

as a function of ion exchange capacity or surface area. In both determinations, the smallest fraction exhibited plutonium concentrations from three to eight times the plutonium concentration of the whole sample.

The displacement in the two curves indicates that the average particle size of the two soils is different. The waterway sediment sample exhibits somewhat larger particle sizes than the soil used to make the synthetic samples. This also explains the fact that the ratio of the concentrations of the smallest size to the average size is greater for the sediment samples. Since the majority of the plutonium is sorbed on the small particles, the presence of large particles serve mainly to dilute the concentration of the whole soil/sediment distribution.

5. Autoradiographic alpha track analysis:(5) An autoradiographic analysis of soil treated with plutonium solutions indicates the general dispersion of plutonium in the soil rather than formation of PuO_2 particulates mixed with the soil. This observation is consistent with the sorption behavior of plutonium on soil and is in

agreement with similar tests performed on the offsite sediment.

6. Proposed bonding mechanisms: Basically, soils are made up of silicate materials and other minerals. Quartz sand has a continuous silicate structure where each silicon atom is bound to four oxygen atoms and each oxygen is bound to two silicons. This continuous structure is interrupted at the surface and in natural systems (where water is abundant), the surface is composed of unsaturated oxygen bonds. That is, each surface oxygen is bound to only one silicon atom. The remaining bond is usually occupied by other cationic species.

Clays are more complicated, but are also based on the continuous silicate structure except that some silicon atoms have been replaced by Mg^{2+}, Al^{3+}, Fe^{3+}, and Fe^{2+} (mostly Al^{3+}). These substituted atoms in the silicate structure result in variations in long range crystal structure. Rather than forming three dimensional silicate networks as in quartz, many clays form two-dimensional sheets which cleve easily for form plates. The surface of these layered sheets that make up the clay particles also exhibit unsaturated oxygen bonds. This, in part, accounts for the higher sorption capacity in clays (relative to the same size silicate particle) since sorption can take place between the silicate layers within the clay particles.

The unsaturated oxygen bonds in natural soils and clays are occupied by cations such as H^+, K^+, Ca^{2+}, Mg^{2+}, or other available cations. The bonding strength order of these cations is:

$$Pu^{4+} > H^+ > Al^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > Na^+.$$

In order to bond to the silicate, an ion must displace or exchange with the cation already bonded:

$$\text{A-Clay} + B^+ \leftrightarrow \text{B-Clay} + A^+.$$

The extent of the exchange depends on the relative strength of the bonds and the relative solution concentrations of the two cations.

Some cations form silicate bonds that are fairly weak (such as Na^+ and K^+) and may be only electrostricted, while other metal cations may form bonds that are much stronger and may even develop covalent character.

Tetravalent plutonium ions are well noted for the formation of strong bonding (complexing) with oxygenated ligands.(6-8) The strength of plutonium oxygen bonds is also indicated by the acidic character of plutonium hydroxide forming hydrous plutonium oxide.

It is not surprising then that plutonium ions can compete with hydrogen ions for the bonding sites on the silicates even when the Pu^{4+}/H^{+} concentration ratio is 10^{-11} or less. The very large bonding potential of plutonium(6-8) suggests that sorbed plutonium cannot be significantly displaced from soil by the concentrations of cations existing in nature.

Chemicals that complex the plutonium(6-9) compete with the silicate particles for the plutonium and tend to reduce the extent of sorption of the plutonium on soil. For example, the formation of plutonium hydrolytic species $PuOH^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^{+}$ and $Pu(OH)_4$ (as well as "polymeric" forms) tends to reduce ion exchange sorption.(10)

However, even at pH 10 the distribution of plutonium in the aqueous phase is only 7.2×10^{-2} (Figure 40).

Some of the hydrolytic plutonium "polymeric" forms may adsorb to the surface of the soil particles, and the precipitation of PuO_2 (H_2O) may be nucleated by the colloidal soil particles when the plutonium concentrations are relatively high ($>10^{-6}$ M).(11,12) These physical adsorption mechanisms are not expected to be extensive at the low plutonium concentrations (10^{-9} M) used for this study.(10)

Moderately strong organic complexing agents, such as citric acid, have been shown to reduce the sorption of plutonium on soil. However, relatively high citric acid concentrations (0.1 M) were required to reduce the sorption to $D_{w/s}$ values of 4.2×10^{-2}.

Soil Erosion and Transport Mechanisms

The extent of soil erosion by surface water depends on:(13)

- The velocity of the water,
- The soil particle-size distribution,

- The degree of consolidation of the soil, and

- The amount of ground cover or root mats holding the soil in place.

The erosion behavior of soil has been reported and is presented in Figure 43.(13,14) The most erodible soil fractions are sands and unconsolidated silts and clays. The effect of consolidation decreases the erosion potential of silts and clays, but has little effect on the larger size fractions.

The effect of ground cover or root mats is to hold the mass of soil in place and reduce total erosion. The upper parts of the plants also tend to reduce the water velocity near the water/soil interface.(13)

At the time of the pipe rupture, most of the plutonium was sorbed onto the subsurface soil surrounding the pipeline and, therefore, was not subject to erosion. The plutonium solution which came to the surface was quickly sorbed onto soils protected by ground cover and root mats (winter conditions). Since there was no rainfall at the time of the rupture, the erosion potential was nearly zero. Had it rained while these conditions prevailed, the erosion of contaminated surface soil would have been minimized by the ground cover and consolidation of the soil. On the

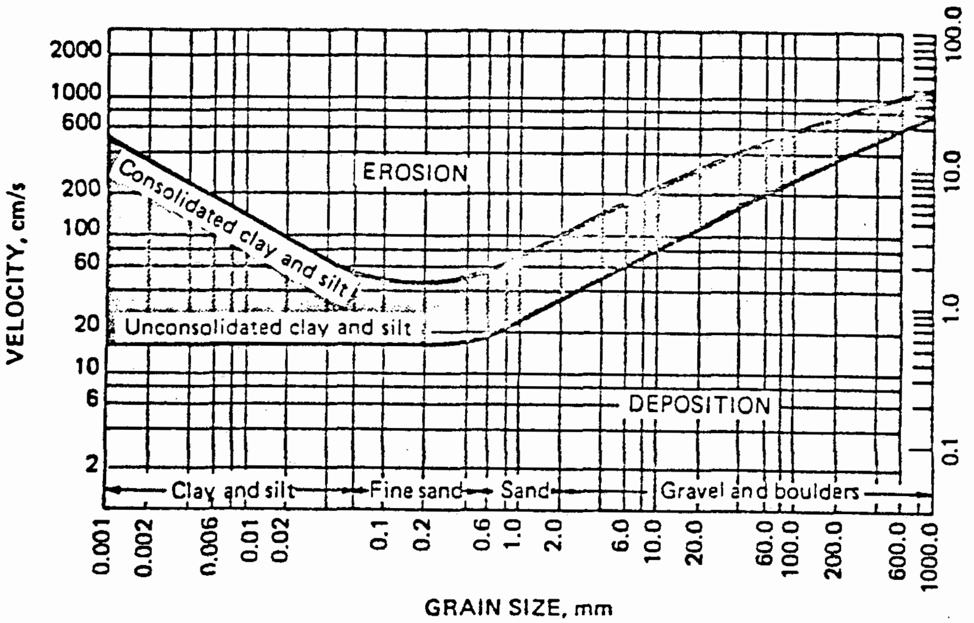


FIGURE 43. Erosion as a Function of Particle Size and Stream Velocity(13,14)

other hand, the presence of plutonium contaminated soil on the 19° slope of the hillside would have been greater than at the rupture site because the velocity of the water would have been higher. Erosion from this grassy hillside, however, is not extensive as indicated by the presence of very little sediment in the concrete flume.

During the period between the rupture, January 23, 1969 and the heavy rainfall on January 28-30, 1969, extensive excavation was taking place at the rupture site. The loosened soil removed from around the ruptured pipeline dropped onto the street, increased the total amount of contaminated soil available for erosion and presented unconsolidated soil rich in sand, clay, and silt particle sizes.

When the rains came on January 28-30, the erosion potential was very high. The large amount of water, collected on the paved surfaces, easily eroded this unconsolidated contaminated soil from the street and excavations to street storm drains and over the hillside where it followed the natural drainage pathways. The velocity of water in all of these surface water drainage channels would have precluded extensive sedimentation until the larger offsite channels and lower stream velocities were encountered.

The movement of plutonium from the rupture site to the runoff hollow probably resulted from erosion of contaminated soil from the outside of drums stored at the end of the street. The flow patterns of water in the area would not have carried the sediment from the rupture site to the runoff hollow. Since only a limited amount of soil was clinging to the outside of these drums, very little plutonium was found in the sedimentation areas of the runoff hollow. The general pathways of erosion of contaminated soil from the rupture site are shown in Figures 44 and 45.

Since the rainfall was very heavy,(3) the suspended and bedloads of uncontaminated erosion products in all of the drainage channels was very large which diluted the concentration of the contaminated sediment by perhaps as much as 1000 times or more.

Water samples taken during this 1969 rainfall indicated plutonium concentrations less than RCG ($<5 \times 10^{-3}$ nCi/ml). The extensive sorption reaction between plutonium and soil was not known to the emergency personnel in 1969; therefore, the absence of plutonium in the water falsely indicated that no significant amounts of plutonium were leaving the site and the situation was under control.

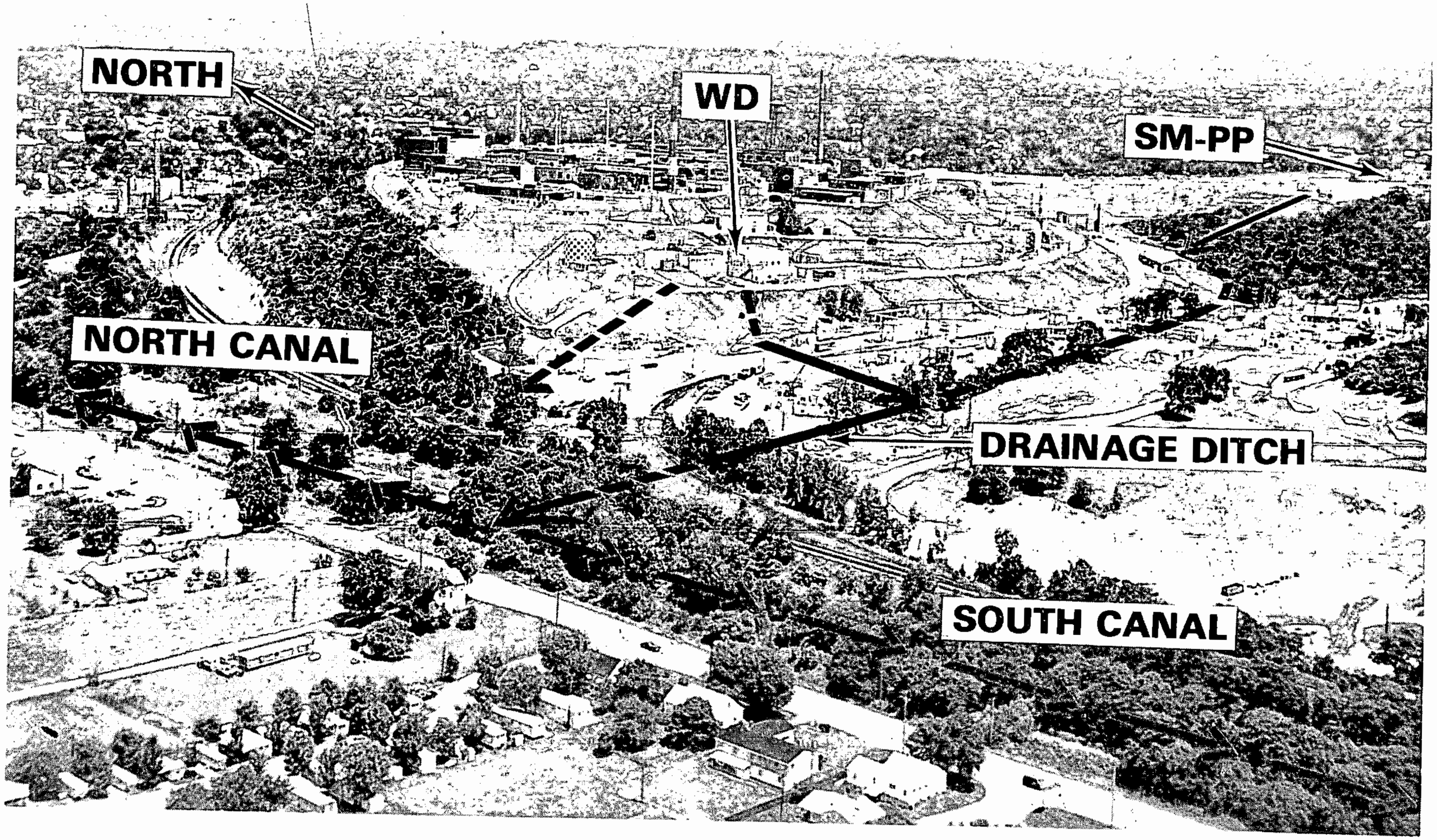


FIGURE 44. Aerial View of Mound Laboratory from the West, Showing Pathways Contaminated Soil Erosion in 1969

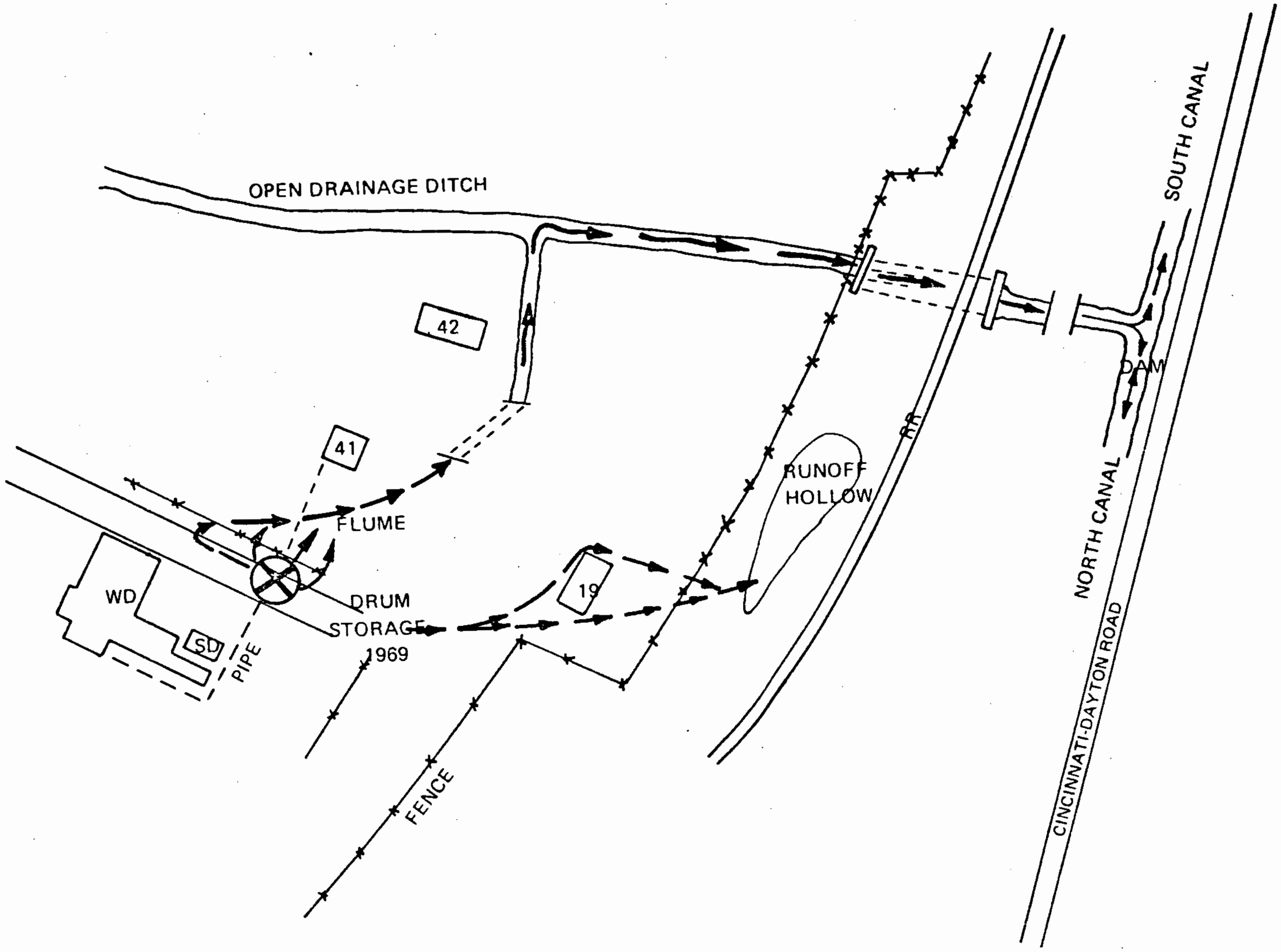


FIGURE 45. Schematic Diagram of Contaminated Soil Erosion Pathways

It is believed that the majority of the plutonium/sediment found offsite was eroded and transported offsite during the heavy rainfall of January 28-30, 1969. An additional smaller amount probably was eroded and transported in subsequent 1969 spring rains(3) before ground cover returned. After the area was cleaned up, grass grew on the hillside, and the soil became consolidated, additional erosion of the plutonium/soil which remained on the hillside would have decreased continually.

Deposit Mechanism

As in the process of erosion, the important parameters for sedimentation of the erosion products are particle size and water velocity including turbulence.(13)

The particle size distribution of erosion products, in a natural water system, exhibits extensive agglomeration due to incomplete dispersion and the presence of natural flocculants in the water. In order to measure the extent of agglomeration that might be expected in the natural system, two types of laboratory sedimentation measurements were performed.

The first test was performed(15) by methods recommended by the American Society for Testing and Materials (ASTM)(16) to determine the basic particle size distribution of the sediment. The second test was performed on an aliquot of the same sediment sample using a modification of the ASTM method to determine the natural particle size distribution of erosion products. In the second test, no dispersant was used and the sedimentation was performed in natural water taken from the sampling site. Everything else was performed(15) exactly as the ASTM method described.

The results of these tests are compared in Figure 46. In the absence of the dispersing agent and in natural water, the smaller particles are extensively agglomerated such that the sedimentation proceeds much faster than would be predicted by the basic particle size of the sediment.

Sedimentation of erosion products in the waterways occurs when the velocity and turbulence of the streams fall below that necessary to maintain the suspension of a particular size range of particles.(13) For example, in very swift sections of the waterways, the bed contains very few deposits, or the deposits are composed mainly of larger gravel and rocks. As the velocity decreases downstream, the deposits indicate successively smaller particle size distributions. This mechanism describes the overall picture of the deposition patterns; however, local variations in the stream velocity such as near an obstruction or on grassy banks of flooded waterways may result in the local deposition of smaller particles.

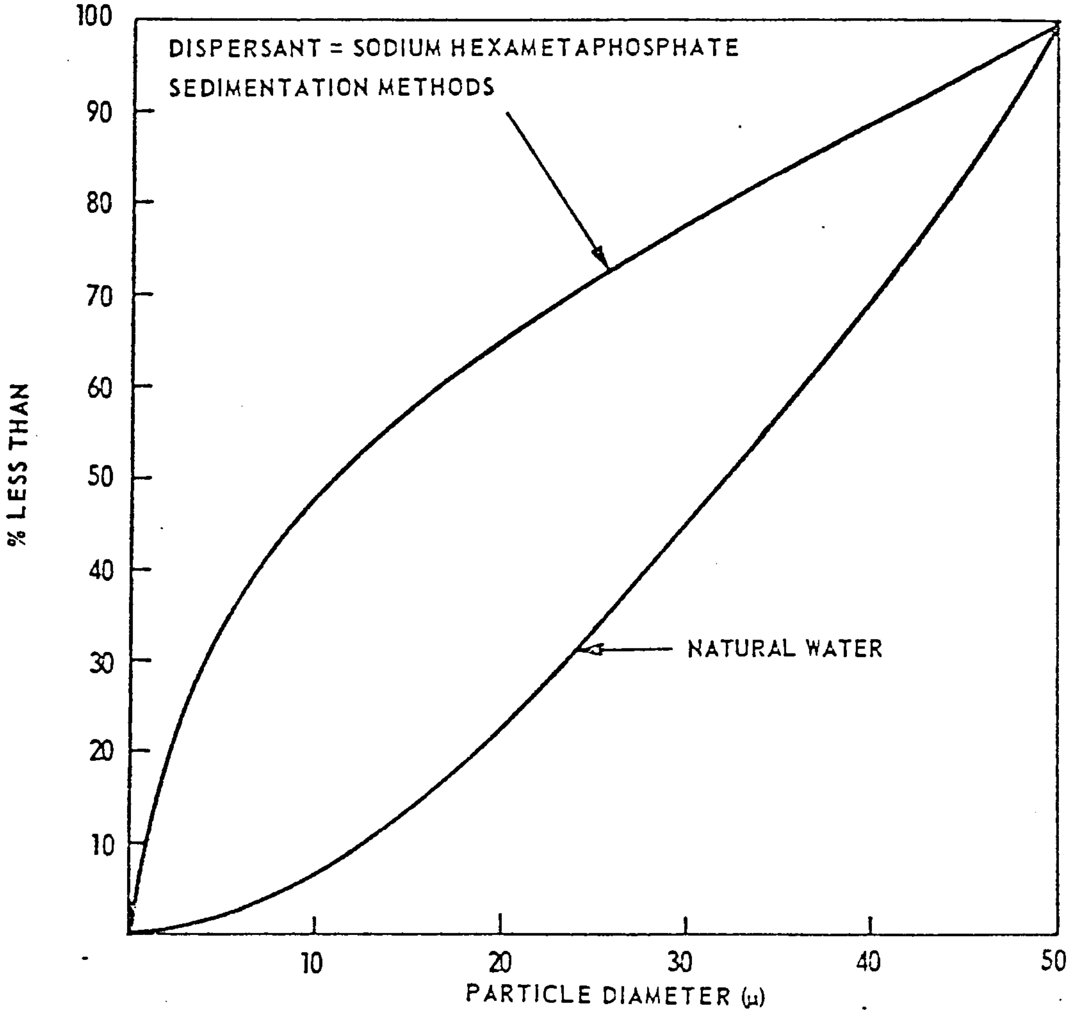


FIGURE 46. Extent of Agglomeration of Erosion Products in the Natural Water System

During the environmental survey sampling program, the size fraction greater than 1000μ was routinely removed from each of the samples and weighed. The percent of this larger size fraction in the first foot is probably indicative of average stream velocity during high velocity waterflows. The percent of the larger size fraction was generally quite large in the sediment of the swift onsite and offsite drainage ditch (central channel). The large size fraction on the grassy banks, which are often flooded, was lower.

In the North and South Canals, an extensive deposition of the >1000 μm size fractions (Figure 47) always preceded the major deposits of the plutonium bearing sediment. This observation indicates the partial classification of particle sizes in the sediment as a result of flow velocity characteristics of the channel and in preferential sedimentation locations.

There are two main plutonium/sediment deposits in the offsite waterways at locations most favorable for erosion products sedimentation. The deepest sediment (and highest plutonium deposits) was found approximately 55 ft north of the earthen dam in the North Canal. Figure 48 shows the differential plutonium inventory distribution along the length of the canal and the profile of the sediment

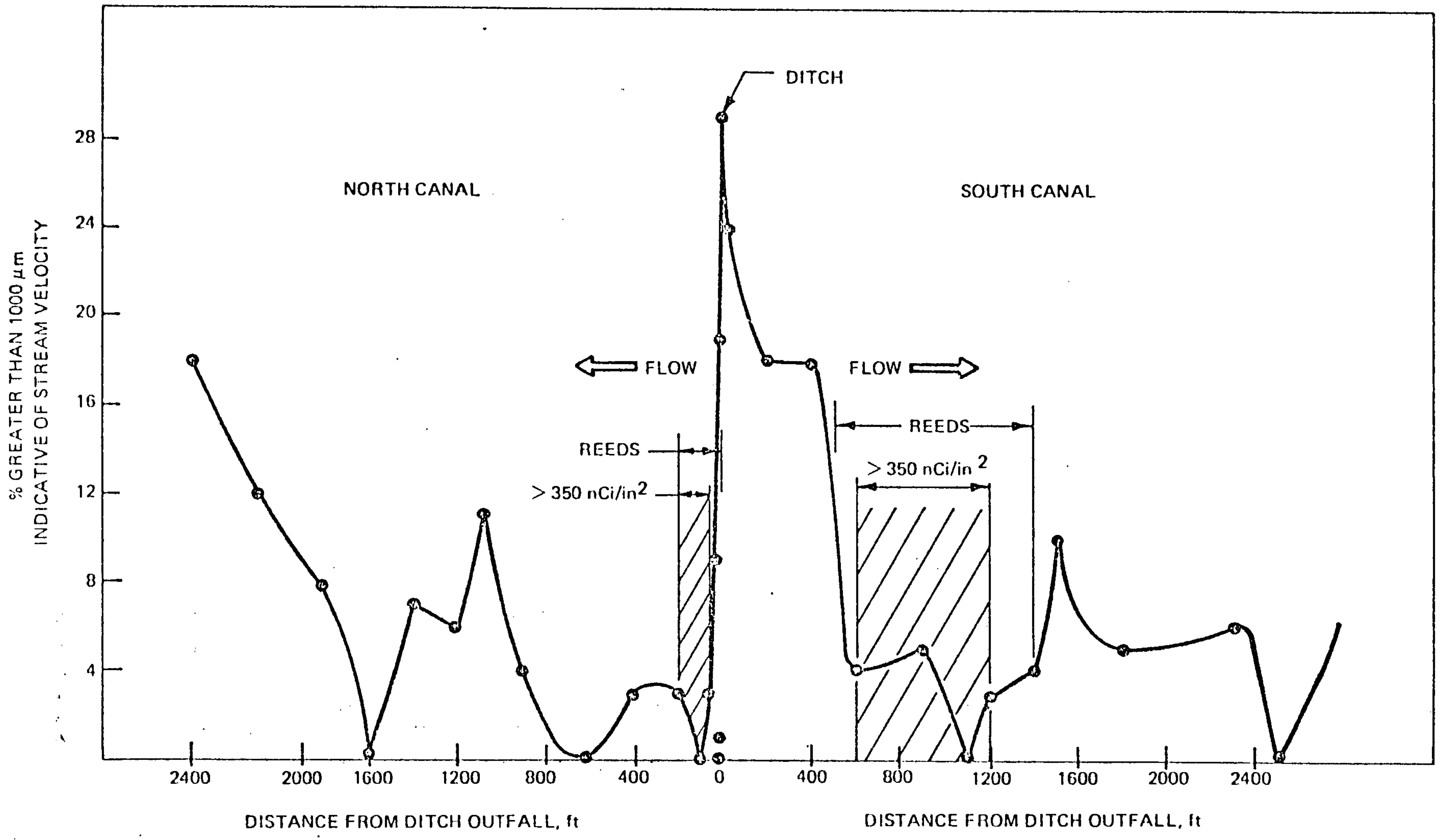


FIGURE 47. Percent of Large Particle Size Fraction in First-Foot Sediment Samples Taken Along the Miami-Erie Canal

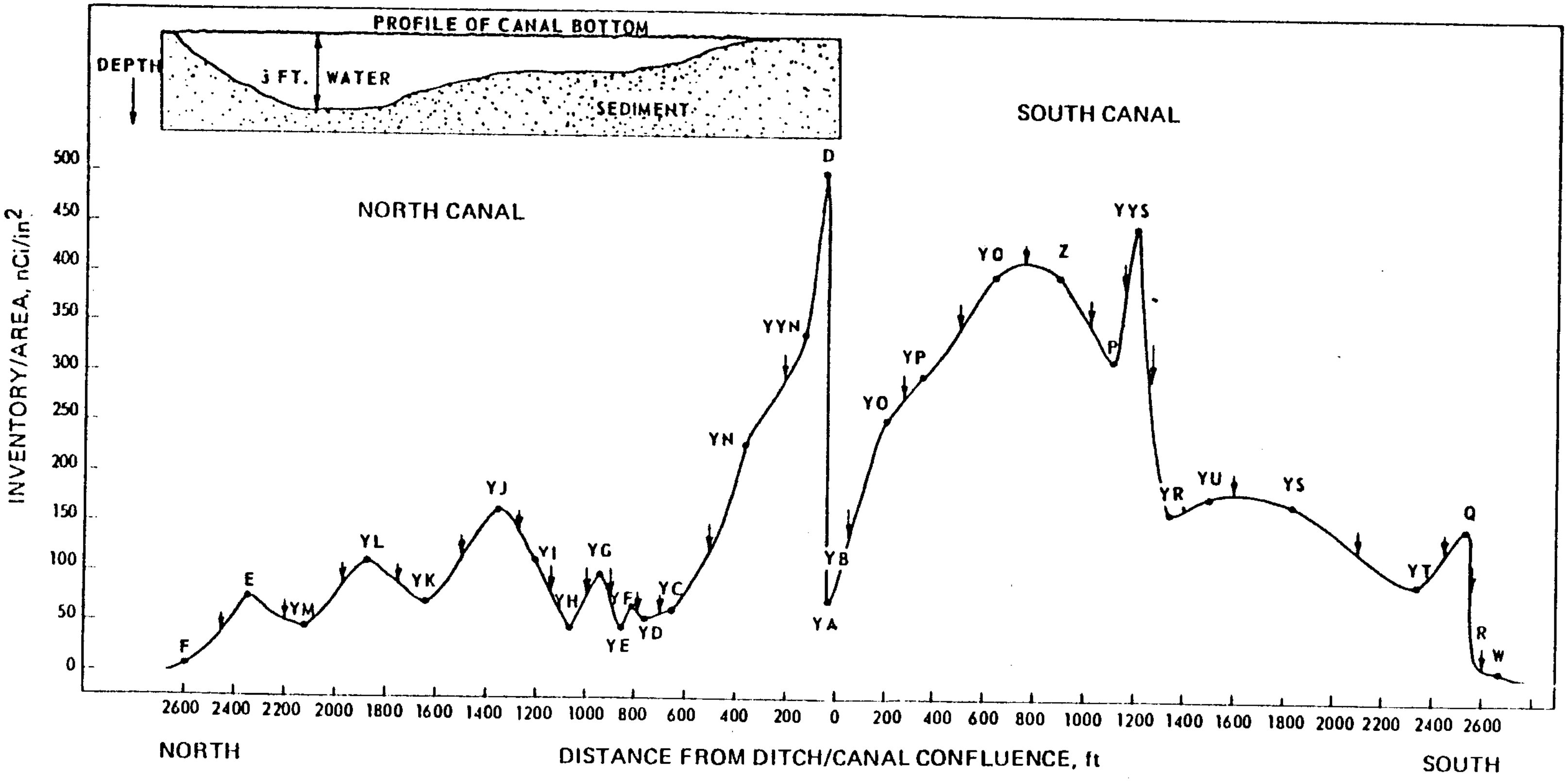


FIGURE 48. Inventory of ^{238}Pu Along the Length of the Miami-Erie Canal

depth in the North Canal. As the turbulent water flows through the pipes to the North Canal, the canal is wide, the water is calm, and the erosion products settle quickly. In addition, the very shallow water in this area has resulted in an extensive growth of cattail reeds which further enhances sedimentation by reducing the velocity and turbulence of the water flow. The result is a build-up of sediment in this area as indicated by the sediment profile.

The plutonium/sediment was deposited in 1969 and has been covered by subsequent sedimentation of uncontaminated erosion products. By this action, the highest plutonium concentrations were buried 3 to 4 ft. There is evidence that some vertical (upward) mixing has taken place during turbulent periods.

The depth of the sediment decreases to the North because of erosion product depletion; however, smaller particles, bearing plutonium, have been deposited in subsequent favorable sedimentation locations. The initial 1969 plutonium deposits in the locations further north, are therefore thinner, and are usually in the first foot of sediment. There is some evidence of minor secondary transport of plutonium sediment from the sediment area north of the dam to locations further north during high turbulent flow conditions. This general trend continues through the system into the south basin of the South Pond and to the North basin into the North Pond, exhibiting deposits of less and less plutonium bearing sediment.

In the South Canal, the initial channel running south of the ditch/canal confluence area is rocky for several hundred feet. Beyond this swift and turbulent zone, another major sedimentation area is evident. At this point, approximately 500 to 600 ft south of the earthen dam, the percentage of >1000 µm particles decreases rapidly, indicating a reduction in the stream velocity. In this area there is also a growth of cattail reeds.

The apparent change in the stream velocity is not as sharp as at the North Canal sedimentation location; therefore, the deposition of plutonium sediment (Figures 47 and 48) is much broader than in the north (~800 ft). In the South Canal sedimentation area, the thickness of plutonium sediment deposit is less, existing mainly in the first 2 ft of sediment. The plutonium inventory trails off in the remaining 1000 ft of the South Canal except for a small additional sedimentation area at the end of the South Canal behind the spillway leading to the overflow creek, where water tends to pool.

The overflow creek is narrow and deep; therefore, the velocity of the water flow is very swift as indicated by very few sediment deposits in this channel. Near the river outfall, sediment containing plutonium tends to collect and deposit. Minor sediment deposits extend downstream in the river along the eastern bank of the river for several hundred feet. This results from the lower velocity of the river near its banks.

The river itself exhibits very little silt and clay deposit. The river bottom was found to be mostly sand and gravel except in selected localized areas such as near the ends of dams.

Due to the minute concentrations of ^{238}Pu (<0.0001 nCi/g) found in the downstream river sediment, it is not possible to statistically prove that the downstream river inventory is different from zero, based on the analytical data. It is likely, however, that some of the contaminated erosion products may have passed through the waterways and were carried down the river. These contaminated erosion products would have been severely diluted by the extremely large amount of uncontaminated erosion products carried by the river and are, therefore, very difficult to detect in the river sediment.

It will be shown later in this report that the river sediment concentrations are insignificant from a health and safety viewpoint. However, in order to place a value on the ^{238}Pu inventory which might have been discharged to the river by this mechanism, a set of conservative conditions were assumed.

- 40 inches of rain ran off the 200-acre drainfield, flowed down the South Canal, through the overflow creek into the river (8.22×10^8 liters or 2.18×10^8 gallons).
- The average suspended erosion produce load in the water at the overflow creek outfall was between 500 and 1000 mg (dry weight)/ℓ. The amount of erosion products discharged to the river, therefore, would have been about 450 to 900 tons dry weight.
- The ^{238}Pu concentration in these erosion products was equal to the highest concentration found in sediment (4.6 nCi/g).

Based on these assumptions, it is estimated that about 1.9 to 3.8 Ci of ^{238}Pu, sorbed onto erosion products, could have been carried down the river as a result of this release.

Summing this estimated amount with the plutonium inventory analytically found deposited in the waterways (5.2 Ci), the total offsite release of plutonium from this incident may have been about 7 to 9 Ci.

Anticipated Future Movement of the Plutonium Deposits

Future water erosion. In general, a portion of the surface plutonium/sediment in each of the waterways will continue to be re-entrained during high-flow periods and deposited downstream. The concentration of these surface deposits will decline as they are diluted by uncontaminated erosion products.

In the North Canal, the majority of the plutonium is buried 1 to 4 ft deep in reasonably consolidated deposits. These deposits are not likely to move except under incredibly extreme flow conditions. In the first 5 years, only 5% of the total North Canal inventory has been transported into the South and North Ponds. The majority of this inventory was probably transported in 1969-70 before the plutonium sediment was consolidated or buried by subsequent sedimentation. The rate of transfer to these ponds is believed to be very small today and should decrease further in the future.

In the South Canal, where waterflow has a considerably higher velocity, more extensive surface erosion could potentially take place. However, this channel is extensively covered with vegetation and the sediment is reasonably well consolidated by the wet/dry cycling. In addition, most of the plutonium is buried and is therefore less susceptible to erosion. For these reasons, extensive movement of the plutonium deposits to downstream areas is not likely. A continuous trickle of surface erosion will probably result in very slight inventory increases in the south half of the South Canal in the future. These deposits will be diluted by noncontaminated erosion products carried by the stream reducing the ^{238}Pu concentration. The future surface deposits at the overfall creek outfall should provide a measure of the erosion from the South Canal.

Surface leaching. According to the distribution ratio of plutonium between water and sediment ($D_{w/s} = 1 \times 10^{-5}$), the concentration of plutonium in the water flowing through these waterways will be very low and will not provide a significant mechanism for transport of the plutonium from the deposits to the river.

Migration through soil. Due to the sorption of plutonium on soil and the very low water permeability of the clay waterway beds,(4) the movement of plutonium through this medium is expected to be insignificant. The rate of movement of the plutonium by this mechanism can be described by:(17)

$$\frac{d[Pu]}{dz} = \frac{dw/dz}{1/D_{w/s} + B}$$

where d[Pu]/dz is the rate of plutonium migration through the clay; dw/dz is the rate of water flow through the sediment; $D_{w/s}$ is the plutonium distribution ratio between water and sediment; and B is the fraction of free volume in the clay.

Water permeability in clay was measured to be 0.1 to 1.0 m/yr,[4] the distribution ratio is 10^{-5}, and the fraction of free volume in the clay is <0.4; therefore, the migration rate can be estimated at about 1×10^{-6} to 1×10^{-5} m/yr.

HEALTH AND SAFETY ANALYSES

The extensive work summarized in the previous sections of this report was performed by Mound Laboratory in order to make a knowledgeable evaluation of the hazards associated with the ^{238}Pu deposited in the waterways adjacent to Mound Laboratory.

It is recognized that the health and safety aspects of plutonium are under public discussion and debate. Most of the debate centers around the setting of national priorities on energy production and fears that general plutonium levels in the environment will increase to a level hazardous to man. This is worthwhile scientific controversy; however, it tends to confuse the general public and generate fear, even when it is not justified by the conditions and circumstances accompanied by accidental releases. Whenever such an accidental release occurs, the public has a right to demand and get a timely, systematic, and realistic evaulation of the hazards it presents to them.

Plutonium, like most chemicals, behaves quite differently under different conditions and circumstances. For this reason, the Health and Safety Analyses presented in this report applies only to the specific set of conditions and circumstances which are present and operable in and adjacent to the waterways near Mound Laboratory.

There has been an honest attempt to make judgments on the conservative side. Overall, the conclusions reached from these health and safety analyses are considered to be substantially on the safe side.

COMPOSITION AND RADIATION PROPERTIES OF ^{238}PU(18)

Plutonium-238 is a manmade element, produced by nuclear reactor irradiation of ^{237}Np. Since Mound Laboratory does not have nuclear reactors, the ^{238}Pu is prepared elsewhere, and sent to this site in a "pure" condition. That is, it contains no significant fission products, and therefore has very little penetrating radiation. The isotopic composition of this plutonium is listed in Table 11 and its associated radioactive impurities are listed in Table 12. The radioactivity is almost entirely short-ranged alpha radiation with a small amount of weak (20 keV) beta radiation from ^{241}Pu. Over 99.9% of the alpha radiation results from the decay of ^{238}Pu which has specific alpha activity of 17.11 Ci/g. The energies of these alpha particles are listed in Table 13.

The energy and amount of penetrating radiation (x-ray and gamma) from ^{238}Pu are listed in Table 14. As can be seen, these dose rates are insignificant at the ^{238}Pu concentrations under discussion.

POTENTIAL HAZARDS OF ^{238}PU

The potential hazards of radiation to man results from external and internal exposure of vital organs. Since ^{238}Pu emits very little penetrating radiation, the potential for external exposure from the amount of ^{238}Pu under consideration is insignificant. The short-ranged alpha and beta radiations cannot penetrate the skin to irradiate vital organs. Therefore, the potential hazard of ^{238}Pu is almost entirely associated with internal exposure. Plutonium taken into the body of man

TABLE 11. Isotopic Composition (Typical of Mound Laboratory ^{238}Pu)(18)

Plutonium Isotope	Principal Decay	Half-Life (yr)	Wt %
236	α	2.85	0.0001
238	α	87.78	80.0
239	α	24082	16.5
240	α	6537	2.7
241	β	14.35	0.7
242	α	3.87×10^5	0.1

TABLE 12. ^{238}Pu Impurities(18)

Isotope	Wt %	Remarks
^{234}U	$\sim$0.19	Increases with Decay of ^{238}Pu
^{237}Np	0.03	
^{241}Am	0.05	Increases with Decay of ^{241}Pu
^{231}Pa	<0.1	
^{232}Th		
^{232}U		
^{235}U		
^{236}U		
^{227}Ac		

TABLE 13. Alpha Emission from ^{238}Pu(18)

Alpha Energy (MeV)	Emission (Ci/g ^{238}Pu)
5.499	12.15
5.456	4.95
5.358	1.5×10^{-2}
5.214	8.6×10^{-4}
4.70	1.2×10^{-5}
Total	17.11

TABLE 14. Computed Penetrating Radiation Dose Rate at One Meter from an Unshielded ^{238}Pu Point Source(18)

Approximate Gamma or X-Ray Energy (keV)	Dose Rate (mR/hr/nCi ^{238}Pu)
17	3.8×10^{-8}
44	1.6×10^{-11}
99	4.3×10^{-12}
150	7.8×10^{-13}
760	4.7×10^{-15}
875	2.3×10^{-13}

deposits in vital organs where the short ranged energetic alpha radiation can irradiate vital cells and may cause harm.

The major entry mechanisms for internal uptake of plutonium in man are:

- Ingestion of plutonium in food, water, or other materials swallowed
- Absorption of plutonium through the skin or wounds
- Inhalation of plutonium from the air.

Therefore, to be taken internally, the plutonium must transmigrate from its present location to materials which might be ingested; onto the skin or in wounds where it might be absorbed; or suspended in the air where it might be inhaled. The path that the plutonium follows to finally be taken internally by man can be described as the "pathway to man." The potential pathways to man for the plutonium under consideration will be the subject of detailed discussion later in this report.

Two groups of scientific experts:

- National Council for Radiation Protection (NCRP)
- International Commission on Radiological Protection (ICRP)

have reviewed the large body of biomedical data which has been collected by experiments on animals as well as from the medical histories of occupational workers who have been accidentally exposed. Based on these data, they have established safe occupational plutonium guidelines or standards (19-21) which are listed in Table 15. The most critical points of reference are bones and lungs where the permissible body burden is established as 40 nCi and 15 nCi, respectively.

TABLE 15. Permissible Total Body and Lung Burdens for ^{238}Pu in Man (22,23)

Critical Reference Organ	Permissible Total Body or Lung Burden: Occupational Workers (nCi)	Permissible Total Body or Lung Burden: Individual in General Population (nCi)
Total Body	300	30
Bone	40	4
Liver	200	20
Kidney	300	30
Lung	15	1.5

Although the occupational standards include safety factors, these standards are reduced by an order of magnitude before they are applied to individuals in the general population.

From these plutonium standards some important RCGs have been derived for plutonium in water and air as are listed in Table 16. If an individual is continuously exposed, during his lifetime, to water or air which has plutonium concentrations at the RCG, he will not exceed a permissible body or lung burden of plutonium.

TABLE 16. Radioactivity Concentration Guides for ^{238}Pu in Uncontrolled Areas(22)

Reference Material	^{238}Pu Radioactivity Concentration Guide (RCG) Soluble Forms	Insoluble Forms
Air	7×10^{-14} μCi/cm^3	1×10^{-12} μCi/cm^3
Water	5×10^{-6} μCi/cm^3	--------(a)
Soil	None	None
Sediment	None	None

(a) Depends on solubility.

To date there is no officially accepted RCG for plutonium concentrations in soil or sediment. The derivation of safe and reasonable RCG values for plutonium in soil and sediment is more difficult than for water and air. Water and air have nearly a constant composition, behavior and properties everywhere, while soil/sediment composition, behavior, and properties vary greatly from place to place.

In addition, because soil and sediment are not normally considered to be in the direct pathway to man, many other factors must be considered to evaluate man's future potential plutonium uptake from this source. These considerations will be discussed in more detail later in this report.

HEALTH AND SAFETY EVALUATION UNDER THE PREVAILING CONDITIONS

From the time of discovery until the full extent of the contamination was known, a continuous health and safety analysis was performed and re-evaluated as the data became available. This analysis was based on actual concentrations of plutonium in the air or of other materials which were similar to those that might be ingested. The final results of this analysis are summarized in Table 17.

TABLE 17. Evaluation of Health and Safety Under Present Conditions

Material Analyzed	RCG	Maximal ^{238}Pu Concentration Found	% RCG	Permissible(a) Ingestion Amount (lb/yr)
Sediment	None	4.56 nCi/g	-	0.9
Water	5×10^{-6} μCi/ml	1×10^{-8} μCi/ml	0.3	-
Air(b) (permanent station continuous)	1×10^{-12} μCi/cm^3	7×10^{-17} μCi/cm^3	0.007	-
Air(c) (worst-case grab samples)	1×10^{-12} μCi/cm^3	3×10^{-15} μCi/cm^3	0.3	-
Vegetation (grass)	None	3×10^{-3} nCi/g	-	1400
Vegetation (algae)	None	1×10^{-1} nCi/g	-	42
Fish (edible portion)	None	5×10^{-6} nCi/g	-	>800,000

(a) Ingestion of this amount could potentially result in an uptake of 0.057 nCi/yr (1/70 of a permissible body burden)
(b) Permanent continuous air sampling station between North and South ponds
(c) Air samples taken one foot above ground at ditch/canal confluence and east of ponds (average value)

Air Concentration

Since inhalation of plutonium is believed to be an important pathway to man for plutonium, measured air concentration was used as one of the major indicators of potential hazards. As a part of the routine environmental survey program, Mound Laboratory has maintained five permanent air sampling stations onsite since 1972. The three sampling stations along the western edge of the site are only a few hundred yards east of the North and South Canals. Prior to 1971, portable air samplers were used to periodically sample the air especially along the boundaries of the Laboratory site and at selected offsite areas. In 1972, additional permanent air samplers were installed at the City sewage plant near the overflow creek, across the river from the Laboratory and in Miamisburg (north) as well as many other locations offsite in other directions and at distances up to 28 miles.

A total of 27 such permanent stations are maintained by the laboratory's environmental staff. From this air sampling data, which are routinely published,(24) it is confirmed that plutonium air concentrations have been and are substantially below the RCG for plutonium in air.

In order to obtain more localized air concentration values, portable air samplers were used to collect samples immediately east (downwind) of the canal and ponds. These samples were taken with higher velocity air flow and much closer (1 ft) to the ground, than the permanent station (3-5 ft) to obtain a worst-case air concentration value. As expected, these localized samples indicated higher plutonium concentrations than the permanent station, but they were still substantially below RCG values. A permanent continuous air sampling station installed in 1975 between the North and South ponds is indicating much lower (by a factor of approximately 40) air concentrations than were found with the portable samplers.

From periodic physical inspections of the contaminated waterways, the contaminated sediment is essentially underwater, moist, or covered with vegetation. These conditions tend to severely limit the potential for suspension of the contaminated sediments in the air. Because the plutonium is strongly sorbed and fixed to the sediment, plutonium airborne suspension behavior is that of the sediment itself. Very little, if any, plutonium is present in PuO_2 particulate form which might separate itself from the sediment and be suspended independently in air.

Based on these considerations:

- The air concentrations of ^{238}Pu are presently substantially below the RCG standards,
- The physical form of the plutonium in the sediment is known, and
- The sediment is underwater, moist, or covered with vegetation;

it is very unlikely that plutonium concentrations in air will approach the RCG standard under prevailing conditions.

Water Concentration

Water samples have been routinely and periodically collected in the canal for years. These samples have consistently indicated concentrations less than the RCG for plutonium in water.(24) Water samples collected in the waterways during this study also confirmed that the water samples are much less than RCG (for water) even when in contact with sediment that may have much higher concentrations. Many samples of contaminated sediment from the various water ways were maintained in contact with the natural water for more than a month to reach "equilibrium." The "equilibrium" distribution ratio (concentration of plutonium in natural water/concentration of plutonium in the sediment) was found to be 10^{-5}. Because of this very low solubility, the plutonium concentration is not expected to approach RCG concentration of plutonium in water.

Concentration in "Ingestible Materials"

As far as can be determined, there is very little vegetation in the immediate area of the waterways which can be described as edible by man. The highest land vegetation ^{238}Pu concentrations were found in the grass contaminated externally by sediment in localized flooding areas along the banks of the waterways. Even if this worst-case land vegetation concentration value is taken as indicative of edible plants and none is removed during preparation, then one would have to consume as much as 1400 lb of this vegetation per year to absorb 0.057 nCi/yr of plutonium (1/70 of body burden dose standard) through the gastrointestinal tract.

Again, there is no known aquatic plant life in these waterways which is normally consumed by man. The highest concentrations found in aquatic plant life were in the green algae. One would be required to eat 42 lb/yr of green algae to make up 0.057 nCi/yr of plutonium.

The waterways do contain some edible fish, mainly bluegills and carp. People in the Miamisburg area occasionally fish in the canals, river and ponds, and consume the few fish they catch. Based on the concentration of plutonium in the edible portions of these fish, they would be required to eat over 800,000 lb/yr of fish to approach the 0.057 nCi/yr uptake value.

As an absolute worst case, one would have to eat almost a pound of the highest concentration sediment found in the waterways per year to get 0.057 nCi/yr of plutonium uptake.

While it might not be impossible for these materials to be consumed in the amounts indicated, it seems extremely improbable. Therefore, it has been concluded that the plutonium deposited in these waterways does not and will not present a credible hazard to the public under the prevailing conditions.

DERIVATION OF ^{238}Pu SEDIMENT CONCENTRATION DECISION GUIDES

Pathway Analysis of Plutonium in the Environment

While it is clear that the ^{238}Pu in the offsite areas near Mound Laboratory does not present a hazard to the public under prevailing conditions, these conditions may be subject to change in the future. To make a definitive determination of these potential future hazards, a rather comprehensive pathway analysis has been performed.

Pathway analysis is an analytical technique for calculating the amount and the concentration of plutonium transmigration from its present state and location, into the materials which might be ingested, absorbed and taken into the body or suspended into the air where it might be inhaled by man and taken into the lungs.

A schematic diagram of the plutonium pathway analyses is presented in Figure 49. In order to perform these analyses, it is necessary to: 1) determine the present state/behavior and location of the reservoir of plutonium; 2) determine a credible worst-case set of future conditions and circumstances which could affect the transmigration of the plutonium along the pathway to man; and 3) experimentally determine or obtain from scientific literature, translocation transfer factors or coefficients which will adequately describe the magnitude of the transmigration of plutonium along the pathway to man.

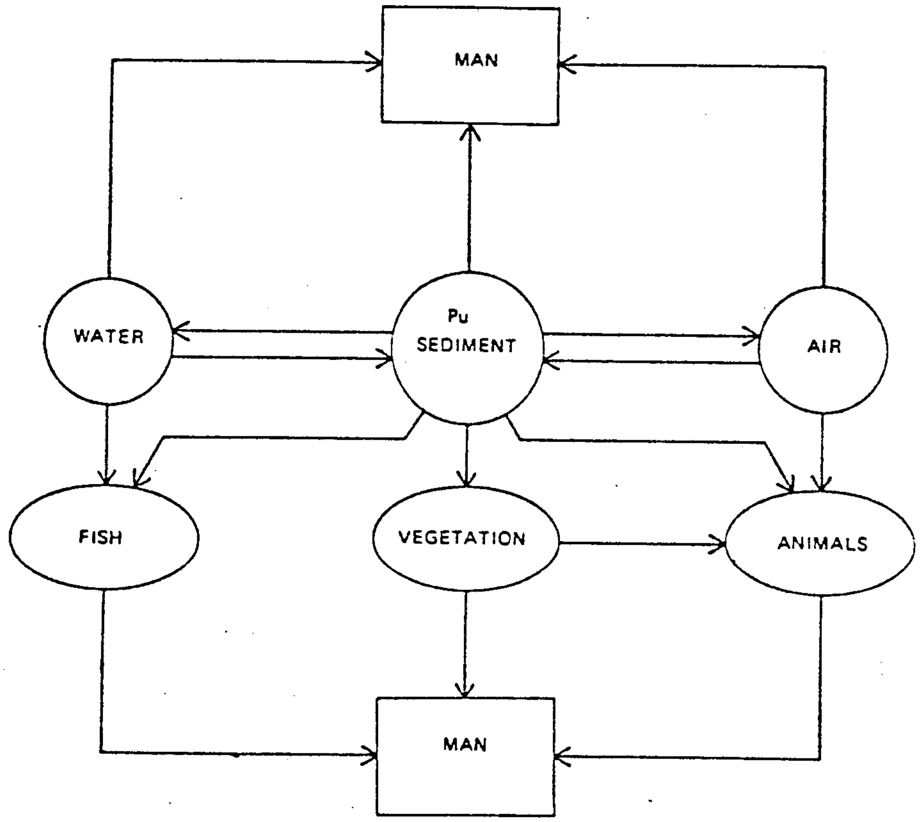


FIGURE 49. Pathways to Man

In early 1974, J. W. Healy(25) of Los Alamos approached a similar problem in order to determine a general interim soil concentration guide from the available scientific information. The soil concentration guideline he proposed (0.225 nCi/g) is less than some of the concentrations found in the sediment of the waterways near Mound Laboratory. It must be remembered, however, that the soil concentration guide he proposed was for general application to widespread contamination in a densely populated area, under all conditions and circumstances, at any location, for an indefinite period. By making his soil concentration guide "for general application," a large number of parameters which are known to vary widely with location, conditions, and circumstances had to be assumed. Among these parameters are:

- The chemical and physical properties of the plutonium
- The chemical and physical properties of the in situ soil
- The interaction and reactions between the plutonium and the soil
- The area and distribution of the contamination
- The present and future land use

- The climatic conditions
- The degree of vegetation and ground cover
- The geography of the contaminated area
- The geology of the area
- The present and future demography of the area.

Because his soil concentration guideline, if adopted, would be applied regardless of these conditions, Healy was more or less obligated under this constraint to assume "worst-case" conditions and parameters in order to avoid underestimating the potential hazard in rather extreme cases.

Healy recognized this difficulty and recommended that specific information regarding a particular situation or event be used in pathway analyses. "Such investigations aimed at a particular situation will always provide better answers than a general standard of this nature and such an approach to individual problems is entirely appropriate."(25)

Taking Healy's suggestion, his general approach to pathway analysis has been expanded and adopted, but information and assumptions specific to this particular situation and location were factored in.

Examination of the major conditions and circumstances in the contaminated area near Mound Laboratory reveals that there are (and will be in the future) substantial differences from the case Healy assumed. The consideration of these differences is critical to a reasonable evaluation of the hazards in this case.

Specific Local Information Available

The major differences between Healy's assumption and conditions near Mound Laboratory are summarized in Table 18.

TABLE 18. Comparison of the Conditions Used By Healy and By Mound Laboratory

Considerations	Conditions Assumed by Healy	Conditions at Mound Laboratory
Extent of Contamination	Wide Spread ~ 39 mi^2	Very small ~ 0.01 mi^2
Physical Nature of Contamination	PuO_2 Fallout (Not fixed)	Pu Sorbed on Sediment (Fixed to Sediment)
Nature of Climate and Soil	Arid Western Soil	Moist Fertile Ohio Soil Large Clay Fraction
Nature of the Area	Wide Open Level Plain	Recessed Canal in River Valley - Lined with Trees
Solubility of Pu	Considered Soluble or Nearly Soluble	Solubility Very Low $\frac{\text{Pu Concentration in Water}}{\text{Pu Concentration in Sediment}} = \frac{1}{100{,}000}$

Nature of the area and degree of ground cover. In Healy's model,(25) he assumes the contaminated area is an open, level, desert plain with little or no vegetation. One can envision this area being raked with high winds to stir up a huge dust cloud from the uncovered, unconsolidated, desert soil.

The waterways near Mound Laboratory, on the other hand, are located in a fertile river valley in Ohio where vegetation is lush and plentiful. The canal and other waterways are recessed into the ground and are generally lined with trees, grass and other vegetation. A large amount of the bed in the South Canal, which is under water only during rainfalls, has been overgrown with vegetation. There is every reason to believe that if the entire waterway system were to dry up, vegetation would soon cover the entire area.

This heavy ground cover of thick root mats would almost certainly reduce the airborne suspension characteristics of the sediment even in high winds. The trees and shielding effect of the recessed nature of the waterways also tend to act as windbreaks which would also moderate the effect of high winds.

The low-form vegetation cover also tends to greatly reduce further water erosion of the contaminated sediment, thus reducing the potential for more widespread redistribution of the contamination.

Climate. Healy assumes(25) a climate typical of the southwestern United States. The rainfall is very sparse in this arid or semiarid desert location and annual average windspeed was assumed to be about 11 mph.

The climate near Mound Laboratory(4) is typical of the central midwest. Summers are rather warm and humid, but temperatures rarely exceed 100°F. Winters are moderately cold with an average of about 2 days of subzero weather. The monthly average temperature and relative humidity are listed in Tables 19 and 20, respectively.

TABLE 19. Temperatures in the Mound Laboratory Area

Month	Average Daily Maximum (°F)	Extreme Maximum (°F)	Average Daily Minimum (°F)	Extreme Minimum (°F)
Jan	39.4	74	23.1	-14
Feb	41.8	73	24.0	-13
Mar	50.5	82	30.7	- 3
Apr	63.7	89	41.1	19
May	73.9	95	51.2	27
Jun	83.2	103	60.9	40
Jul	86.9	107	64.2	48
Aug	85.5	104	62.6	42
Sep	79.1	102	55.1	29
Oct	67.8	91	44.4	19
Nov	52.0	81	33.2	- 1
Dec	40.9	71	24.6	-13
Annual	63.7	107	42.9	-14

TABLE 20. Relative Humidity in the Mound Laboratory Area

Month	Relative Humidity at Four Times Per Day, Hour (EST)			
	01	07	13	19
Jan	80	81	71	75
Feb	79	80	67	71
Mar	76	79	58	64
Apr	75	77	55	60
May	79	78	54	61
Jun	82	80	55	61
Jul	81	81	52	58
Aug	81	84	52	61
Sep	80	85	50	62
Oct	78	84	52	65
Nov	77	81	61	68
Dec	80	82	69	74
Annual	79	81	58	66

The annual average precipitation is about 40 in./yr and is rather evenly distributed throughout the year as shown in Table 21. Snowfall averages about 27 in./yr.

TABLE 21. Precipitation in the Mound Laboratory Area

Month	Precipitation Normal (in.)[a]	Precipitation No. of Days >0.5 in.[b]
Jan	3.66	2
Feb	2.62	2
Mar	3.61	2
Apr	3.74	2
May	4.14	3
Jun	4.71	4
Jul	3.40	2
Aug	3.03	1
Sep	3.28	2
Oct	2.53	1
Nov	3.12	2
Dec	2.75	2
Annual	40.59	25

(a) Based on 30 years of record
(b) Based on 10 years of record

The median annual wind velocity is about 8.5 mph predominantly from the south and west. The seasonally median wind velocity is listed in Table 22.

TABLE 22. Wind Velocity in the Mound Laboratory Area

	Median Wind Velocity (mph)	Frequency of Wind in Excess of 24.2 mph (%)
Winter	9.9	0.8
Spring	9.5	0.6
Summer	6.9	0.2
Autumn	7.5	0.3
Annual	8.5	0.4

The climate at Mound Laboratory, therefore, results in higher average soil moisture and less wind erosion than might be expected in the arid setting Healy(25) describes. Most extreme winds observed in the Mound Laboratory area are associated with storms which deliver heavy rainfall. Therefore, under these conditions, the airborne concentration of suspended soil might be expected to decrease rather than increase.

Properties of the sediment. The physical and chemical properties of the soil or sediment are quite important since the transmigration of the plutonium along the pathway to man and behavior in the environment is largely controlled by these properties as has been discussed previously. The sandy desert soil assumed by Healy would be expected to behave entirely differently from the sediment found in the waterways in Ohio.

The sediment properties expected to affect the behavior of the plutonium in the environment are:

- Large clay/silt fraction
- Low water permeability
- Dries to very hard, difficult to grind material
- Large ion exchange capacity
- Calcareous ($CaCO_3$)
- High acid neutralization capacity
- Agglomerates in natural water
- Remains agglomerated in dry state.

The sediment in the waterways results from the water erosion of the glacial till and natural sedimentation processes. One of the most important features of the sediment is the very large clay and silt fraction which varies from 49 to 92% of the sediment as shown in Table 23. As a result, the sediment exhibits low water vertical permeability (0.1 to 1.0 m/yr)(4) and dries to a very hard mass similar to pottery clay. When this drying occurs, the surface cracks from shrinkage; however, very few fines are formed unless the mass is mechanically broken up. This very hard dry mass is very difficult to grind into small particles. A sample was air dried, broken, and ground in a mortar and pestle until it would pass through a 50 µm screen. The particle size distribution of this powder is shown in Figure 50. It should be noted that only about 2 to 3% of the powder is less than 5 or 6 µm (aerodynamic diameter = 10) which is considered respirable.

TABLE 23. Physical Composition of Sediment

Components	Composition (%) A	Composition (%) B
Clay and Silt	92	49
Fine sand	8	28
Medium sand	-	10
Coarse sand	-	5
Fine gravel	-	6
Coarse gravel	-	2

The major chemical constituents are clay (mostly hydromicas), $CaCO_3$ (calcite), $CaMg(CO_3)_2$ (dolomite), Fe_3O_4 (magnetite), SiO_2 (sand), organic materials, and water.

The large clay fraction is composed of mostly hydromicas with some kaolinite and montmorillonite.

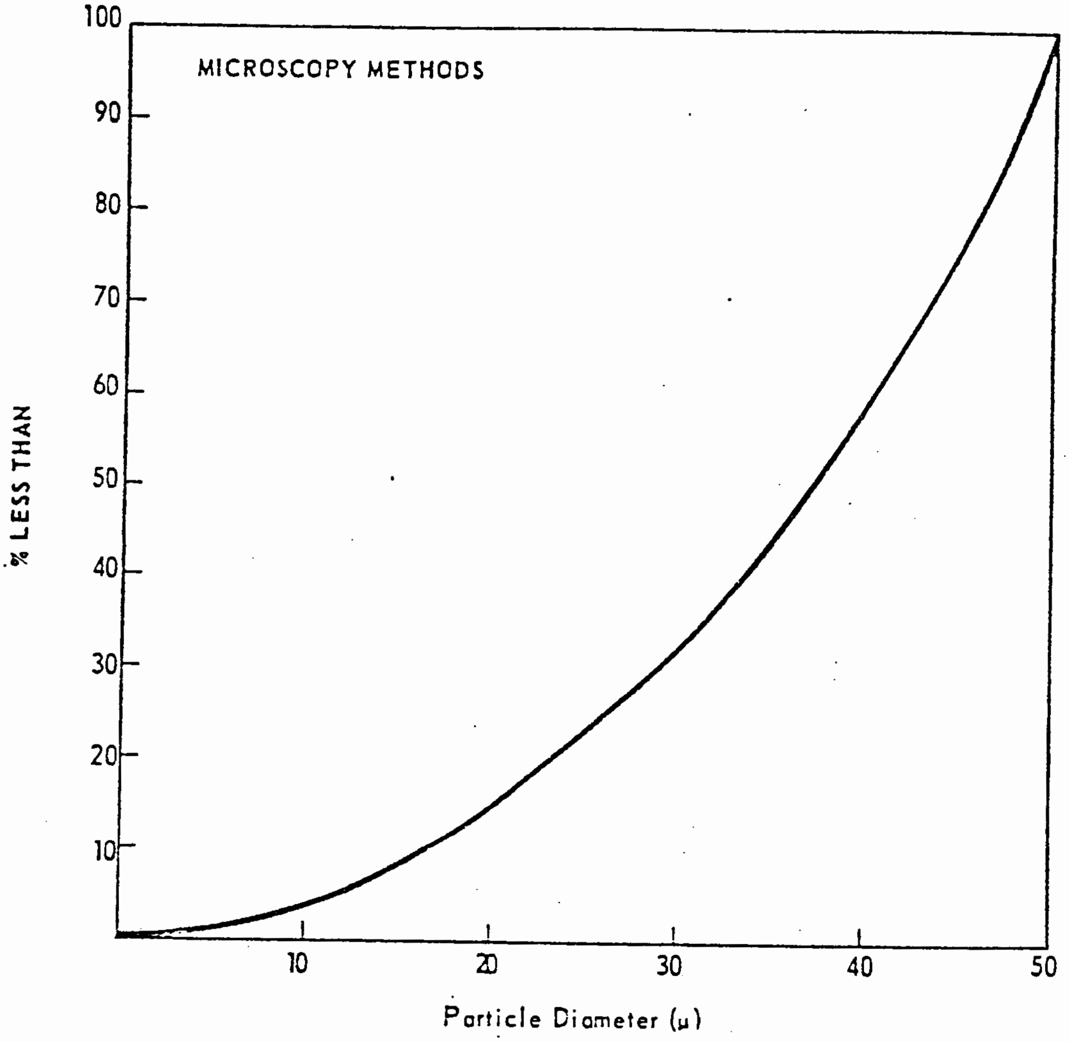


FIGURE 50. Agglomerated Particle Size Distribution of Soil which was Dried and Ground to Less than 50 μm

The sediment is very calcareous containing a large amount of calcite ($CaCO_3$) and dolomite ($CaMg[CO_3]_2$).

The clays account for most of the ion exchange capacity and surface area while the calcareous constituents account for the buffer capacity (acid neutralization) and the pH of the natural surface water. These soil properties and their values are listed in Table 24.

TABLE 24. Chemical Properties of Sediment

Property	Value
pH of water in equilibrium with sediment	7.5 - 8.3
Acid neutralization capacity	4 meq/g
Ion exchange capacity	20 meq/100 g

From the time of the release of the plutonium solution to the onsite soil, the properties of the soil and erosion products controlled the behavior of the plutonium. It is expected that the properties of the contaminated sediment will continue to be one of the major controlling factors in the transmigration of the plutonium along the pathway to man.

Physical nature and characteristics of the contamination. The physical form of the contamination in Healy's analysis(25) is assumed to be fine PuO_2

particulate material such as would be present in nuclear fallout or from the release of fine PuO_2 powder. When such fine particulate PuO_2 powder is freshly deposited on soil, it tends to exhibit behavior independent of the soil properties. With time, however, these tiny PuO_2 particles become mixed with the soil and/or fixed onto soil particles and the airborne resuspension properties of the PuO_2 decreases.(26-29)

This process proceeds (depending on the nature of the soil and the climate) quite rapidly at first exhibiting half times of 35 to 70 days(26-27) over the first 6 to 8 months.

This reduction in resuspension behavior apparently approaches a lower limit in a few years since 20-year deposits have been reduced by only a factor of 1000.(30) It seems reasonable that a lower limit might represent the resuspension characteristics of the soil itself.

Samples of sediment in the waterways at Mound Laboratory have been examined by an independent testing laboratory, LFE,(5) using autoradiographic techniques to detect particulate PuO_2 content, by examination of the alpha tracks. Very few observable PuO_2 particles were detected in these samples. The radioactivity was generally quite diffuse throughout the sample. This observation is consistent with the information presented in the cause analyses regarding the nature of the release. An acidic plutonium solution was released to onsite soil. The acidity was neutralized by the calcareous soil and the plutonium was strongly sorbed to the silt and clay fractions of the soil.

Since the plutonium is chemically sorbed onto the soil, it can be considered fixed in that the plutonium is not free to act physically independent of the soil. Under these conditions, one would expect the resuspension properties of contaminated sediment (from the beginning) to be similar to the behavior of well-aged fallout deposits.

Suspension characteristics of contaminated soil at Mound Laboratory were estimated by measuring the air concentration 2 ft above the ground under prevailing conditions. The ground contamination levels were measured by surface FIDLER Survey using the 17 keV x-rays emitted as a result of ^{238}Pu decay. This technique is responsive predominantly to soil ^{238}Pu concentration in about the top 0.1 cm of soil(31) ("very surface" of the soil). The measured suspension factors, K m^{-1} (defined as the air concentration in $\mu Ci/m^3$/surface contamination ($\mu Ci/m^2$), are listed in Table 25.

TABLE 25. Resuspension Factors Estimated on Mound Laboratory Soil

Geometric median of maximum values	3×10^{-9} m^{-1}
Geometric median of minimum values	5×10^{-10} m^{-1}
Geometric median value	1×10^{-9} m^{-1}
Maximum value on downwind edge	1.6×10^{-8} m^{-1}
Minimum value on downwind edge	9.0×10^{-10} m^{-1}
Maximum value on upwind edge	1.8×10^{-9} m^{-1}
Minimum value on upwind edge	3.2×10^{-10} m^{-1}

These resuspension factors are comparable (perhaps lower) to those measured on the 20-year-old contamination in the GMX area at NTS which are in the 10^{-8} to 10^{-9} m^{-1} range.(30) These values indicate that the sediment even if allowed to dry would exhibit a factor of about 1000-fold less contaminated airborne suspension than was assumed by Healy.(25)

Chemical behavior of the contamination. Although Healy(25) assumes the contamination is in the form of PuO_2 particles which are generally sparingly souble, he considers the contamination soluble or partially soluble in most cases. For example, he assumes complete solubility in the ingestion and absorption intake mechanisms and partial solubility for inhalation. He makes these assumptions because the chemical behavior of the contamination in his case is truly unknown. The solubility of the plutonium in the contaminated sediment under the action of various reagents has been measured and these values are listed in Table 26.

TABLE 26. Distribution Ratios (Water/Sediment) and Solubility of Plutonium from Sediment

Solution	Distribution Ratio Water/Sediment $D_{w/s}$	Solubility (%) (20 ml Solution/1 g Sediment) S
Canal Water	1×10^{-5}	2×10^{-2}
Dilute Acid Initial pH = 1 Final pH = 5.5	1×10^{-5}	2×10^{-2}
Moderate Acid Final pH = 1	1.6×10^{-3}	3.1
High Acid (8M HNO_3)(a)	2.5×10^{-1}	83
Moderate Base pH = 10	Clay disperses	(61)(b)
Complexing Agent (0.1 M citrate)(a)	4.2×10^{-2}	46

(a) Tamura (ORNL)
(b) Pu believed to be sorbed to colloidal clay suspension

When the sediment is placed in the natural water and permitted to reach equilibrium, the plutonium distribution ratio between the water and sediment was found to be 10^{-5} which demonstrates the extent of the sorption reaction. When placed in mild acid solutions (pH 1), the calcareous soil neutralizes the acid and the distribution ratio remains unchanged. When sufficient acid is introduced to adjust the solution to a final pH of 1, then the distribution ratio is slightly increased (more in solution) to 1.6×10^{-3}. Even when placed in strong acid (8 $\underline{M}$ HNO_3), the plutonium is not completely removed from the sediment. The 8 $\underline{M}$ HNO_3 is also a complexing agent for plutonium, in that the high nitrate ion concentration would tend to assist the plutonium into solution forming $Pu(NO_3)_6^{2-}$.

The distribution ratio of plutonium between 0.1 $\underline{M}$ citric acid is 4.2×10^{-2}, indicating again that moderately strong complexing agents in reasonably high concentrations do not completely remove the plutonium from the sediment.

The behavior of the sediment in strong alkaline solutions is probably partially related to a physical reaction rather than being completely due to chemical formation of plutonium hydrolytic species and desorption of the plutonium. In strong bases, the clay fraction tends to become dispersed in the solution and is difficult to remove from solution. The apparent increase in solubility may be due, in part, to plutonium sorbed onto colloidal clay suspended in the solution.

The exact nature of the sorption reaction and the plutonium species sorbed on the soil is not unambiguously known at this time; however, from the solubility data, the bonding is quite strong and silicate bonding is believed most likely as discussed previously.

The plutonium is sorbed mostly on the clay and silt fraction of the sediment which has a very high ion exchange capacity and specific surface area. It has been demonstrated that the extent of sorption increases with decreasing surface median particle size indicating a surface area or ion exchange capacity dependence as shown in Figure 51. The smallest fully dispersed size fraction, however, exhibits no more than four to eight times the plutonium concentration measured on the full range of particle sizes in the sediment. Under normal circumstances,

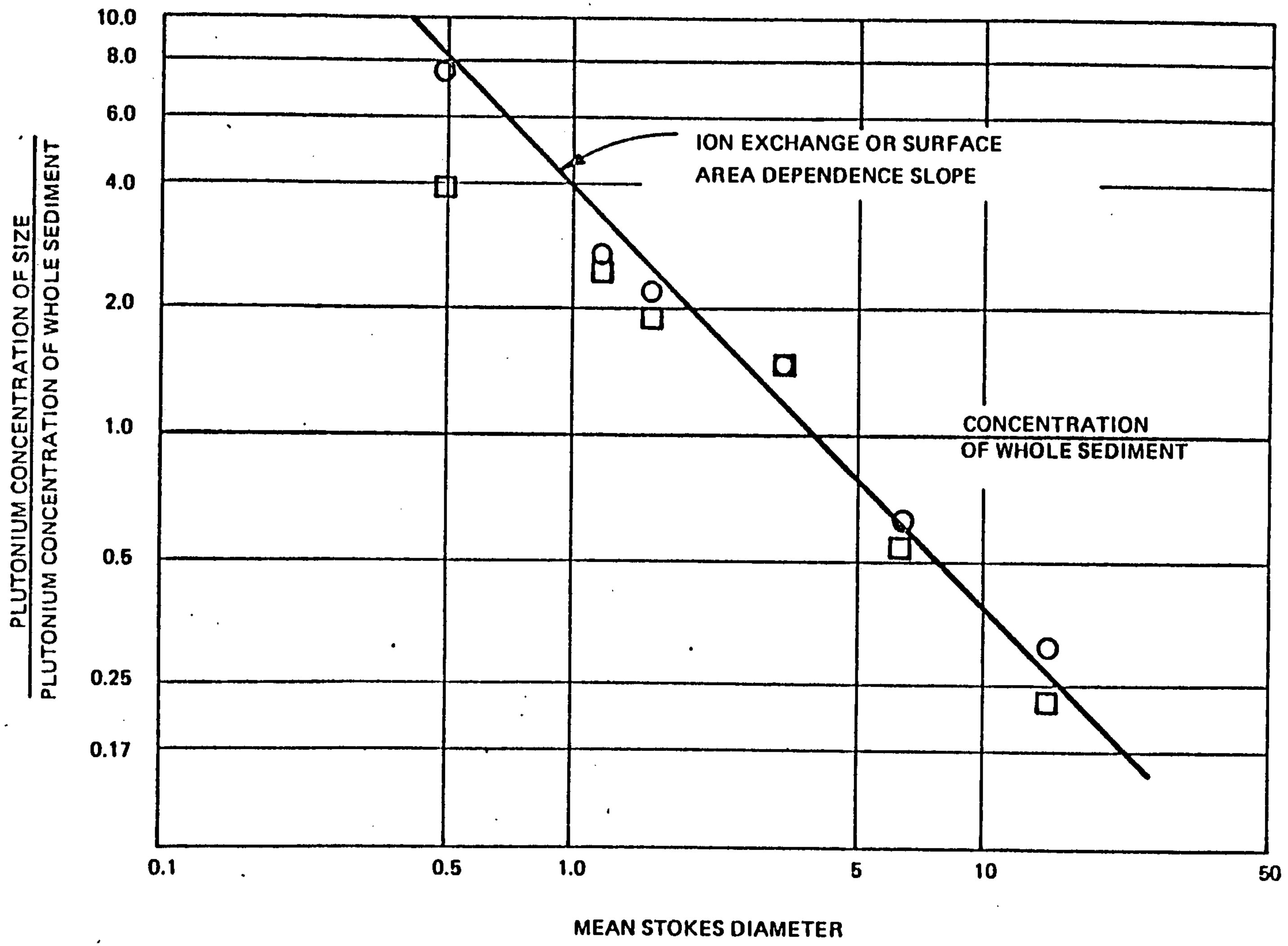


FIGURE 51. Variation of ^{238}Pu Concentration in Sediment as a Function of Fully Dispersed Particle Size

however, the sediment remains highly agglomerated and the particle size dependence of the plutonium concentration should be much less dramatic. These large agglomerated particles exhibit the surface area and ion exchange capacity and, therefore, plutonium concentration of the smaller particles from which they are constituted.

Distribution of the contamination. The distribution of the contamination assumed by Healy is quite different than is observed in this case. The contamination he assumes is idealized to be on the "very surface" of the desert soil and evenly distributed throughout the area.

In this case, the contaminated sediment is very unevenly distributed with regard to both area and depth profile as has been described previously. The deposition of the sediment was controlled by sedimentation conditions which vary greatly within the waterways. No attempt will be made to use an area-wide average concentration value for the 0.01 mi^2 area even though the concentration varies over greater than four orders of magnitude. Instead the maximum values will be used in all cases as though it were evenly distributed throughout the 0.01 mi^2 area. The localized nature of these maximum values, however, is clearly less hazardous than the case Healy describes.

Because events which resulted in these contaminated sediment deposits occurred in 1969, the major part of this contamination has been buried beneath the surface by continued sedimentation of uncontaminated sediment. This buried plutonium presents a less hazardous condition than the surface deposited contamination assumed by Healy because the plutonium under the surface is not available to man. In the future, some of the more concentrated buried plutonium contaminated sediment could potentially be brought to the surface and, therefore, will be considered. However, it is expected that such occurrences would be localized and that dilution with less contaminated sediment would occur.

<u>Extent of the contamination</u>. Healy assumes a very widespread contaminated area in his pathway analysis. Although he does not state the exact size, it has been estimated from his wind resuspension model that the area might be as large as 39 mi^2. He generally assumes the uniform surface contamination to be omnipresent in a densely populated area, even to the very doors of the homes and businesses.

At Mound Laboratory, the significant contamination is confined to the sediment in the beds of the waterways or to very localized areas along the immediate banks where minor but frequent flooding and sediment deposition has occurred. The total area (even the area under water) with contamination levels greater than 0.001 nCi/g including the runoff hollow, ditch, North Canal, two ponds, South Canal, and overflow creek is about 277,000 ft^2 or 0.01 mi^2.

This 0.01 mi^2 area will most certainly present a lesser hazard than the widespread contamination area Healy assumes.

This area is not expected to expand significantly in the future. The overwhelming source of water to these waterways is the Mound Laboratory site drainfield. This water must pass through the culverts under the railroad before reaching the canal waterway system. These culverts tend to set a maximum waterflow rate to those contaminated waterways. In June 1974, the area observed a very intense 6-inch rainfall in 24 hours. During this storm (which has about a 100-year return frequency), the Mound Laboratory side of the culvert was completely submerged and the culvert system was transmitting the water at about the maximum rate. The system did not flood beyond the localized areas described as flooding areas.

Major Assumptions Regarding Future Conditions

The major assumptions about future conditions are guided by the philosophy of selecting most credible worst-case conditions with regard to health and safety for each pathway considered. This philosophy was applied in order to avoid underestimating the potential hazard to the public. It is believed that these assumptions are truly worst case and add substantial safety to the analyses.

- It is assumed that the plutonium contaminated sediment will remain in the waterways for at least 70 years.

- The maximum values of the ^{238}Pu concentration at the "very surface," "first foot," and "any depth" have been assumed to be evenly distributed over the entire 0.01 mi^2 area of the waterways.

- The public is assumed to consume 10% of their intake of sediment, food, and water from the contaminated area.

- As much as 10% of the mud or dust which the public normally has on their skin, in wounds, on their clothing, and in their homes continuously is assumed to come from the contaminated waterways.
- The entire waterway system is assumed to be permanently dry.
- The public will visit the contaminated area daily (8 to 24 hours) for the entire 70 years of life.

Sediment Concentration Decision Guides Estimated by Pathway Analyses

Using the information specific to this situation, the assumption regarding credible worst-case future conditions and "best value" pathway parameters from the scientific literature, plutonium concentration decision guides for the sediment were calculated using pathway analytical techniques.

These decision guides are defined as the critical plutonium concentration in the sediment of the waterways which could, under credible worst-case conditions, result in a plutonium uptake in man approaching maximum permissible dose levels with a continuous lifetime exposure of 70 years.

The decision guides include an additional safety factor of 10 which was applied to account for uncertainties in the pathway parameters and changes that are anticipated in the plutonium dose standards. The decision guides were then compared to the plutonium concentration found in the sediment of the waterways in order to determine if a significant hazard will exist even under these maximum credible worst-case conditions.

Ingestion pathways. Materials ingested or swallowed by man pass through the gastrointestinal tract (GIT) in about 24 hours. The GIT has been found to absorb only a small fraction of soluble plutonium forms ingested. The ICRP reports(20,23) that only 3 x 10^{-3} % of the soluble plutonium passing through the GIT is absorbed by the body, the remainder passing in the stool, leaving no reservoir for future absorption. Tests have also shown that insoluble forms of plutonium are absorbed to even a lesser degree by the GIT.(32) The presence of complexing agents, such as citrate ions, have been shown to increase absorption probably by increasing the solubility of the plutonium in the GIT.(25)

Before plutonium can be absorbed into man, however, it must first transmigrate from the sediment deposits to the GIT. The pathways describing this transmigration considering soil or sediment directly, water, vegetables, meat from both wild and domestic animals and fish, are summarized in Figure 52.

1. Accidental or deliberate ingestion of sediment or soil: Sediment and soil are not normally a part of the human diet and usually are ingested only accidentally. The pathways considered for this accidental ingestion are shown in Figure 53. The sediment can be transferred to hands and then to the mouth.

Sediment can be transferred mostly by water action to the surface of food plants which are ingested. Part of the sediment which is suspended in air and taken into the respiratory system is transferred into the GIT.

The amount of soil or sediment that might be transferred from dirty hands into the mouth has not been experimentally determined and probably occurs only sporadically. A worst-case upper limit of this value might be developed by the

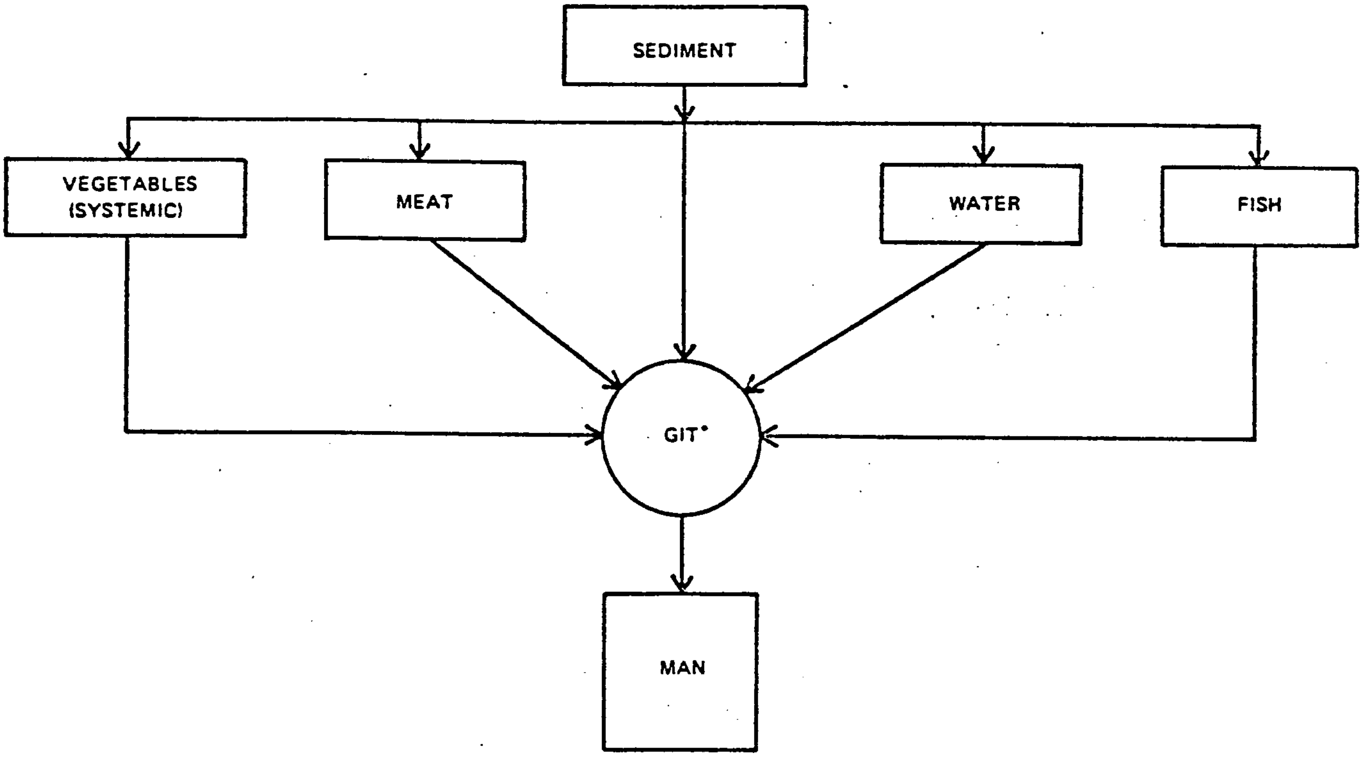


FIGURE 52. Ingestion Pathways

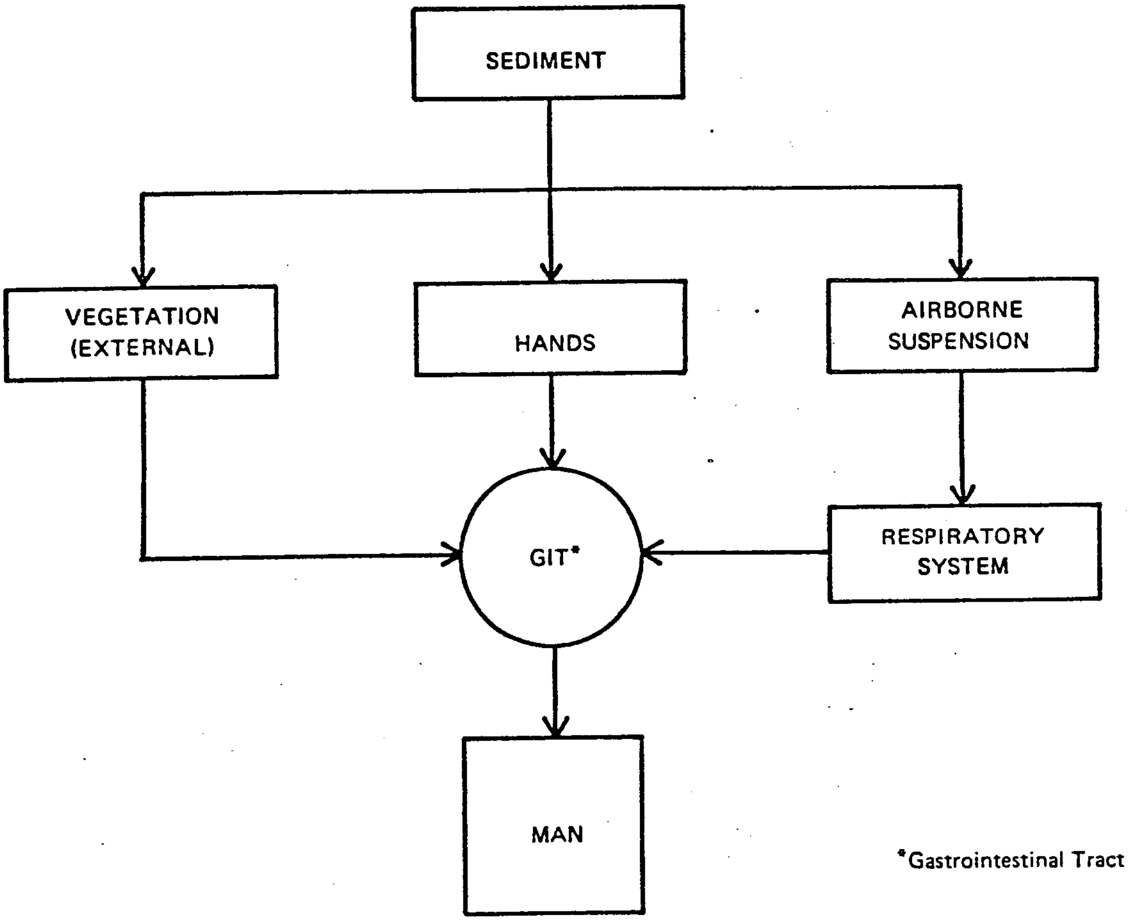


FIGURE 53. Pathways for Ingestion of Sediment

following logic. The surface area of the hands, fingers and about one-third of the forearm is assumed to be of the order of about 1000 cm^2. Healy(31) assumes that a person might have as much as 0.1 mg/cm^2 of dust on the skin constantly all his life. This would mean that an individual might have as much as 0.1 g on his hands. Assuming that this much dirt is constantly present and as a worst case, 10% of this dirt was transferred to the mouth and swallowed per day, up to 3 to 4 g of total dirt might be accidentally ingested per year. This value compares favorably with the 2 g/yr soil accidentally ingested by a person living continuously in a desert environment which was assumed by Martin.(33) Healy assumes as much as 36.5 g/yr for a desert environment which seems quite high. For accidental soil ingestion in the case under study here, in a nondesert environment 3 to 4 g of total soil intake per year seem quite adequate as a worst case. Additionally one need not assume that all the dirt deposited on the hands and arms would originate in the beds of the contaminated waterways. If 10% of all the dirt assumed to be on the hands comes from the waterway sediment, the contaminated sediment ingestion rate would be about 0.3 to 0.4 g/yr.

Healy estimates as an upper limit that young children might be subject to a higher uptake potential from this source because of their tendency to get dirtier, and to put their hands in their mouths. He believes the rate may be an order of magnitude higher at least for 1 year. Applying this safety factor of 10, it will be assumed that as a worst case, 3 to 4 g of sediment might be transferred to the mouth and ingested per year to account for more or less deliberate ingestion during 1 year of life.

The fraction of the sediment which is transferred from the respiratory system to the GIT is assumed by the ICRP(20,23) to be 0.625 of the total amount inhaled. The amount of dust in the air in this area ranges between 40 to 1000 $\mu g/m^3$ of air. It will be shown later that only about 1% of this dust can be assumed to come from the contaminated area.

A person breathes air at the rate of about 20 m^3/day and thus would inhale from 0.2 to 0.5 g of dust per year, but only 0.002 to 0.005 g would be from the contaminated area. This is insignificant relative to the transfer from hand to mouth.

The amount of sediment deposited on vegetation might be as much as 10 μg/cm^2. One would expect that these would be washed prior to ingestion and only 10% of this sediment would be actually ingested. It has been estimated the specific surface area of leafy food plants is 6.45 cm^2/g.(34) The average amount of vegetables consumed by people in North America is 73,000 g/yr,(34) and as before, one need only assume 10% (as an upper limit) or 7300 g would come from the contaminated area. Combining these values would result in the ingestion of about 0.05 g of sediment from this source which is well within the uncertainty of the amount transferred from hand to mouth.

The worst-case amount of soil ingested as a lifetime average is therefore assumed to be about 0.3 to 0.4 g. Children, during 1 year, might ingest as much as 3 or 4 g deliberately.

The "sediment concentration decision guide" was calculated for ingestion of sediment as shown in Table 27 and found to be about 52 nCi/g for deliberate ingestion for 1 year and 520 nCi/g for accidental ingestion.

TABLE 27. Sediment Concentration Decision Guide Based on Ingestion of Sediment/Soil

Decision Guide Equation for Ingestion of Sediment:

$$DG_{(sediment)} = \left(\frac{B/T_e}{G_s F_{m/gi}}\right)\left(\frac{1}{S}\right) = 52 \text{ nCi/g (deliberate/1 year)}$$

$$= 520 \text{ nCi/g (accidental)}$$

Pathway Parameters:

B	= permissible body burden	= 4 nCi
T_e	= years of exposure	= 70 years
G_s	= amount of sediment ingested	= 3 to 4 g/yr (deliberate) 0.3 to 0.4 g/yr (accidental)
$F_{m/gi}$	= fraction absorbed from GI tract	= 3×10^{-5} g/yr
S	= overall safety factor	10

2. Ingestion of natural water in equilibrium with sediment: It is not expected that anyone would deliberately consume water from this source since the water is quite dirty. However, a small amount might be swallowed if swimming is permitted or someone falls in the waterways. The pathway considered for ingestion of water is shown in Figure 54.

Previously, the distribution ratio ($D_{w/s}$) of plutonium between water and sediment has been discussed. The concentration of plutonium in water is only 10^{-5} fraction of the concentration in sediment under "equilibirum" conditions.

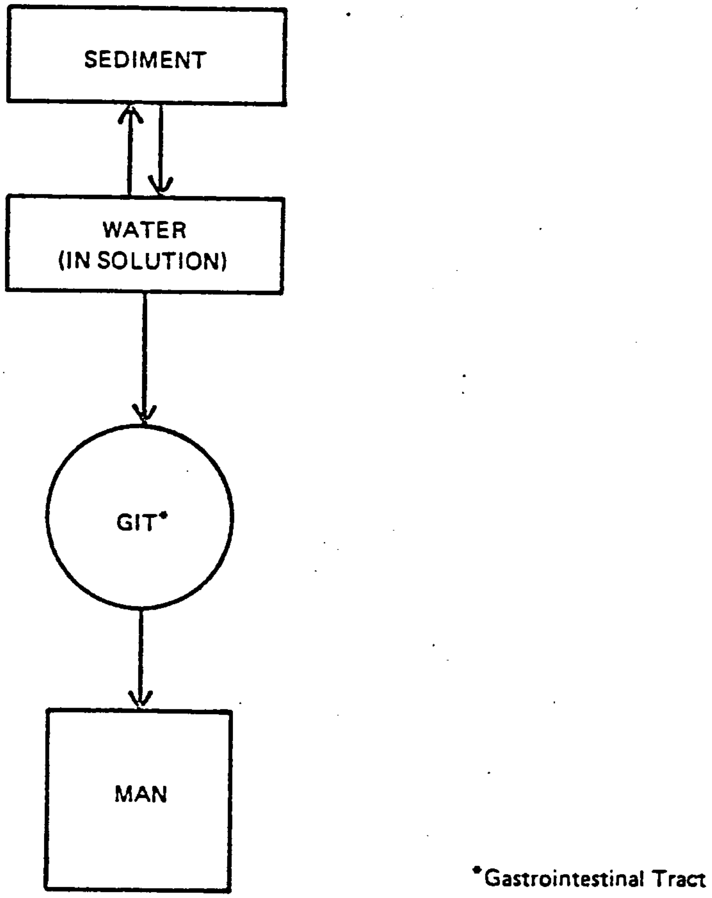


FIGURE 54. Pathway for Ingestion of Water

Since the consumption rate of water (as water) is about 1 liter/day or 365,000 g/yr, an uptake of 36,500 g/yr (10% of total intake) is assumed as a worst case upper limit. Safe water ingestion from this area might limit the sediment concentration to about 522 nCi/g as shown in Table 28.

TABLE 28. Sediment Concentration Decision Guide Based on Ingestion of Water

Decision Guide Equation for Ingestion of Water:

$$DG_{(\text{sediment})} = \left(\frac{B/T_e}{G_w D_{w/s} F_{m/gi}}\right)\left(\frac{1}{S}\right) = 522 \text{ nCi/g}$$

Pathway Parameters:

B	= Permissible body burden	= 4 nCi
T_e	= years of exposure	= 70 yr
G_w	= amount of water ingested	= 36,500 g/yr
$D_{w/s}$	= ratio water/sediment concentration	= 10^{-5}
$F_{m/gi}$	= fraction Pu absorbed by GI tract	= 3×10^{-5}
S	= Overall safety factor	= 10

Sediment, which might be swallowed with the small amount of water during swimming, can be assumed to be part of the sediment ingestion amount previously considered.

3. Ingestion of vegetables grown in sediment: At the present time there is little, if any, edible vegetation growing in or near the contaminated waterways. In this pathway, Figure 55, the plutonium in the sediment must first be taken up systemically into the plant and then consumed by man. Previously (sediment ingestion) the external deposit of sediment on the plant has been considered.

Plants show very little tendency to extract plutonium from soils. In 1970, Romney(35) grew clover in soils contaminated with plutonium solutions for several years. Each year he harvested the top parts of the clover and analyzed for plutonium. He found that the concentration in the clover tops tended to increase from year to year probably as the root structure developed and maintained more contact with the soil. The ratio ($F_{p/s}$) of plutonium concentration taken into the plant and the plutonium concentration in the soil seemed to follow the empirical equation:

$$F_{p/s} \simeq 1.91 \times 10^{-5} \exp [0.4971(5-1)].$$

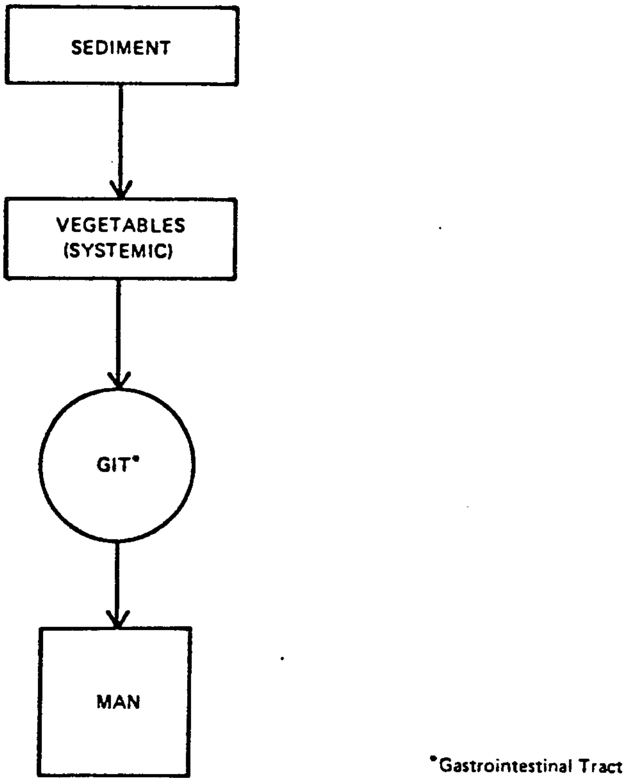


FIGURE 55. Pathway for Ingestion of Vegetables

After 1 year $F_{p/s}$ reached a value of about 2×10^{-5} and then after 5 years increased to 1.40×10^{-4}.

Because almost all vegetable crops consumed by man are annual plants, it seems safe enough to use Romney's first year uptake value ($\sim 2 \times 10^{-5}$).

Wildung and Garland(36) recently have suggested that the plutonium uptake in root crops may be substantially higher than in leafy vegetation. On the basis of tests they performed on barley plants, the root uptake was found to be up to eight times higher than for the barley shoots. It is somewhat understandable that the small feeder roots of barley might exhibit a large uptake; however, the cellular structure and function of the massive roots that are consumed by man might be expected to take up much less plutonium than the tiny barley roots.

The potential for a larger plutonium uptake in man from the root crop portion of the diet is believed to be adequately offset by the "worse case" assumptions regarding the dietary intake from this area.

Coleman(34) estimated the average vegetable consumption in North America to be 73,000 g/yr. Most vegetables consumed on a yearly basis are grown on commercial farms and purchased fresh or canned. Since the contamination is confined to the waterways and the immediate banks, the vegetation to be considered in this case must be grown in these confined areas.

As a worst case, it is assumed that no more than 10% of the total dietary vegetable intake would be grown in this contaminated sediment. The sediment concentration necessary to result in an uptake of 0.057 nCi/yr was estimated to be 1300 nCi/g as shown in Table 29.

TABLE 29. Sediment Concentration Decision Guide Based on Ingestion of Vegetables

Decision Guide Equation for Ingestion of Vegetables:

$$DG_{(\text{sediment})} = \left(\frac{B/T_e}{G_s F_{v/s} F_{m/gi}}\right)\left(\frac{1}{S}\right) = 1300 \text{ nCi/g}$$

Pathway Parameters:

B	= permissible body burden	= 4 nCi
T_e	= years of exposure	= 70 yr
G_s	= amount of vegetables ingested (10% of total dietary intake)	= 7300 g/yr
$F_{v/s}$	= ratio plant/sediment concentration	= 2×10^{-5}
$F_{m/gi}$	= fraction Pu absorbed from GI tract	= 3×10^{-5}
S	= overall safety factor	= 10

4. Ingestion of meat from animals grazing or living in contaminated waterways: Presently there is no known consumption of animals from this waterway area since it is undeveloped land inside the City of Miamisburg. However, as a worst case, the ingestion of the muscle portion of both small and large animals will be considered. The transmigration pathway of plutonium from the sediment through animals to man is shown in Figure 56.

Martin(33) has considered this pathway in a desert environment for ingestion of large animals (beef). From his pathway analysis, he estimates that the ratio of plutonium concentration in the muscle to the concentration in the soil to be about 2×10^{-5}. To account for smaller animals which may burrow in the banks of the waterways, this value was increased by a factor of 10 in this analysis.

If 10% of the 74,000 g of meat(34) or 7400 g were consumed from this area, the sediment concentration guide would be safety between 129 and 1290 nCi/g as summarized in Table 30.

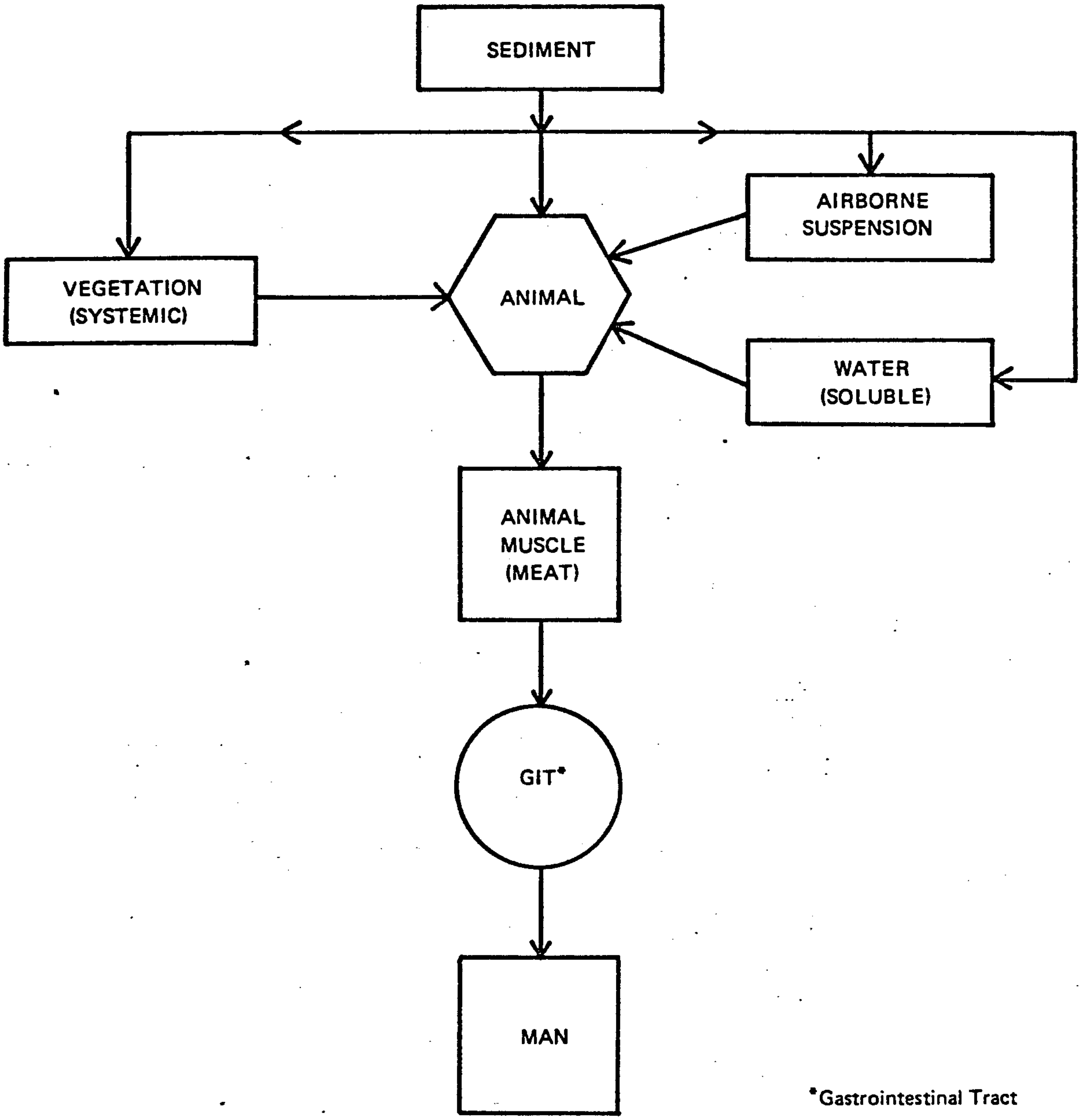


FIGURE 56. Pathway for Ingestion of Meat

TABLE 30. Sediment Concentration Decision Guide Based on Ingestion of Meat

Decision Guide Equation for Ingestion of Water:

$$DG_{(\text{sediment})} = \left(\frac{B/T_e}{G_a F_{a/s} F_{m/gi}}\right)\left(\frac{1}{S}\right) = 129 - 1290 \text{ nCi/g}$$

Pathway Parameters:

B = permissible body burden = 4 nCi

T_e = years of exposure = 70 yr

G_a = amount of muscle ingested = 7400 g/yr

$F_{a/s}$ = ratio muscle to sediment = 2×10^{-5} (large animals) 2×10^{-4} (small animals)

$F_{m/gi}$ = fraction Pu absorbed from GI tract = 3×10^{-5}

S = overall safety factor = 10

5. Ingestion of fish from the contaminated waterways: The fish in the waterways are mostly bluegill and carp. The public occasionally fish in the canals and ponds and eat the bluegills. The carp are not usually consumed, but are edible.

The pathway from the sediment to man through ingestion of fish is shown in Figure 57. The pathway from sediment to fish might included ingestion of water, biota, and sediment or absorption of plutonium from the water. The

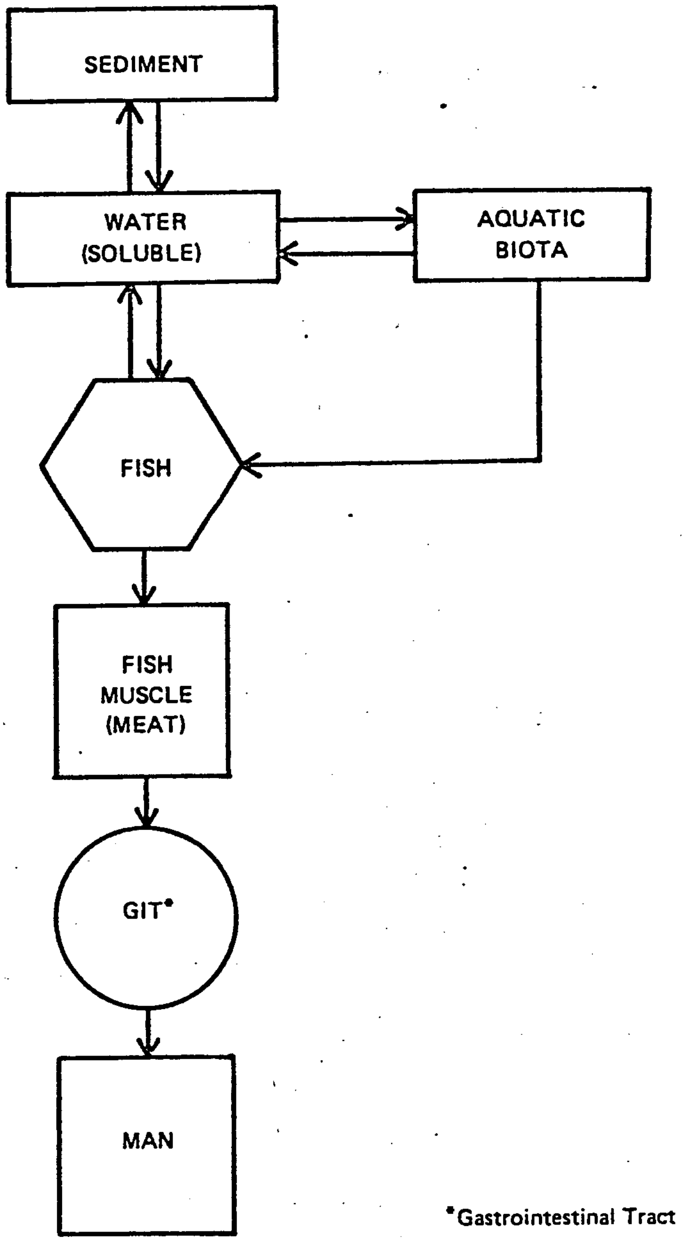


FIGURE 57. Pathway for Ingestion of Fish

^{238}Pu concentration in each of the components is assumed to be in equilibrium with the other components and all are related to the water concentration.

The concentration of plutonium in the water is controlled by the sediment/water equilibrium which has a water to sediment distribution ratio of 10^{-5} as discussed previously. Noskin(37) has reported that the edible portion of the fish might have a ^{238}Pu concentration four or five times higher than the water concentration. The highest concentration factor of ^{238}Pu in the fish (carp) taken from the waterways indicates this fish to water ratio might be considerably less (0.5 to 1.0) than Noskin's value; however, the age of these fish is not known and Noskin's value will be assumed.

Coleman(34) reports the average fish consumption by man is about 9000 g/yr. Since the fish population in these waterways (except the river) is quite limited, it is assumed that 10% of the total fish consumed (or 900 g/yr) were taken from the contaminated waterways.

Using the parameters and assumptions described above, the sediment concentration decision guide for the fish ingestion pathways was estimated to be 4230 nCi/g as summarized in Table 31.

TABLE 31. Sediment Concentration Decision Guide Based on Ingestion of Fish

Decision Guide Equation for Ingestion of Fish:

$$DG_{(sediment)} = \left(\frac{B/T_e}{G_f D_{w/s} F_{f/w} F_{m/gi}}\right)\left(\frac{1}{S}\right) = 4230 \text{ nCi/g}$$

Pathway Parameters:

B	=	permissible body burden	= 4 nCi
T_e	=	years of exposure	= 70 years
G_f	=	amount of fish ingested	= 900 g/yr
$D_{w/s}$	=	ratio of water to sediment concentration	= 1×10^{-5}
$F_{f/w}$	=	ratio of fish to water concentration	= 5
$F_{m/gi}$	=	fraction ^{238}Pu absorbed through GI tract	= 3×10^{-5}
S	=	overall safety factor	= 10

Absorption pathways. Contaminated sediment deposited on the skin and in wounds might be absorbed into the body. The intact skin provides an excellent barrier against this pathway to man.

The entry of solid or insoluble material by this mechanism is negligible and even the rate of absorption of soluble plutonium is very small. Langham(38) measured the rate of absorption of a 0.4 M HNO_3 solution of plutonium through the skin of a human subject and found the rate to be less than 1×10^{-2} % per day. (This acidity might be high enough to cause some skin change and increase absorption.) After reviewing the animal and human absorption studies performed with acidic solution of plutonium, Healy(25,39) recommends an upper limit for absorption rate to be about 1.4×10^{-2}% per day for soluble plutonium.

Data on the rate of absorption through open wounds indicate that this rate may be 10 to 100 times faster than through intact skin.(25)

In order for plutonium to transmigrate from the contaminated sediment to man, it must be deposited on the skin or in wounds, become solubilized, and then absorbed into the body. The pathways for these mechanisms are shown in Figure 58.

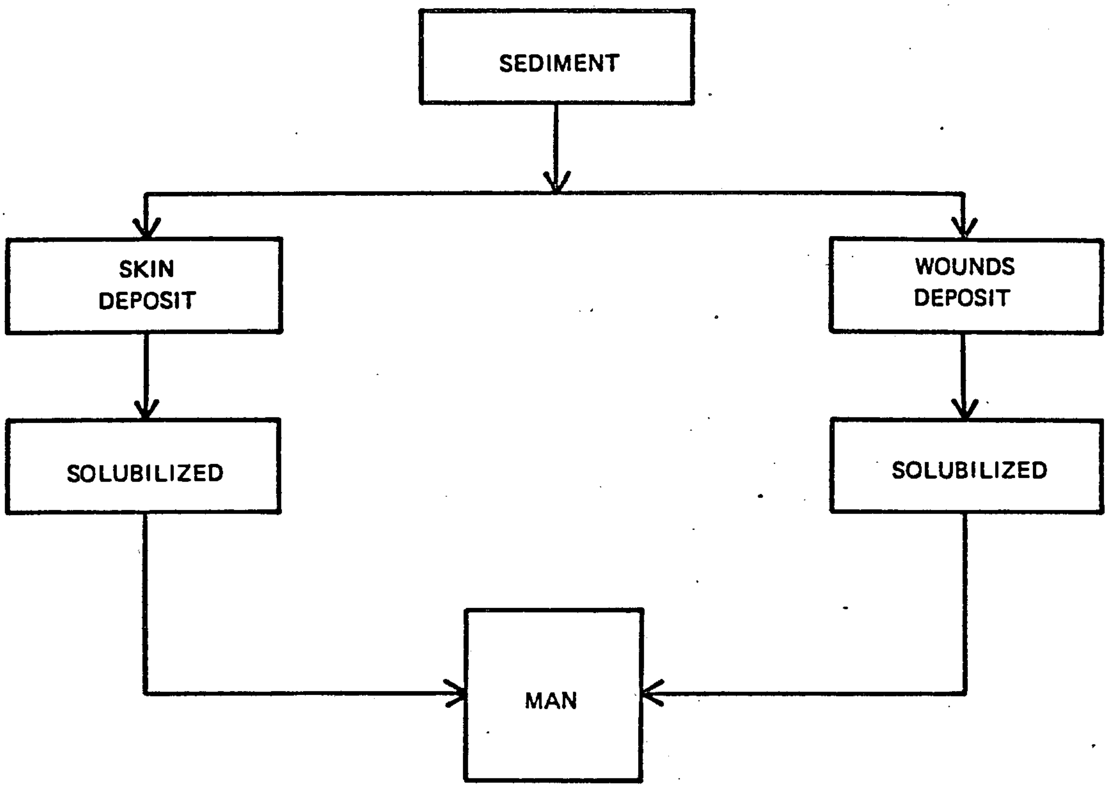


FIGURE 58. Absorption Pathways Through Skin and Wounds

1. Absorption through intact skin: The amount of total dirt which may be deposited on the skin was estimated by Healy(25) to be about 1.0 g/m^2 of skin area. Since the skin area of a "standard man" is estimated at 1.85 m^2,(39) this amounts to about 1.85 g of dirt deposited continuously on the skin 24 hr/day for a lifetime.

If a person is clothed, and this part (90%) of the skin is protected,(39) the amount of dirt on the exposed areas might be as high as 10 g/m^2. Tests performed with the silty-clay sediments indicate the appearance of this amount of deposit is very muddy and might be unreasonable for a continuous lifetime deposit especially with periodic bathing.

But, even if this amount of dirt were deposited, one would not expect all of it to come from the contaminated waterways. For these reasons, a deposition of 0.1 g/m^2 on the 1.85 m^2 individual is believed to safely represent a worst-case upper limit for skin deposits of sediment from the contaminated waterways. The solubility of the plutonium in the sediment deposited on the skin is assumed to be of the order of 10^{-2} % if there is about 2 ml ($0.001\ \text{ml/cm}^2 \times 1850\ \text{cm}^2$ of skin area exposed) of perspiration continuously in the skin areas where the sediment is deposited.

The sediment concentration guide considering absorption through intact skin was estimated to be greater than 6000 nCi/g as shown in Table 32.

TABLE 32. Sediment Concentration Decision Guide Based on Absorption Through Skin

Decision Guide Equation for Absorption Through Skin:

$$DG_{(\text{sediment})} = \left(\frac{B/t_e}{(G/a)_s A_m R_{abs} d/y S_{w/s}}\right)\left(\frac{1}{S}\right) \simeq 6000 \text{nCi/g}$$

Pathway Parameters:

B = permissible body burden = 4 nCi

T_e = years of exposure = 70 yr

$(G/a)_s$ = Amount of sediment deposited per unit area (10% of total dirt) = $0.1\ \text{g/m}^2$

A_m = skin area, standard man = $1.85\ \text{m}^2$

R_{abs} = absorption rate through skin = 1.4×10^{-4}/day

d/y = days per year of absorption = 365 days

$S_{w/s}$ = fraction of plutonium soluble = 1×10^{-4}

S = overall safety factor = 10

2. Absorption through wounds: If no more than 1% (0.185 m^2) of the skin area is continuously abraided, the uptake by absorption through wounds would lead to about the same decision guide as for intact skin as shown in Table 33.

TABLE 33. Sediment Concentration Decision Guide Based on Absorption Through Wounds

Decision Guide Equation for Absorption Through Wounds:

$$DG_{(\text{sediment})} = \left(\frac{B/T_e}{(G/a)_s A_w R_{abs} d/y S_{w/s}}\right)\left(\frac{1}{S}\right) \approx 6000 \text{ nCi/g}$$

Pathway Parameters:

B	= permissible body burden	= 4 nCi
T_e	= years of exposure	= 70 yr
$(G/a)_s$	= amount of sediment/unit area of wounds (10% of total dirt)	= 0.1 g/m
A_w	= area continuously abraided (1% of total skin area)	= $1.8 \times 10^{-2} m^2$
R_{abs}	= absorption rate through wounds	= 1.4×10^{-2} /day
d/y	= days/year of absorption	= 365 days
$S_{w/s}$	= fraction of plutonium soluble	= 1×10^{-4}
S	= overall safety factor	= 10

Inhalation pathways

1. Introduction: Before the contaminated sediment can enter the inhalation pathway to man

it must first be suspended in the air and exhibit a particle size range which can be breathed in and deposited in the lungs. These pathways are shown in Figure 59.

At the present time, the sediment is showing very little tendency to become airborne because it is underwater, moist, or covered with vegetation. These conditions tend to suppress or eliminate the air suspension potential of the sediment. If, however, in the future, the surface hydrology is altered to reduce or eliminate the water flow in these waterways, this would potentially affect the suspension characteristics of the sediment.

Even without the extensive surface waterflow now observed, these waterways cannot be assumed to take on desert-like conditions. More likely, it can be safely assumed that the beds of the waterways will revert to the conditions in the area nearby which are not subject to extreme flooding. Therefore, if the waterflow was somewhat permanently decreased or eliminated, the beds of the waterways would be expected to become overgrown with thick vegetation in 1 or 2 years. That this assumption is valid is

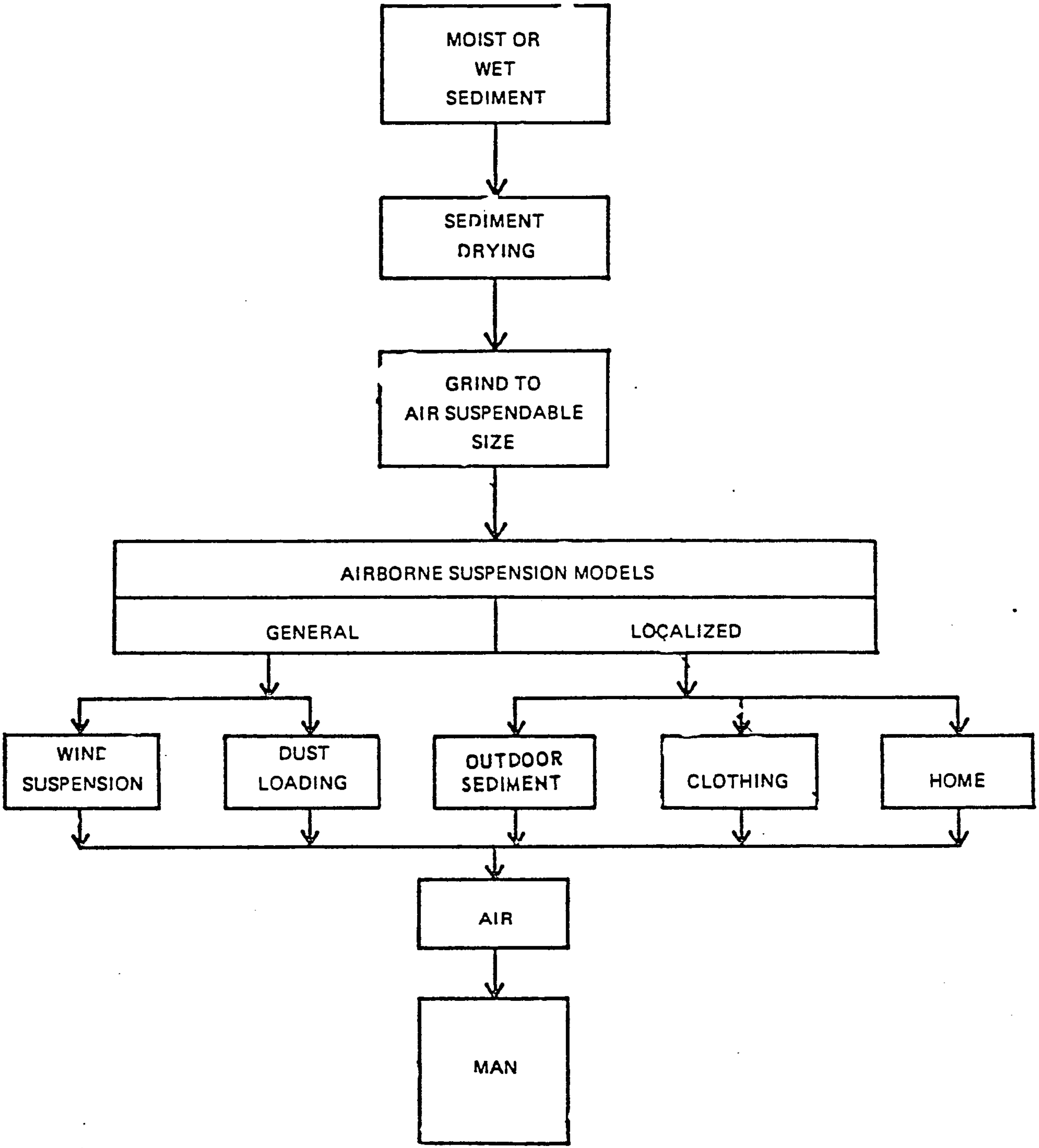


FIGURE 59. Pathways for Inhalation

indicated by the conditions prevalent in the South Canal. This portion of the waterway is subject to considerable variation of flow, ranging from a small flow in a central meandering channel under low flow conditions to a high flow that fills the entire bed during storms. The canal bed, other than the area of the meandering low flow channel, is completely overgrown with thick grass, weeds, brushes, and other plants. This extensive ground cover severely reduces the suspension of the sediment in air by providing a physical barrier against wind, mechanical disturbance, saltation, etc., and by keeping the surface relatively moist.

In the interim, while the vegetation gets established, the surface may dry out during one or two dry periods in summer or fall. When extreme drying occurs, the silty clay sediment dries, almost like pottery clay, to a very hard cake. In the waterways, the sediment tends to form large agglomerate masses which are not subject to airborne suspension. These masses, thoroughly dried, are very hard and difficult to grind, but under extreme mechanical disturbance might be reduced to air suspendable size. To determine the particle size distribution that might result from extreme mechanical grinding, a typical sample of the sediment taken from the top of a core sample was air and vacuum dried at temperatures less than 40°C (104°F). This action produced a very hard cake, about 2 inches in diameter and 1 inch thick, and almost no fine material. Next, this cake was broken and ground to pass through a 50 μm screen simulating an extreme mechanical disturbance. An agglomerate particle size distribution analysis (Figure 51) performed by microscopy methods indicated that only about 2.1% of these particles were in the respirable size range, less the ∿6 μm (equivalent to a aerodynamic diameter of 10 μm). The mass median diameter was about 35 μm. A very small fraction of the sediment would be reduced to the respirable size range even under dry conditions and extreme mechanical disturbance. In addition, when this powder is rewetted, it seems to return to its original state. After the next rainfall, all sediment in the waterways which had been subjected to mechanical abuse would be reconsolidated. Therefore, continuous dry conditions or repeated mechanical action would be required to maintain the sediment in suspendable form. This is contrary to the nature of local weather conditions. In all probability, if these waterways were no longer needed to carry surface water and were allowed to dry, the city would fill the waterway beds to provide more level land. This action would bury the plutonium sediment deposits and virtually eliminate the air suspension potential.

Very few of these moderating conditions and circumstances were used in the pathway analysis performed because they are very difficult to define quantitatively.

Several methods have been used to estimate air suspension characteristics. General or widespread airborne contamination behavior is examined using dust loading and wind plume suspension models. Localized air concentrations near the waterways or resulting from sediment contamination of personal clothing and homes are estimated from airborne resuspension factors.

Using these models to define the pathway to man, the sediment concentration which would potentially result in air concentration approaching levels permitted by the RCG for air were calculated.

The ICRP recommends two RCG values reflecting the solubility of the plutonium inhaled. The "insoluble" air RCG (1 x 10^{-12} μCi/cm^3) was established to prevent the accumulation of a permissible lung burden (1.5 nCi) with a lifetime continuous exposure. The "soluble" RCG (7 x 10^{-14} μCi/cm^3) was established to prevent the accumulation of a permissible body burden with a continuous lifetime exposure.

The "insoluble" RCG is usually applied to PuO_2 forms which are relatively insoluble and tend to remain in the lungs for an extended period of time. The "soluble" RCG relates to inhalation of very soluble forms like acidic $Pu(NO_3)_4$ solutions.

While the plutonium sorbed on the sediment is probably more soluble in lung fluids than the refractory forms of PuO_2, it is almost insoluble when compared to acidic plutonium nitrate solutions. Therefore, it was assumed, due to the relative insolubility of the plutonium/sediment in reasonably harsh conditions and the worst-case nature of the suspension mechanisms, that the insoluble RCG for air (1 x 10^{-12} $\mu Ci/cm^3$) is severe enough to adequately define the hazardous levels of plutonium in sediment.

2. Inhalation estimated by a dust-loading model: Under normal circumstances, there is a sizable concentration of dust in the air. The source of these airborne particulates varies from location to location, but usually results from soil suspension in primarily agricultural areas, from automobiles and industry in urban areas. In any case, the airborne dust loading at any location orginates from very wide areas.(25) Localized air concentrations can be enriched temporarily from a single ground source or small area where mechanical disturbance is occurring, but this affect is transient and averaged out over a period of time will be insignificant.

The dust loading in this area varies from about 40 $\mu g/m^3$ to 100 $\mu g/m^3$. How much of this dust is suspended soil is not known, but the fossil fuel electrical generation station to the southwest is known to greatly affect the dust loading.

If it is assumed, as a worst case, that the dust loading values reflect only airborne soil suspendion and that the area supplying dust (a reference location) is much greater than 1 mi^2, the sediment concentration in the air near the waterways (area = 0.01 mi^2) that are assumed to be dry would contribute less than 1% of the total dust.

Since the dust load model implies a general average air concentration, it has been assumed as a worst case that the public in this area would be exposed to this air, 24 hours/day for 70 years.

The sediment concentration which would potentially result in exposure of the public to air concentrations approaching the RCG value for air has been estimated as shown in Table 34. This pathway model results in a sediment concentration decision guide of about 100 to 250 μCi/g.

TABLE 34. Sediment Concentration Decision Guide Based on Inhalation: Dust Loading Model

Decision Guide Equation for Inhalation (Dust Loading)

$$DG_{(\text{sediment})} = \left(\frac{RCG(\text{air})}{C_p A_s / A_p}\right) \cdot \left(\frac{1}{S}\right) = 100\text{-}250 \text{ nCi/g}$$

Pathway Parameters:

RCG(air) = permissible air concentration (^{238}Pu) = 1×10^{-9} nCi/cm^3

C_p = total dust loading this area = 40×10^{-12} to 100×10^{-12} g/cm^3

A_s = area of contaminated sediment = 0.01 mi^2

A_p = total area supplying particulate matter to this area = >1 mi^2

S = overall safety factor = 10

3. Inhalation estimated by a wind suspension model: When the wind blows over an area, it tends to pick up loose soil particles from the surface and form a dust cloud or plume. The airborne particles rise and are subsequently dispersed in the air or deposited downwind.

Many factors determine the amount (and rate) of soil particles which will be picked up by the wind. Among these factors are wind velocity and turbulence, particle size, ground moisture, ground cover and surface roughness.

The depletion of airborne soil concentrations resulting from deposition or dispersion also depends on many factors. Among these factors are soil particle density and size, particle settling velocity, wind velocity, and wind stability.

The maximum concentration of dust downwind from a particular source is, therefore, a balance between the pickup of soil particles and their deposition and dispersion downwind. Healy(25) considered these factors and presented a wind generated dust plume model to estimate the maximum airborne contamination downwind of a strip of contaminated soil.

A detailed discussion of Healy's plume calculation is beyond the scope of this report. He performed a calculational parameter study assuming the contaminated strip is of various widths but infinitely long. The infinite length assumption tends to reduce the effect of minor changes in wind direction. Using an 11 mph wind (5 m/sec), he assumed a range of particle properties and wind stability characteristics and calculated a plume parameter or concentration integral which defines the dust concentration at 1 meter above the ground as a function of the dust particle pickup rate, R_p, the contamination level on the ground per unit area, Ω, and the wind velocity, as shown below:

$$I = \frac{x\bar{u}}{R_p \ \Omega}$$

These concentration integral values are presented as a function of contaminated strip width and wind stability in Figure 60.

As was discussed previously, the wind at Mound Laboratory blows mostly from the south and west. These extremes correspond to a wind direction essentially perpendicular or across the waterways and parallel along the length of the waterways. The dimensions of the contaminated waterway beds presented to a west or southwest wind is assumed to be an average of about 49 feet wide (15 m) and infinitely long. In this case, the assumption of infinite length is probably justified since the waterways are very long (6890 ft) relative to the width.

For a south or southwest wind, a contaminated strip is assumed to have a width of 6890 ft

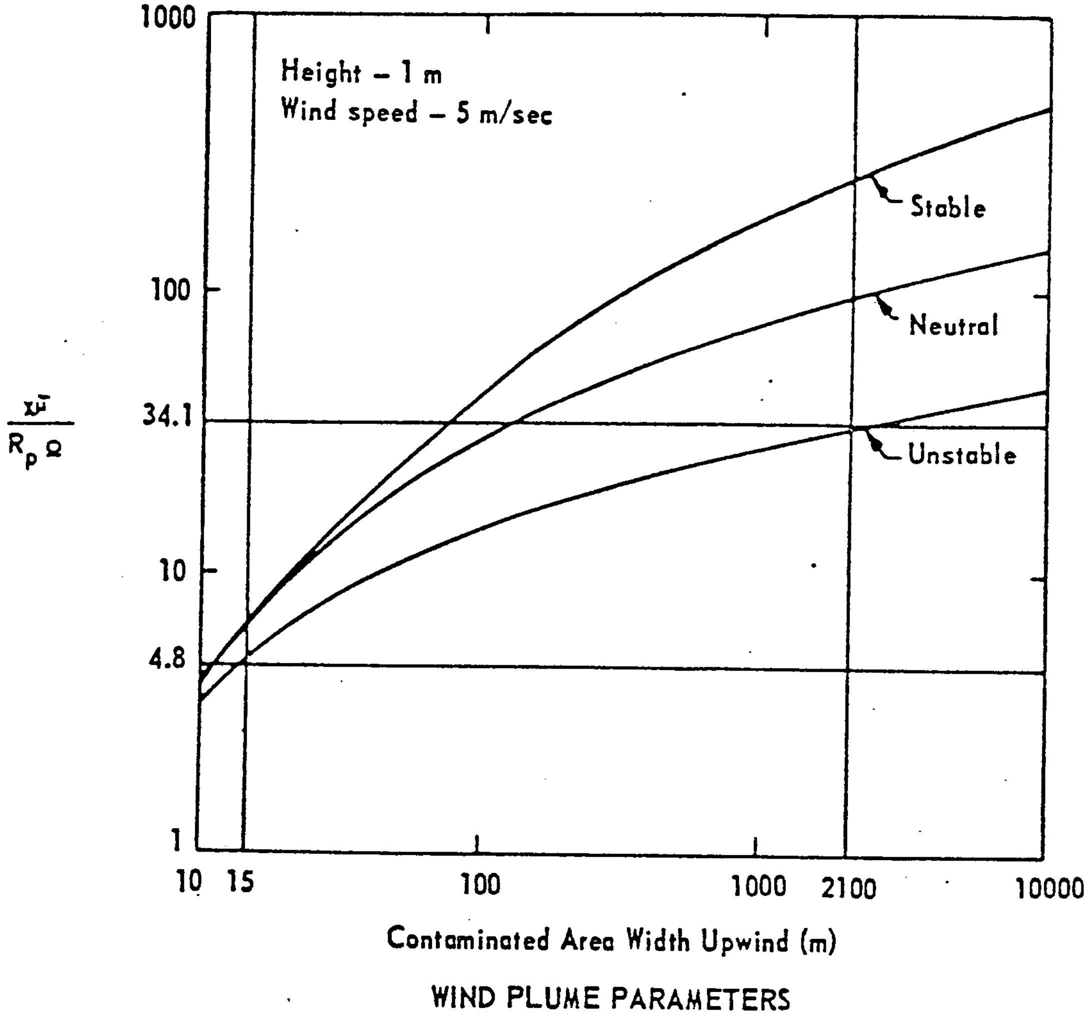
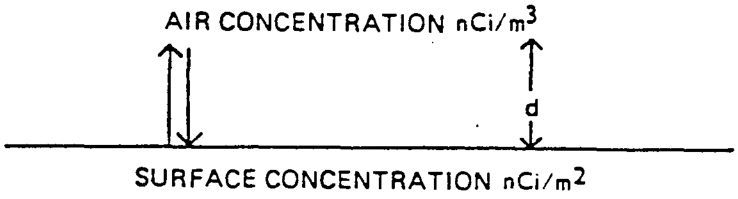


FIGURE 60. Calculated Concentration Integrals (plume parameters)

(2100 m) and an infinite length. This assumption is clearly worst case since this would define a contaminated area very much larger than is observed. However, using these width assumptions the extreme concentration integrals were taken from Figure 62 to be 4.8 for the 15 m strip (west wind) and 34.1 for the 2100 m strip (south wind). Healy's assumption of an unstable 11 mph wind is not substantially different than is observed in this area and was adapted in the pathway calculation.

Using ZnS particles to simulate fresh fallout, Healy(25) determined a pickup factor, R_p to be 2×10^{-8}. Therefore, this value applies to fresh fallout and is not applicable to this case where the plutonium is fixed to the soil. As has been stated previously, the suspension properties of the contaminated sediment is controlled by the soil properties and should be similar to fallout contamination on soil which has been well aged and permitted to become fixed onto the soil.



$$K = \left(\frac{\text{AIRBORNE CONCENTRATION nCi/m}^3}{\text{SURFACE CONCENTRATION nCi/m}^2} \right) \text{m}^{-1}$$

FIGURE 61. Resuspension Factors

The wind pickup factor, R_p, has been estimated to be 2 x 10^{-12} sec/m^2 for the 20-year GMX area at NTS.(25) This value was selected to represent the wind pickup factor in this area.

Healy(23) assumes that only the top 0.1 cm (or the very surface) of the soil is vulnerable to wind suspension. Using a sensitivity of about 1.6 g/cm^3 then, there are about 1600 g/m^2 of particles available for suspension.

As in the case of dust loading, the wind suspension of dust much be considered generally distributed and as a worst case the public might be exposed to this air 24 hours/day for 70 years.

With these assumptions and parameters, the sediment concentration which potentially could result in the exposure of the public to air concentration approaching the air RCG is calculated as shown in Table 35. These sediment concentration decision guides based on wind suspension for the dry waterway were then estimated to be between 183 to 13,000 nCi/g.

TABLE 35. Sediment Concentration Decision Guide Based on Inhalation: Wind Suspension Model

Decision Guide Equation for Inhalation (Wind Suspension)

$$\mathrm{DG(sediment)} = \left(\frac{\mathrm{RCG(air)}}{\dfrac{\chi \bar{u}}{R_p \Omega_w} \quad \dfrac{R_p}{\bar{u}^2} \quad \bar{u}(G/a)_w} \right) \cdot \left(\frac{1}{S} \right) = 183\text{-}1300 \ \mathrm{nCi/g}$$

Pathway Parameters:

RCG(air) = permissible air concentration (^{238}Pu) = 1×10^{-3} nCi/m^3

$\dfrac{\chi \ \bar{u}}{R_p \Omega_w}$ = dust concentration integral (plume parameter = N/S 34.1
= E/W 4.8

$R_p/\bar{u}^2$ = wind pickup rate constant = 2×10^{-12} sec/m^2

$\bar{u}$ = wind velocity = 5 m/sec

$(G/a)_w$ = sediment available for suspension per unit area = 1600 g/m^2

S = overall safety factor = 10

4. Inhalation estimated by resuspension factors: A useful technique for estimating the air concentrations, which might be present in the immediate area of the contamination, is defined by the resuspension factors.

The resuspension factor, Km^{-1}, is defined as the ratio of the air concentration per unit volume to the ground concentration per unit area as shown in Figure 61. This parameter does not relate to any particular mechanism for air resuspension of ground contamination but is simply a functional measure of the air concentration which would be expected in the immediate area of the ground contamination under prevailing conditions.

Resuspension factors have been reported for a variety of conditions and circumstances (10^{-2} to 10^{-11})(27,28,40) and vary over about nine orders of magnitude. When these values are sorted according to the condition prevailing at the time,

- Nature of the contamination
- Amount of ventilation (indoors or outdoors)
- The nature of the surface (hardness, smoothness)
- The amount and nature of the mechanical disturbance,

The range of values falls into a pattern as shown in Table 36.

TABLE 36. Summary of Resuspension Tests on Outdoor Soil

Nature of Contamination	Disturbance	Km^{-1}
Fresh Fallout	Low	10^{-7} to 10^{-6}
Fresh Fallout	Auto Traffic	10^{-6} to 10^{-5}
Aged Fallout (20 yr)	Low	10^{-9}
^{91}Y sorbed on soil	Low	10^{-9}
^{238}Pu sorbed on soil at Mound Laboratory	Low High	10^{-9} 10^{-8}

The resuspension factors measured for fresh PuO_2 fallout particulates deposited on outdoor soil during nuclear testing range from 10^{-7} to 10^{-6} under low mechanical disturbance conditions.(28) (In areas where the surface is rocky or paved, the resuspension factors may range up to 10^{-3} due to these smoother and harder surfaces and because little mixing with noncontaminated surfaces can occur.)

Mechanical disturbances (even automobile traffic) usually increase the resuspension factor by a factor of 10 to 100.(39) Steward(28) and others(26) recommend a resuspension factor of 10^{-6} m^{-1} for fresh fallout under quiescent conditions increasing this value to 10^{-5} m^{-1}

for moderate activity. As the fresh fallout becomes aged, fixed to the soil or mixed with the soil, the resuspension characteristics of the contamination apparently approaches the soil suspension characteristics. The resuspension factor measured at the GMX area (20-yr-old deposit) is estimated at about 10^{-9} m^{-1}.(30,33) This represents a reduction of about three orders of magnitude from the time it was originally deposited.

Interestingly, the suspension of radioactivity, which is sorbed onto soil is apparently controlled by soil suspension characteristics without aging. A test performed with $^{91}YCl_3$ solution sorbed onto soil indicated a 10^{-9} m^{-1} resuspension factor.(28) Plutonium-238 sorbed onto Mound Laboratory soil also indicated a resuspension factor of about 10^{-9} m^{-1} as has been discussed previously.

On this basis, sediment would exhibit a resuspension factor of about 10^{-9} m^{-1} from the time of sorption.

Using Healy's "very surface" criteria,(25) the amount of sediment available for resuspension is assumed to be 1600 g/m^2.

In this case, since the resuspension factor defines the air concentration only in the immediate area of the waterway beds, it has been assumed that the public would be exposed no more than 8 hours a day, every day, for 70 years.

The sediment concentration in the dry waterway beds which could potentially result in exposure of the public to air concentrations approaching the RCG for air was estimated, as shown in Table 37.

TABLE 37. Sediment Concentration Decision Guide Based on Inhalation: Resuspension Factors

Decision Guide Equation for Inhalation (Resuspension Factors)

$$DG_{(\text{sediment})} = \left(\frac{\text{RCG (air)}}{(\text{Km}^{-1})\ (\text{G/a})_r F_t} \right) \cdot \left(\frac{1}{S} \right) = 188\ \text{nCi/g}$$

Pathway Parameters:

RCG (air) = permissible air concentration ^{238}Pu = 1×10^{-3} nCi/m^3

Km^{-1} = resuspension factor = 1×10^{-9}/m

$(\text{G/a})_r$ = resuspendable sediment per unit area = 1600 g/m^2

F_t = fraction of time exposed/day (8 hours/day) = <0.3

S = overall safety factor = 10

The sediment concentration decision guide based on resuspension factors was established at 188 nCi/g. During periods of high mechanical disturbance, the RCG might be exceeded temporarily; however, these short-term exposures will not affect the overall evaluation significantly.

5. Inhalation estimated from clothing contamination: Should a person contaminate his clothing with waterway sediment and perform a vigorous activity, one might expect an increased inhalation exposure. This is assumed to be due to the more active mechanical disturbance, the drier nature of the dust deposit, and the proximity of the clothing to the mouth and nose. As a measure of assurance that this mechanism is not underestimated, the normal sediment resuspension factor has been increased by three orders of magnitude to about 10^{-6} m^{-1}.

Healy(25) assumes that 10 g/m^2 of dust might be present on clothing in a desert area. While it would certainly be less in this area and all of it need not be assumed to be contaminated sediment, a value of 1 g/m^2 of sediment dust on the clothing seems to be safe.

One can logically assume that the clothing, removed for sleeping, would not be subject to mechanical agitation. Therefore, it is assumed that a person would, in the worst case, only be exposed to this source 16 hours a day, every day, for 70 years.

Using these parameters and assumptions, the calculation of sediment dust concentration which might result in an exposure of the public to air concentrations approaching the RCG for air is summarized in Table 38.

TABLE 38. Sediment Concentration Decision Guide Based on Inhalation: Personal Clothing Contamination

Decision Guide Equation for Inhalation (Clothing)

$$DG_{(\text{sediment})} = \left(\frac{RCG(\text{air})}{(Km^{-1})_c (G/a)_c F_t}\right) \cdot \left(\frac{1}{S}\right) = 150 \text{ nCi/g}$$

Pathway Parameters:

$RCG(\text{air})$ = permissible air concentration ^{238}Pu = 1×10^{-3} nCi/m^3

Km^{-1} = clothing resuspension factor = 10^{-6}/m

$(G/a)_c$ = grams sediment per unit area of clothing = 1 g/m^2

F_t = fraction of time exposed/day (16 hr/day) = 0.67

S = overall safety factor = 10

The sediment concentration decision guide is estimated at 150 nCi/g based on clothing contamination.

6. Inhalation from home contamination: Sediment from the waterways might be tracked into nearby homes or carried in on clothing. The total amount of soil that might be considered to be continuously in the home is not known. However, one can safely assume, with normal routine cleaning, that the soil in the home will not exceed 10 g/m^2. This amounts to about three pounds of dirt in a modest 1500 ft^2 house.

For the purpose of this pathway one need not assume that all dirt in the house originated in the contaminated waterways. Therefore, as with personal clothing, the sediment deposition in the home will be assumed to be 1 g/m^2 of floor space.

Because some of the floors are harder and have a smoother surface than outside soil and because the ventilation may be low and cannot disperse the dust, the outside resuspension factor has been increased, by a factor of 1000, to

10^{-6} m^{-1} as a worst case. Even though this is a localized concentration, the daily exposure time has been assumed to be 24 hours a day, every day, for 70 years to account for persons who spend a great deal of time working in the house.

The worst-case sediment concentration, to potentially result in RCG air concentrations, in nearby homes has been estimated as shown in Table 39. The sediment concentration decision guide based on this pathway is estimated to be of the order of 100 nCi/g.

TABLE 39. Sediment Concentration Decision Guide on Inhalation: Home Contamination

Decision Guide Equation for Inhalation (Home)

$$DG_{(\text{sediment})} = \left(\frac{RCG(\text{air})}{(Km^{-1})_H (G/a)_h F_t}\right) \cdot \left(\frac{1}{S}\right) = 100 \text{ nCi/g}$$

Pathway Parameters:

$RCG(\text{air})$ = permissible air concentration ^{238}Pu = 1×10^{-3} nCi/m^3

$(Km^{-1})_H$ = resuspension factor (indoors) = 10^{-6}/m

$(G/a)_h$ = grams of sediment per unit area of home (10% of total dirt) = 1 g/m^2

F_t = fraction of time/day exposed 24 hr/day = 1.0

S = overall safety factor = 10

APPLIED AND IMPLIED SAFETY FACTORS IN SEDIMENT CONCENTRATION DECISION GUIDES

In the previous section, the sediment concentration decision guides were estimated for a number of worst-case pathways. In effect, these decision guides attempt to answer only the question: "What sediment concentration in or around these waterways should cause the slightest concern about allowing the plutonium sediment deposits to remain in these locations based only on health and safety considerations?"

In order to avoid underestimating the potential hazard, a number of directly applied and implied safety factors have been built into the analyses.

- The overall dose standards recommended for continuous lifetime exposure to occupational plutonium workers were reduced by a factor of 10 before they were applied to the general public in this analysis. The occupational internal dose standards also contain safety factors for they have protected workers and scientists working with plutonium for many years. It is a high recommendation, that no one is known to have been killed or significantly harmed(41) by internal exposure to plutonium at much higher levels than the occupational standard. Few other safety standards have been this successful.

- An honest attempt was made in this analysis to develop as many pathways to man as possible, even to the point of forcing the issue on a few.
- An attempt was made to develop not only an overall worst case, but the maximum credible worst case for each pathway.
- Pathway parameters which have not been experimentally evaluated were estimated with great caution. An attempt was made to deliberately choose a value many times the value considered reasonable just to remain on the safe side.
- The best values for measured parameters reported in the scientific literature were used in the pathway analyses.
- A continuous exposure, 8 to 24 hours/day, every day, for a 70-year lifetime was assumed in all pathways.
- An overall additional safety factor of 10 was applied to each pathway decision guide to account for anticipated future reduction of the plutonium dose standards and uncertainties in the pathway parameters.

Now as the decision guides are compared to the actual plutonium concentration found in the waterways, some additional safety factors are implied.

- These decision guides will be compared with the maximum values (rather than an average or mean value) found on the surface in or near these waterways as though they existed evenly throughout the entire 0.01 mi^2 area.

- Next, the decision guides will be compared with the <u>maximum</u> first-foot value and the maximum worst-case value found at any depth as though these concentrations existed at the surface and were evenly distributed over the 0.01 mi^2 area. The fact is that these maximum subsurface concentrations are found in a very small fraction of the total contamination area.

Overall then, the sediment concentration decision guides and their application to the evaluation of hazard to the general public in this particular situation is considered substantially on the safe side from a health and safety standpoint.

OVERALL HEALTH AND SAFETY EVALUATION

The plutonium sediment concentration guides developed in the previous section are summarized in Table 40. These guides indicate the plutonium concentrations in sediment, which under credible worst-case conditions, could potentially result in a plutonium uptake approaching the dose standard in a lifetime (70 yr) of continuous exposure. Plutonium concentrations in sediment which are less than the concentration decision guides are considered to be safe.

TABLE 40. Sediment Concentration Decision Guides For Waterways Near Mound Laboratory

Ingestion	Sediment Concentration (nCi/g)
Sediment	52-520
Water	520
Vegetables	>1000
Animals, large	>1000
Animals, small	129
Fish	>1000
Absorption	
Skin	>1000
Wounds	>1000
Inhalation	
Dust Loading	100-250
Winds Suspension	183-1300
Resuspension Factor	188
Clothing Contamination	100
Home Contamination	150

In order to make the long-term health and safety evaluation, the maximum plutonium concentrations found in or near these waterways are compared with the decision guides. The maximum concentrations found are subdivided into the concentrations at the "very surface," in the first-foot, and at any depth as listed in Table 41.

TABLE 41. Maximum Sediment/Soil ^{238}Pu Concentration Found in Waterways Near Mound Laboratory

Very Surface (Available)	Maximum Concentration Found (nCi/g)
Sediment Surface in Waterways	0.450
Immediate Waterway Banks	0.060
Contiguous Land Areas	0.001
First Foot (Potentially Available in Future)	
Sediment in Waterways	3.8
Banks	0.010
Contiguous Land Areas	0.0004
Any Depth (Worst-Case Available in Future)	
Sediment in Waterway	4.6
Banks	0.060
Contiguous Land	0.001

The "very surface" concentration represents the plutonium contaminated sediment or soil that would be available to man. The maximum value found was 0.45 nCi/g, which is at least two orders of magnitude less than the worst decision guide pathway.

The first-foot concentrations represent the plutonium-contaminated sediment which, if it were brought to the surface by some action, could potentially be available to man. The only locations where exposing the first-foot concentration would lead to increased surface concentrations of plutonium is in the actual beds of the North and South Canals. The highest first-foot concentration, 3.8 nCi/g, is found near the middle of the South Canal, which is, at least, an order of magnitude less than the worst-case pathway decision guide.

The high concentration found at any depth represents the worst-case potential available plutonium because the probability of being brought to the surface decreases with depth. The highest plutonium concentration (4.6 nCi/g) was found buried 3 to 4 ft in sediment in the North Canal. This too is substantially below the decision guides for all the worst-case pathways.

Based on worst-case pathway analyses, the overall conclusions about the health and safety aspects of the plutonium deposited in waterways near Mound Laboratory are:

- The ^{238}Pu does not and will not, in the future, present a hazard to people living in this area or the public at large.
- There is no apparent reason to restrict the use of the area in or near the waterways because of the plutonium deposits.

REFERENCES

1. B. Robinson, D. R. Rogers, W. H. Westendorf and H. A. Black, Mound Laboratory ^{238}Pu Study: Offsite Analytical Data May-December 1974, (to be published as MLM-2251).

2. R. M. Emery and D. C. Klopfer, Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem: Phase I, Limnological Characterization and Isotopic Distribution, BNWL-1867, Battelle Pacific Northwest Laboratory (September 1974).

3. Miami Conservancy District, Dayton, Ohio, Rainfall Records for Miamisburg, Ohio (1961-1974).

4. Dames and Moore, Consulting Engineers.

5. Tests performed by LFE Environmental Analysis Laboratory, Richmond, California.

6. J. M. Cleveland, The Chemistry of Plutonium, Gordon and Breach Science Publishers, New York, New York (1970).

7. O. J. Wick (ed.), Plutonium Handbook, A Guide to the Technology, Gordon and Breach Science Publishers, New York, New York, (1967).

8. J. J. Katz and G. T. Seaborg, The Chemistry of the Actinide Elements, John Wiley and Sons, Inc., New York, New York (1957).

9. H. Metivier and R. Guillaumont, "Hydrolyse du Plutonium Tetravalent," Radiochem. Radioanal. Lett., 10 27-35 (1972).

10. B. U. I. Grebenshchikova and Y. P. Davydov, "A Study of Pu(IV) in Dilute Solutions of Nitric Acid," Radiokhimiya 3, 155-164 (1961).

11. D. W. Ockenden and G. A. Welch, "The Preparation and Properties of Some Plutonium Compounds, Part V: Colloidal Quadrivalent Plutonium," J. Chem. Soc., London, 3358-3363 (1956).

12. A. Brunstad, "Polymerization and Precipitation of Plutonium(IV) in Nitric Acid," Ind. Eng. Chem., 51 38-40 (1959).

13. J. Gilluly, A. C. Waters and A. O. Woodford, Principles of Geology (3rd edition), W. H. Freeman and Company, San Francisco, California (1968).

14. A. Sundborg, *Geografiska Annaler*, *38* (1956).

15. Bowser and Morner Testing Laboratory, Dayton, Ohio.

16. "Standard Method for Particle-Size Analysis of Soils," ASTM D422-63 (reapproved 1972), in *1975 Annual Book of ASTM Standards, Part 19*, American Society for Testing and Materials, pp. 67-77.

17. F. Helfferich, *Ion Exchange*, McGraw-Hill Book Company, Inc., New York, New York (1962).

18. D. R. Rogers, *Properties of ^{238}Pu Radioisotopic Fuels: Properties of ^{238}Pu*, Mound Laboratory report in preparation.

19. *Basic Radiation Protection Criteria*, NCRP Report No. 39, National Council on Radiation Protection, Washington, DC (January 1971).

20. *Recommendations of the International Commission on Radiological Protection (adopted September 17, 1965)*, ICRP Publication 9, International Commission on Radiological Protection, Pergamon Press, Oxford (1966).

21. *Background Material for the Development of Radiation Protection Standards*, Report No. 1, Federal Radiation Council, U.S. Dept. of Commerce (May 13, 1960).

22. *Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure* (Recommendations of the National Committee on Radiation Protection), NBS Handbook 69, National Bureau of Standards (June 5, 1959).

23. *Recommendations of the International Commission on Radiological Protection*, ICRP Report No. 2, International Commission on Radiological Protection, Pergamon Press, Oxford (1959).

24. Mound Laboratory Annual Environmental Monitoring Reports.

25. J. W. Healy, *A Proposed Interim Standard for Plutonium in Soils*, LA-5483-MS, Los Alamos Scientific Laboratory (1974).

26. W. H. Langham, *Biological Considerations of Nonnuclear Incidents Involving Nuclear Warheads*, UCRL-50639, Lawrence Livermore Laboratory (April 1969).

27. R. L. Kathern, Toward Interim Acceptable Surface Contamination Levels for Environmental PuO_2, BNWL-SA-1510, Battelle Pacific Northwest Laboratory (April 1968).

28. K. Steward, "The Resuspension of Particulate Material from Surfaces," in Surface Contamination, B. R. Fish (ed.), Pergamon Press, New York, New York (1964), pp. 63-74.

29. R. H. Wilson, R. G. Thomas and J. N. Stannard, Biomedical and Aerosol Studies Associated with a Field Release of Plutonium, WT-1511, University of Rochester (1960).

30. L. R. Anspaugh, "The Use of NTS Data and Experience to Predict Air Concentrations of Plutonium Due to Resuspension on the Eniwetok Atoll," in The Dynamics of Plutonium in Desert Environments, P. B. Dunaway and M. G. White (ed.), NVO-142 Nevada Operations Office (July 1974), pp. 299-310.

31. J. W. Healy and W. J. Smith, Contamination Limits for Real and Personal Property, LA-5579-PR, Los Alamos Scientific Laboratory (April 1974).

32. Recommendations of the International Commission on Radiological Protection, Publication ICRP-19, International Commission on Radiological Protection (1972).

33. W. E. Martin, S. G. Bloom and R. J. Yorde, Jr., "Plutonium Transport and Dose Estimation Model," in The Dynamics of Plutonium in Desert Environments, P. B. Dunaway and M. G. White (ed.), NVO-142, Nevada Operations Office (January 1974), pp. 331-360.

34. J. R. Coleman, Radiological Dose Model for Plutonium Fueled Space Nuclear Systems, SNS-NUS-934, NUS Corporation (August 1972).

35. E. M. Romney, H. M. Mork, and K. H. Larson, "Persistence of Plutonium in Soil, Plants, and Small Mammals," Health Phys., 19, 487-491 (1970).

36. R. E. Wildung and T. R. Garland, "Influence of Soil Plutonium Concentration on Plutonium Uptake and Distribution in Shoots and Roots of Barley," J. Agr. Food Chem., 22, 833-835 (1974).

37. V. E. Noshkin, "Ecological Aspects of Plutonium Dissemination in Aquatic Environments," Health Phys., 22, 537-549 (1972).

38. W. H. Langham, "Physiology and Toxicology of ^{239}Pu and Its Industrial Medical Control," Health Phys., 2, 172 (1959).

39. J. W. Healy, Surface Contamination: Decision Levels, LA-4558-MS, Los Alamos Scientific Laboratory (1971).

40. J. Mishima, "A Review of Research on Plutonium Releases During Overheating and Fires," Hanford Atomic Products Operation Report HW-83668 (1964).

41. R. D. Evans, A. T. Keane, M. M. Shanahan, "Radiogenic Effects in Man of Long-Term Skeletal Alpha-Irradiation," in Radiobiology of Plutonium, B. J. Stover and W. S. S. Jee (eds.), The J. W. Press, Department of Anatomy, University of Utah, Salt Lake City, Utah (1972), p. 431.

FOLLOWING D. R. ROGERS' PRESENTATION

QUESTIONS AND ANSWERS

Ames: Don, will you be doing any more work on this in the future?

Rogers: Yes. We plan to continue the work at the deposit in the South Canal and in the North Canal as well, to see if we can gain a little more knowledge on the mobility of the plutonium. Based on our estimates right now, we feel that the discharge to the river is in the ballpark of about 10 mCi/yr. In addition to that, we hope to do some more work on the interactions between plutonium and the soil at our site. We hope to develop a better understanding of the plutonium polymerization reactions this year; where they occur and where they do not. Generally speaking, almost every time someone speaks of plutonium in a near neutral solution, it is assumed that plutonium is polymerized. At the really low concentrations present in the environment, this is difficult to envision.

Serne: Is your distribution coefficient unitless?

Rogers: The units are milliliters per gram.

Lini: At the time of your release, were your solutions acidic? Was the plutonium species being released, plutonium (IV) nitrate?

Rogers: Yes. Mostly tetravalent plutonium nitrate.

Lini: Then do you think that the plutonium is being sorbed on the clay, and not being deposited as plutonium oxide?

Rogers: That's right. It's being neutralized in situ by the soil carbonates and simultaneously being sorbed onto the clay silt fraction of the soil.

Lini: Is the plutonium sorbed on the clay silt fraction irreversibly?

Rogers: No, it's not sorbed irreversibly, but it is strongly sorbed.

Lini: Then it has been exchanging potentially in the ionic form.

Rogers: Or whatever species that was sorbed. I don't think we know enough from these studies to speak of the species sorbed, at least not precisely. That's the reason I call these <u>distribution ratios</u> rather than <u>distribution coefficients</u>. What I am talking about here is the total concentration of plutonium in the aqueous stage divided by the total concentration of the plutonium regardless of speciation. One can write a lot of equations and attempt to predict an awful lot, but it is a very complex system and before I would want to make a judgment as to exactly what's going on, I would do a great deal more work.

Wildung: Do you have studies to determine if the distribution ratio changes with aging?

Rogers: The distribution ratio of the plutonium sorbed onto the canal sediment will be examined again this year. But remember that the distribution coefficient that we measured in 1974 which was 5 years after the incident, agreed fairly well with the distribution coefficients we measured on fresh solutions in the laboratory. Therefore, we do not not expect to detect changes within this time frame.

Wildung: I was wondering if you still had some of that contaminated soil from the first spill, that has been maintained under reasonably constant conditions of temperature and moisture, which you can retrieve and then compare with samples that were aged.

Rogers: I don't really understand what you are saying.

Wildung: Aged in the environment, subject to the normal wetting, drying, freezing, thawing cycles.

Rogers: Do you mean the original spill area?

Wildung: Yes, the question of changes in solubility which occur with aging in the environment that has been raised many times.

Rogers: Well, we've got it in the sediment, of course. The sediment is still there. We have that material left that we can look at from time to time. We have a small amount of material that we found on the hillside involved in the original 1969 release. I think T. Tamura (ORNL) and several other people have a sample of it, and, of course, we still have some of it left.

Wildung: That would be interesting to study.

Nyhan: Even more interesting might be to do a field evaluation of soluble plutonium.

Wildung: That's what I meant. You have some techniques you can use to compare.

Nyhan: What I mean is in situ measurements of the soluble plutonium which is out in the streams or in the canals.

Rogers: We measured that. That's where we got the distribution coefficients. We measured both in sediment and in the water. That depends a great deal on how fast the water is flowing and other factors, but once these sediment/ water samples are collected together and maintained for a time together, that's when we measured the distribution coefficients to determine the maximum amount that would go into the water and the amount that would be left on the soil. It gives you a pretty good feeling, as a matter of fact, that you don't have quite as much to worry about from a health and safety viewpoint, as you might have expected from plutonium sorbed on sediment. Of course now this safety factor depends a great deal on what the plutonium distribution ratio of the material is at a particular location. But at our location the large sorption distribution ratios would seem to give added protection for the water system.

Nyhan: What I meant was, during your talk you noted that your distribution ratio gave you a minimal estimate of an hour to move the plutonium into some of these soil profiles.

Rogers: Oh, you mean as a function of the soil size distribution?

Nyhan: No. Distribution of plutonium absorbed onto the soil versus plutonium in solution from your laboratory study. And I guess that indicates to me that samples that are aged out in the field might give you a different answer, i.e., if you could measure the plutonium concentration immediately and not by taking the samples that are bottled, bringing them back to the lab and filtering them, as is done in most environmental monitoring routine activities.

Rogers: Make the separation right there?

Nyhan: Yes. The solution that comes through is analyzed immediately for plutonium with no waiting period and possible time for a reaction between plutonium and sediments. I don't known the best way to do this, but it's a thought.

Rogers: The difficulty I have, though, is sorting out the movement by this chemical sorption-desorption mechanism and the feelings I have that there is sediment particle movement within the sediment itself. This physical movement is supported by some of the Rocky Flats work that tends to make that look like maybe a dominant mechanism of movement over the diffusion model. That seems very possible to me. Before we can make judgments on whether or not these two mechanisms exist and how much more work is required. You may be able to sort the mechanisms by studying migration through rock. You can get some of these rates of movement by sorption-desorption through rock where you are sure you are not watching small silicious particles filtering through. But in soil I'm not too sure that we will ever really be able to sort those two mechanisms.

Nyhan: You also mentioned during your talk that you've got a situation where you've got fine textured sediments in the canals. What about the stream banks? Do the stream bank soils have higher concentrations of silt and clay?

Rogers: In some of the canals you can get down into the original stream banks that have not been disturbed, there is packed clay. When the canals were built they formed the banks with packed clay. They have almost no permeability at all.

Nynan: That's interesting. At Los Alamos we have just the opposite situation of coarse alluvium in the steam channels and finer textured soils. No, I guess it's the same situation, except to a different degree. About 80 to 90% of the alluvium in the stream channel is sand-sized materials or larger, and stream banks are about 40% silt and clay.

Rogers: Yes, that's typical of normal distribution. When you have a fast channel flowing, one would expect the fine material to be swept on, except near the banks where there is a bit more drag. As a matter of fact, in the South Canal area there in the central meandering channel which is reasonably fast flowing, you do find that this channel contains somewhat coarser sediment than just up on the canal base which is covered with vegetation. Obviously the vegetation, as you would expect, tends to still the turbulence and causes a quieter condition for sedimentation of small particles.

Nyhan: The difference is of course that we're seeing uptake of plutonium by the stream bank, whereas you're not.

Rogers: But you see, ours didn't go into that stream in solution. Ours went into that stream as sediment. Now that may be different from the situation you have. Our effluent we piped directly to the river. Apparently the currents in that river are a bit more pronounced than I realized because I expected to find a lot muddier bottom to that river. It is mostly sand and gravel.

Serne: Maybe you should check for seasonal trends. Maybe you'll get a spring runoff that flushes fines and in fall low flow rates deposit mud or fine material.

Bruns: I had one question on your resuspension factors. Did you make a study on varying the wind speed?

Rogers: No, I did not. As a matter of fact, during this period when we did this, the wind speed varied from about 0 to 5 mph.

Bruns: So these are 0-5 mph values.

Rogers: During the actual time the samples were being taken, we are not sure because we don't have a meteorological station. We wish we had this information now.

FIELD AND LABORATORY OBSERVATIONS ON PLUTONIUM OXIDATION STATES

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ABSTRACT

Test methods for evaluating Pu oxidation state species in experimental samples were developed and tested. These methods, which are based on solvent extraction and coprecipitation principles, enabled the elucidation of Pu(VI) and Pu(IV) monomeric species in laboratory soil-water equilibration studies, plutonium dioxide dissolution studies, and in seepage solution collected near a solid waste burial ground. The methods employed also allowed the identification of soluble polymeric Pu species which do not revert to monomeric forms upon acidification.

INTRODUCTION

Soluble Pu species present in the environment may influence the rate of Pu entry into food chains. In evaluating the short- and long-term behavior of Pu released to the biosphere, solubilization reactions capable of mobilizing Pu require elucidation. Such mobilization mechanisms may involve the formation of organic and inorganic complexes which stabilize Pu in solution. The oxidation state of Pu can exert an effect which may be confused with organic complexation. For example, if Pu(VI) were a stable oxidation state, it should behave somewhat like U(VI). Since uranyl ion forms strong carbonate complexes, Pu(VI) carbonate complexes should also be stable. Because soluble uranyl carbonate is an important species of U in natural waters, similar behavior might be expected for Pu(VI). In addition to carbonate complexing, Pu(VI) forms a more soluble hydroxide than Pu(IV)$^{(2)}$ and would dominate the soluble species present in a mixture of solid phase (Pu(IV) and Pu(VI)) hydroxides.

However, Pu(VI) is easily reduced by organic substances that occur naturally in the environment.$^{(1)}$ A comparison of the Pu(IV)-Pu(VI) and U(IV)-U(VI) redox couples will reveal that Pu(VI) is much more readily reduced than U(VI). Since U(IV) only forms in anaerobic sediments, it is reasonable to assume that Pu(VI) reduction will occur in less reductive environments. Such comparative studies have not been reported, however.

The purpose of the research reported in this paper was to determine the Pu oxidation state species present in various experimental or laboratory media. The identification of these Pu species was a requirement necessary for interpreting why soluble Pu species were found in experiments devoid of soluble organic complexing groups. Furthermore, the observation that Pu was leaching from a solid waste burial ground required that the mechanism be resolved, since either organic chelating agents or oxidation state could account for the observed leaching species.

Pu VALENCE DETERMINATIONS

General

To understand the factors influencing the distribution of Pu between aqueous and solid phases, it is essential that the oxidation state species present in environmental media be understood and quantified. Furthermore, to understand Pu mobility in the environment, species identification is critical. To accomplish these needs, recognized separation techniques for evaluating actinide oxidation states at tracer levels have been adapted and tested. The information presented here represents a part of these efforts.

The requirements for determining the nature of Pu species in solution at tracer levels must be met by radiochemical methods. These methods fall into two general classes: solvent extraction and coprecipitation. Solvent extraction, as used in this paper, covers two systems: chelation, whereby extraction selectivity for Pu(IV) can be accomplished by conducting extractions from strong acid solutions; and ion association extractions, where the species partitioning into the organic solvent is a Pu-nitrate complex. Coprecipitation methods rely on the carrying of Pu species which because of their low concentrations do not themselves form a distinct precipitate. To form precipitates, Zr(IV), Pr(III), or Th(IV) are used in micro amounts to carry Pu(III) and/or Pu(IV), and U(VI) is used to carry Pu(VI) [and Pu(V) if selectively oxidized to Pu(VI).

An important aspect of these radiochemical procedures for determining Pu oxidation states is that the methods employed must not alter the actual distribution of species. This requirement has been of major concern in the application of the procedures to be discussed. By employing both and coprecipitation methods, the authors have found it possible to determine ionic Pu(IV) and Pu(VI) as well as Pu species which behave as "polymer", all in the same solution. The separation methods have been applied to a number of different experimental systems with satisfactory results. However, only extended usage will validate the general applicability of the methods.

RADIOCHEMICAL DETERMINATIONS: Pu(IV) AND Pu(VI)

Extensive studies have been conducted on the separations chemistry of the transuranium elements. An excellent treatment of the early literature has been assembled by Hyde.(5) A brief discussion of methods tested and used in the present study is presented here since much of the source material was found in progress reports of the Manhattan Project which are not widely available.

Zr-Iodate: Zirconium (IV) forms a very insoluble iodate which carries Pu(IV) and Np(IV) practically quantitatively(5) Iodate rapidly oxidizes Pu(III) so that it coprecipitates as Pu(IV) (2). Hexavalent actinides do not carry. Iodate precipitates Pu polymer(2) so that any polymer present probably carries with the $Zr(IO_3)_4$, although depolymerization may also occur in the presence of iodate. Thorium can also be used as a carrier in place of Zr.

Pr-Fluoride: Insoluble rare earth fluorides carry the III, IV, and V actinide oxidation states, but hexavalent species do not coprecipitate(5) Plutonium(VI) is, however, partially reduced by impurities in HF, requiring the presence of a holding oxidant.(6,8) Dichromate has been used for this purpose. In 1 M HNO_3, oxidation of Pu(IV) by dichromate at room temperature is very slow(8) and can be neglected if the separation is conducted rapidly. Polymer carries with the precipitate, being depolymerized in the process (Reference 3, Procedure 2). Plutonium V is oxidized to Pu(VI).

TTA-Xylene: Ionic Pu(IV) selectively extracts from 1 M acid solutions into organic phases containing thenoyltrifluoroacetone (TTA). Plutonium III, V, and VI do not extract appreciably from 1 M acid.(9) Plutonium polymer does not extract.(2)

Hexone: Hexone (methylisobutylketone) extracts the nitrate salts of Pu(IV) and Pu(VI) from acid solutions.(2) Trivalent actinides and Pu(V) do not readily extract.(2) With an aqueous phase 1 M in HNO_3 and 3.5 - 4.0 M in $Ca(NO_3)_2$, the partition coefficient (organic-Pu/aqueous-Pu) for both Pu(VI) and Pu(IV) is about 30.(2) If hexone extraction is used following the TTA-xylene extraction step, only Pu(VI) is the extracting species. Polymer does not extract. Plutonium V will extract (as VI) in the presence of BrO_3^-.

Uranyl Acetate: One of the few precipitation procedures selective for hexavalent actinides is sodium uranyl acetate.(5) Uranium (VI), plutonium(VI), and neptunium(VI) form isomorphous acetate compounds. The procedure which is detailed was adapted from that report by Connick.(4) Dichromate is present as a "holding oxidant" because the added acetate may have reducing impurities. Omission of dichromate in our work has resulted in low yields, although whether reduction to Pu(V) was the cause has not been tested. Tetravalent Pu has not carried significantly under the test conditions, indicating no appreciable oxidation by dichromate occurs in the procedure. This is due to conducting the precipitation from 1 $\underline{M}$ HNO_3.

Diethyl Ether: From an aqueous phase 10 $\underline{M}$ in ammonium nitrate and 1 $\underline{M}$ in nitric acid, Pu(VI) preferentially extracts into diethyl ether (partition coefficient of 1.0).(3) Plutonium(IV) extracts only to the extent of 4%. The ether should be prescrubbed with 2 $\underline{M}$ HNO_3-0.1 $\underline{M}$ sodium dichromate to reduce the subsequent extraction of nitric acid from the salting solution and to destroy peroxides. Traces of dichromate remaining in the ether are lowered by scrubbing with 1 M nitric acid. This procedure is a classical method for Pu(VI), but is not recommended because of the difficulties in manipulating diethyl ether. It is diagnostic, however.

RADIOCHEMICAL SEPARATION PROCEDURES: Pu(IV) AND Pu(VI)

1. Zr-Iodate. The sample is made 2 M in HNO_3, 0.1 - 1.0 mg of Zr is added per milliliter, and KIO_3 is added to 0.05 - 0.1 M final concentration. The iodate precipitate forms immediately upon mixing. After 5 min of digestion, the sample is centrifuged and the precipitate washed with 2 M HNO_3 - 0.01 M KIO_3 solution. After centrifugation, the washed precipitate (if a small amount of Zr was used) is transferred to a tantalum planchet, dried, heated in a flame, and alpha counted. Larger amounts of Zr (i.e., from large volumes) are dissolved in 1 M HNO_3 - 0.05 M sodium bisulfite; a small amount ($\leq$ 0.5 mg) of praseodymium is added, followed by HF (final concentration 1 M), and the Pu carried on PrF_3. Zirconium is largely left in solution. The aqueous phase from the $Zr(IO_3)_4$ precipitate contains Pu(VI). This Pu can be assayed by reduction (sodium bisulfite) and carrying on PrF_3. Bisulfite destroys iodate and reduces Pu(VI).

2. Pr-Fluoride (the "holding oxidant" method): In an ice bath (optional), an aliquot of the solution to be analyzed is made 1 M in HNO_3 followed by making the solution 0.5 M in H_2SO_4 and 0.02 M in sodium dichromate. Praseodymium is also added ($\leq$0.5 mg). The solution is made 2 N in HF with freshly treated 30 N HF. The HF is treated by adding dichromate to color the acid slightly yellow. After mixing, the precipitate is digested for 5 min at room temperature, centrifuged, washed with 1 M HNO_3 - 1 M HF containing a trace of dichromate. The precipitate is then mounted on a tantalum disk or dissolved if solvent extraction (TTA) is desired, particularly if ^{241}Am is present.

3. TTA-Xylene: A 0.5 M TTA (in xylene) solution is shaken for 10 min with an equal volume of aqueous sample acidified to 1 M HNO_3. After phase separation, the aqueous phase is re-extracted with 0.5 ml of TTA-xylene for 5 min. The combined TTA-xylene phases are then backwashed with fresh 1 M HNO_3 for 10 min. The TTA-xylene phase is then evaporated on a stainless steel planchet, flamed, and counted. When TTA-xylene extraction from a PrF_3 precipitate is desired, the PrF_3 is dissolved in 1 ml of 1 M HNO_3 - saturated boric acid solution. Five drops of 3 M $NaNO_2$ is added and the mixture let stand for 10 minutes. The TTA-xylene extraction step is then used.

4. Hexone: Following the TTA-xylene step, the first raffinate is made 3.5 - 4.0 M in $Ca(NO_3)_2$ and extracted for 3 min with an equal volume of hexone. Most of the hexone is removed and the extraction repeated. The hexone is pretreated with 1 M HNO_3 - 0.01 M $KBrO_3$ solution to destroy reductants and equilibrate the hexone with acid. The hexone phase contains Pu(VI) and is evaporated on a stainless steel planchet, flamed and counted.

5. Uranyl Acetate: The sample is made 1 M in HNO_3 and 20 - 40 mg/ml of UO_2^{2+} carrier is added. Solid $NaNO_3$ is then added to a final concentration of 5.0 M. Immediately after adding sodium dichromate (final concentration 0.01 M), solid sodium acetate (final concentration 3 M) is added and mixed. The precipitate forms immediately. After 5 min, the precipitate is centrifuged, washed with 0.5 M sodium acetate - 0.5 M acetic acid - 3 M $NaNO_3$ solution. The washed precipitate is dissolved in 1 M HNO_3, ^{242}Pu or ^{236}Pu tracer added, and the solution reduced with hydroxylamine (0.1 M final concentration). The reduced Pu is separated from uranium by a PrF_3 step followed by solvent extraction (TTA-xylene). Any uranium carry-through may interfere with ^{242}Pu resolution; ^{236}Pu is therefore a better internal tracer, although not essential. Plutonium-242 is used in this laboratory. Alpha spectrometry is required for these internal standards.

RECOMMENDED DETERMINATIONS

The following methods are recommended. The order of preference is:

A. TTA-xylene extraction followed by hexone extraction. One to two ml sample volume is recommended.
   1. Purpose: extract Pu^{4+}, then PuO_2^{2+}.
   2. Advantages: rapid, quantitative, determines only Pu species which revert to ionic forms in 1 M HNO_3 (i.e., Pu polymer is not readily dissolved).

B. $Zr(IO_3)_4$ or PrF_3 (holding oxidant procedure).
   1. Purpose: carry Pu(IV), including polymer.
   2. Advantages: useful for separations from large volumes.
   3. Disadvantages: time-consuming, polymer carries, Am and Cm also carry. Internal standard (^{242}Pu(IV)) desirable.
   4. Plutonium(VI) in the supernatant is reduced with hydroxylamine or sodium bisulfite, then carried on PrF_3.

C. Uranyl Acetate
   1. Purpose: carry Pu(VI) only.
   2. Disadvantages: time consuming, introduces alphas from U which must be decontaminated.
   3. Advantage: specific for Pu(VI).

TESTING AND APPLICATIONS OF VALENCE DETERMINATIONS

TEST AND REFERENCE SOLUTIONS

To quantify results and prepare reference Pu solutions with known oxidation states, simple methods for valence preparation are desirable. Heating Pu in 8 M or stronger nitric acid insures all Pu(IV).(10) Heating Pu in 70% perchloric acid at 195°C for 15 min forms Pu(VI) with no residual oxidant.(10)

Table 1 presents a comparison of the methods on known and unknown mixtures of Pu(IV) and Pu(VI). Sample 1 was a stock solution of concentrated Pu which was oxidized to Pu(VI) by heating in 1 M HNO_3. The valence distribution was then determined by spectrophotometric techniques. Sample 2 was a dilution of this solution. The results of the chemical separations show that essentially the same valence distribution was determined. Sample 1 was about 0.1 M in Pu, while the concentrations used for the tests on sample 2 were near 10^{-8} M. Utilizing ^{237}Pu, Pu(IV) and Pu(VI) species were tested at about 10^{-13} M Pu. These results are presented for solutions 3 and 4. The master ^{237}Pu solution also was tested and found to contain both oxidation states. Thus, it was treated as an unknown mixture and the various procedures tested. These latter results are tabulated for sample 5. Samples 6 and 7 represent analog actinide species with more stable valences.

TABLE 1. Comparison of Methods for Plutonium Valence State Determination

Sample	Method	Valence Determined	Results, %	
			(IV)	(VI)
1. Concentrated Pu solution	Spectrophotometric	IV, VI	2-3	97-98
2. Dilution of (1)	TTA-xylene	IV	2	---
	Pr-fluoride	IV^a	4	---
	Zr-iodate	IV^a	2	---
	U-acetate	VI	---	97
	Hexone	VI	---	98
3. Tracer ^{237}Pu(IV)	Pr-fluoride	IV^a	96	---
	U-acetate	VI	---	2
4. Tracer ^{237}Pu(VI)^b	Pr-fluoride	IV^a	1	---
	U-acetate	VI	---	96
5. Unknown mixture of ^{237}Pu Oxidation States	TTA-xylene	IV	12	---
	Zr-iodate	IV^a	12	---
	Th-iodate	IV^a	12	---
	Pr-fluoride	IV^a	12	---
	Diethyl ether	VI	---	89^c
	U-acetate	VI	---	88
6. ^{233}U(VI)	Pr-fluoride	IV	1	
7. ^{234}Th(IV)	Pr-fluoride	IV	96	

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[a] Pu(III) also determined if present.

[b] Prepared by oxidizing with dichromate.

[c] Calculated from published partition coefficient after determining fraction in ether phase.

The results for the various samples demonstrate that the adapted procedures provide adequate accuracy and consistency, allowing their use in testing unknown systems. However, unknown systems must be carefully evaluated by more than one method, recognizing the fact that as unknowns, many factors may influence the results. At present, Pu(V) cannot be distinguished from Pu(VI) as the separation conditions probably oxidize Pu(V), therefore appearing as Pu(VI). The radiochemical separation procedures that were discussed represent the basic steps necessary to accomplish the separations. It is recommended that a radiochemist be consulted to finalize the application of the methods to a researcher's particular needs. It is recommended that preliminary tests be made on Pu solutions of known oxidation state before applying the methods to unknown samples. A convenient method of further verifying the oxidation states present is to add ^{242}Pu(IV) to the sample and conduct the extractions or precipitations. The recovery of the added and indigenous Pu can then be compared by alpha spectrometry.

BEHAVIOR OF Pu AND Cm IN WHITE OAK LAKE WATER

For two consecutive years (October, 1974 and September, 1975) White Oak Lake (WOL) water samples were collected for study. White Oak Lake is an impoundment which receives effluents from ORNL operations and has transuranic activities higher than global fallout levels. Insights into the environmental solution chemistry of the transuranium elements were thus sought by selective studies. A part of the data derived from this work is presented to illustrate the relative behavior of Pu and Cm, and suggest the existence of different Pu forms which may be related to discharges from a solid waste burial ground (Table 2). The data on the burial ground investigation will follow in a subsequent section. For the 1974 sample, most of the Pu was associated with the particulate phase (greater than 0.45 μm). There appears to be a difference in the ^{238}Pu/^{239}Pu activity ratios associated with the less than 0.45 μm filtered fraction (soluble) and the total sample. The difference in Pu activity ratios appear small when the total vs. the soluble fraction is examined for both samples. However, the Pu activity ratios associated with the soluble Pu and retained by an anion exchange resin are larger than the soluble fraction as a whole; i.e., the anionic ratio doubled in both the 1974 and 1975 samples. The cation exchange resin results for 1974 further suggest that the changes in ratios are real; that is, the ratio (1.3) is less than the total soluble ratio (3) indicating that an anionic form is preferentially being retained by the anion exchanger but not the cation exchanger. The amount of Pu (1975 sample) which passed a nominal 10,000 molecular weight Amicon membrane was essentially the same as the total soluble fraction and had the same activity ratio, indicating non-colloidal associations. However, when the soluble fraction was passed through the anion resin, the amount of retained Pu dropped to a value (0.10 dpm/liter) which was significantly (50% confidence level)

TABLE 2. Behavoir of Pu and Cm in White Oak Lake Water Samples Collected in October 1974 and September 1975

		1974		1975	
Transuranic	Fraction	dpm/l	ratio[a]	dpm/l	Ratio[a]
Plutonium	Total	0.73	0.8	0.8-1.4[b]	0.9
	> 0.45 μm	0.64	0.7	---	---
	< 0.45 μ	0.09	3 ± 1	0.16	1.3
	< 10,000 MW	---	---	0.14	1.3
	Anionic	0.09	6 ± 3	0.10	2.7
	Cationic	0.013	1.3 ± 0.5	---	---
^{244}Curium	Total	1.8-2.5	---	0.5-0.9[b]	---
	< 0.45 μm	1.1	---	0.38	---
	< 10,000 MW	---	---	0.30	---

[a] Ratio ^{238}Pu/^{239}Pu.

[b] L. D. Eyman, personal communication.

different from the total in solution (0.16 dpm/liter). The ^{238}Pu/^{239}Pu activity ratio likewise increases, again suggesting preferential ^{238}Pu retention by the anion column.

Since the 1 σ counting error for the data typically was about 10%, the individual numerical values are of less importance than the fact that a certain consistency appears in the data. The fact that the Pu was present at such low concentrations necessitates that any conclusions drawn remain tentative. However, the data, when taken as a whole, suggest two important conclusions: first, much of the ^{238}Pu activity associated with the soluble fraction appears to carry a negative charge, and the ^{238}Pu appears more soluble than ^{239}Pu. Secondly, Cm is more soluble than Pu, as indicated by the lower distribution between total and soluble fractions.

Behavior of Pu in Burial Ground Seepage Water

A source of the soluble ^{244}Cm and ^{238}Pu activity in WOL water appeared to be seepage from a solid waste burial ground (no. 5), located north of a tributary creek (Melton Branch) feeding WOL. The distance from where this seep enters the creek to the WOL water sampling location is 1.8 kilometers. Levels of Pu alpha activity above background concentrations have been found in soil taken from the vicinity of the seeps and in samples taken at intervals downslope to Melton Branch (about 45 meters in distance). The dominant Pu isotope present is mostly ^{238}Pu (T. Tamura, personal communication). The trenches located in the burial ground fill through infiltration of precipitation and overflow during the wetter winter months. This soaking leaches radioactivity out of the buried waste and trench overflow moves it downslope into Melton Branch. Remedial measures to minimize water infiltration into the trench have been completed (J. O. Duguid, personal communication).

In July 1974, seepage solution was collected from a sump located below one of the burial trenches and filtered through a millipore 0.45 μm membrane. The results of Pu and Cm analyses are in Table 3. The solution was subsequently stored in a polyethylene bottle with no measures taken to preserve the sample.

In December 1975, following the testing of the valence determination procedures, an attempt was made to determine if the solubility characteristics of ^{238}Pu noted in the seeps and suggested by the ^{238}Pu behavior in WOL could be explained by oxidation state chemistry. The total activity determined for the two dates showed that ^{244}Cm largely disappeared from solution during the 1.5 year sampling interval, while the ^{238}Pu activity remained about the same (50-60 dpm/liter). This finding is surprising because the solution had a pH of 7.9 and a HCO_3^- concentration of 9.1 m$\underline{M}$. Plutonium should be less soluble than Cm in this medium. However, Pu can theoretically exist in three oxidation states at this pH, and each oxidation

TABLE 3. Preliminary Observations on the Behavoir of ^{238}Pu in Burial Ground Seepage Solution

Date and Type Analysis	^{238}Pu (dpm/l)	^{244}Cm (dpm/l)
July 1974		
Total, <0.45 μm	60 ± 6[e]	700 ± 70
December 1975		
Total, < 0.45 μm	50 ± 5	70 ± 7
Pu(IV)[a]	a. 10 ± 1 b. 11 ± 1 c. 12 ± 1	
Pu(VI)[b]	a. 36 ± 3 b. 31 ± 3 c. 38 ± 3	
Pu(VI) UO_2[c]	29 ± 3	
Pu(VI) Ether[d]	18 ± 2	

[a] PrF_3, holding oxidant procedure.

[b] PrF_3, after reduction of supernatant from (a).

[c] Uranyl acetate method.

[d] Ethyl ether extraction.

[e] Uncertainties based on 2 S.D. of counting error.

state has its own unique chemistry. The oxidation state test procedures indicated that only about 20% (11 dpm/l) of the Pu existed as Pu(IV). Most of the Pu which did not coprecipitate on the initial PrF_3 (i.e., Pu(III) or Pu(IV)), carried when the raffinate was treated to convert Pu species (i.e., Pu(VI)) to forms which will carry on PrF_3. The uranyl acetate and ether extractions also indicated, at least qualitatively, the presence of Pu(VI). The ether data is the least definitive; however, the extraction procedure is sensitive to interferences like $SO_4^{=}$, F^-, etc., which could be in the waste solution. Plutonium (V) could be present and would not extract.

Soluble complexes like EDTA, etc., would likely keep Pu(IV) in a soluble state. However, previous testing demonstrated that even these strong chelates do not prevent Pu(IV) from carrying in the PrF_3 procedure. When ^{242}Pu(IV), ^{237}Pu(IV), and ^{237}Pu(VI) oxidation states were added to aliquots of the seepage solution, the known oxidation states behaved as expected when the PrF_3 and UO_2^{2+} precipitations were conducted. This behavior suggests the absence of significant interferences which might have held Pu in solution, resulting in major errors in the normal Pu precipitation behavior. Thus a significant fraction of the Pu was hexavalent, and not organically-complexed Pu(IV).

EVIDENCE OF Pu(VI) IN SOLUTIONS CONTACTED WITH HIGH-FIRED PuO_2

Leaching studies with high-fired (1150°C) PuO_2 had indicated that only a small fraction (less than 10%) of the alpha activity leachable from PuO_2 extracted into TTA-xylene (i.e., Pu^{4+}). A batch-type equilibration study subsequently showed that about 95% of the soluble Pu present in a neutral, dilute carbonate (approximately 10^{-4} $\underline{M}$ NH_4HCO_3) solution contacting plutonium dioxide microspheres was Pu(VI) or Pu(V). Five percent behaved as Pu(IV). No Pu(III) was found.

To illustrate this, valence species determinations after 500 hr of solution contact are presented in Table 4. The methods used to evaluate the valance distribution in the solution contacting the microspheres included both precipitation and solvent extraction techniques. The total Pu present was determined by alpha spectrometry. Americium-241, which contributes to the 5.5 meV ^{238}Pu count, was determined using the $^{239}Pu/^{238}Pu$ ratio determined from a mass analysis supplied with the oxide sample.

The Zr-iodate method showed that the amount of Pu(IV) in the solution was approximately 0.18×10^{-10} $\underline{M}$. The amount of Pu(VI) present was then determined by reducing the Pu which did not carry with Zr and precipitating it with PrF_3. This value was 3.7×10^{-10} $\underline{M}$. Solvent extraction using TTA-xylene and then hexone determined essentially the same Pu species distribution. When the PrF_3 procedure was conducted using either the holding oxidant modification or an initial reduction step to convert Pu(VI) to a precipitable form, evidence for Pu(VI) was found. Plutonium(VI) determined by the U-acetate procedure agreed with the hexone-determined value.

TABLE 4. Valence Distribution of Soluble Pu Species Contacting High Fired PuO_2

Analytical Method	Valence Determined	Pu	
		$(10^{-10}\ \underline{M})$	(dpm/ml)
1. Total	---	4.3	14.1 ± 1.2[c]
2. (a) Zr-Iodate	IV[a]	0.18	0.6 ± 0.3
(b) Pr-Fluoride (reduced)	VI	3.7	12.2 ± 0.7
3. (a) TTA-Xylene	IV	0.15	0.5 ± 0.3
(b) Hexone	VI[b]	3.5	11.5 ± 1.3
4. Pr-Fluoride (holding oxidant)	IV[a]	0.71	2.3 ± 0.5
5. Pr-Fluoride (reduced)	All	3.1	10.1 ± 2.1[d]
6. U-Acetate	VI	3.7	12.1 ± 1.5[d]

[a] Pu(III), if present, coprecipitates.

[b] Raffinate from TTA-xylene extracted with hexone.

[c] Uncertainties based on 2 S.D. of counting error.

[d] Assuming 95% carried on respective precipitate, ^{242}Pu (10.0 dpm) was added to U-acetate precipitate prior to subsequent steps and used to correct for recovery.

Other oxide equilibration experiments have shown that in addition to ionic Pu(IV) and Pu(VI) in the aqueous phase, a form of Pu refractory towards solvent extraction but carrying on the Zr or Pr precipitates was present. This Pu activity also sediments in the ultracentrifuge, indicating the presence of polymer-like material. Some of most of the "ionic" Pu(IV) originated from this material during TTA extraction. It therefore appears possible, as discussed in the methodology section, to detect polymer forms by comparing results from the solvent extraction and precipitation methods.

SOIL CLAY SORPTION STUDIES

Additional evidence of the importance of Pu valence species can be illustrated by discussing the results of Pu sorption studies. In the course of studying the influence of soil clay constituents on actinide element sorption, it was observed that when ^{238}Pu was added as Pu(IV), large amounts of the added Pu remained in solution after many weeks of equilibration. In fact, this observation was the stimulus to develop the oxidation state procedures. These observations are illustrated in Table 5.

The clay fraction of a Miami silt loam soil was treated to first remove organic matter and also to remove organic matter plus free iron oxides.$^{(1)}$ When the distribution of Pu between clay and solution was determined, both the minus organic matter (-O.M) and blank (no clays present) replicated treatments showed

TABLE 5. Sorption of ^{238}Pu(IV) to Treated Clays [pH 4.0, 5×10^{-3} M $Ca(NO_3)_2$]

Time and Treatment	Percent Sorbed	Evidence of Polymer or Pu(VI)[a]	K_d[b]
3 Weeks			
Clay	99.86	---	2.9×10^5
-O.M.	50.0	---	4×10^2
-Fe + O.M.	99.8	---	2×10^5
Blank(c)	71	---	---
18 Weeks			
Clay	99.8	No	---
-O.M.	61.5	Yes	3.5×10^2
-Fe + O.M.	99.9	No	---
Blank	71.7	Yes	---
52 Weeks			
Clay	99.9	< 20%(VI)	1.9×10^5
-O.M.	99.8	50%(VI)	8.1×10^4
-Fe + O.M.	99.8	< 20%(VI)	8.1×10^4
Blank	78.6	25%(VI)	---

[a] By TTA extraction, PrF_3 precipitation (holding oxidant method) and hexone extraction.

[b] K_d is defined as the ratio of the amount adsorbed to the amount adsorbed to the amount in solution. Units are ml/g.

[c] No clays present.

low sorption of Pu. At 3 week equilibration, 50% of the Pu in the -O.M. treatment had sorbed, while 71% of the Pu in the blank treatment had disappeared from solution. After 18 weeks, TTA-xylene extractions on the soluble Pu in all experiments suggested the presence of Pu(VI) or polymer (i.e., non-TTA extractable Pu was present). After 52 weeks of equilibration, application of the then-developed procedures revealed that Pu(VI) was indeed present and constituted a significant fraction of the soluble Pu in the -O.M. and blank treatments. The Pu(VI) apparently formed through disproportionation(2) and was stable even after 52 weeks. This observation suggests that sorption studies using Pu(IV) need to be carefully examined because the soluble species which do not sorb may be a different oxidation than that initially added. The problem would be more pronounced with ^{239}Pu because of the higher mass associated with each radiodecay event of that isotope. In the study briefly described here, ^{238}Pu was added at about 0.6 ppm (Pu mass/clay mass). This is a very high level, although the presence of strong sorption surfaces often requires such levels for Pu detection.

CONCLUSIONS

Due to the absence of reducing substances, Pu(VI) appears to be stable in the aqueous solutions tested. It should be stressed that the amount of Pu(VI) present in the systems described represented a small fraction of the total Pu present. The exception was the burial ground leachate where much of the Pu was Pu(VI). However, the source (burial ground) may contain primarily Pu(IV). The finding of Pu(VI) species in the PuO_2 dissolution study is especially significant. To the authors' knowledge, Pu(VI) has never been identified as a species that is present in environmental-type PuO_2 systems. In fact, no determinations of monomeric Pu species have been reported for any environmental studies.

The observation that Pu(VI) [or possibly Pu(V)] contributes to the Pu present in a number of experimental systems stresses the necessity for Pu valence state identification. Such determinations are essential if the environmental mobilization mechanisms of Pu are to be understood. Thus, when trace amounts of soluble Pu are found in solutions containing large amounts of insoluble Pu (such as PuO_2) the conclusion should not be immediately reached that organic complexes of Pu(IV) are responsible for the solubilization. The evidence reported here suggests that Pu(VI) needs to be considered as well.

REFERENCES

1. E. A. Bondietti, S. A. Reynolds, M. H. Shanks, Environmental Plutonium Chemistry, I. Reactions of Plutonium with Environmental Organic Substances, submitted to Soil Sci. Soc. Amer. Proceedings (1976).

2. J. M. Cleveland, The Chemistry of Plutonium, Gordon and Breach Science Publishers, Inc., New York (1970).

3. G. H. Coleman, The Radiochemistry of Plutonium, National Academy of Sciences-National Research Council, NAS-NS 3058, National Bur. Std., Springfield, Virginia (1965).

4. R. E. Connick, J. W. Golman, and A. C. Wahl, USAEC Report, CN-363, (Manhattan Project Report) (1942).

5. E. K. Hyde, "Radiochemical Separation of the Actinide Elements," Ch. 15. The Actinide Elements (Seaborg, G. T., Katz, J. J., Eds.), McGraw-Hill Book Company, Inc., New York (1954).

6. D. E. Koshland, USAEC Report CN 2041 (1945).

7. L. M. Lavkulch, and J. H. Wiens, Comparison of Organic Matter Destruction by Hydrogen Peroxide and Sodium Hypochlorite and Its Effects on Selected Mineral Constituents, Soil Sci. Soc. Amer. Proc. 34 (1970) 755-758.

8. W. H. McVey, USAEC Report CN-1588 (1944).

9. A. M. Poskanzer, and B. M. Foreman, Jr., "A Summary of TTA Extraction Coefficients," J. Inorg. Nucl. Chem. 16 (1961) 323-336.

10. J. Rydberg, and L. G. Sillen. "Combination of Unit Processes for Isolating Plutonium." Acta Chem. Scand. 9 (1955) No. 8, 1241-1251.

FOLLOWING E. A. BONDIETTI'S PRESENTATION

QUESTIONS AND ANSWERS

Polzer: Can you distinguish Pu(V) from Pu in the other oxidation states? In other words, can you say that Pu(V) is not present?

Bondietti: First of all, no one even agrees whether Pu(V) carries with the fluoride or not, even neptunium (V). Plutonium (V) is presumably very easy to oxidize. In the PuF_3 system you have dichromate as a holding oxidant. Dichromate in the cold and in 1N/nitric acid will not oxidize Pu(IV) to Pu(VI) over the time required for the analysis. We tested this as I said before. You find references in the literature that say cold dichromate will oxidize Pu(V) to Pu(VI). If there is any Pu(V) present, it would be oxidized to Pu(VI) and would not carry. The hexone extractions are also not definitive. We pretreat with bromate to get any reducing substances out, and the same thing with ether to get the peroxides out of the ether. There might be traces of these things around that would oxidize any Pu(V) to Pu(VI). They do oxidize Pu(IV) to Pu(VI). I made sure that we did not get into that trap. Based upon the literature and doing my own research, I'm afraid that if any Pu(V) is there, (and maybe a lot of this you see as Pu(V)), it gets oxidized to Pu(VI). I don't know. We are working on this.

Rai: Do you have any information on the pH and Eh of these solutions?

Bondietti: This is pH 7. That's pretty close. It's in equilibrium with the atmosphere. Why it's coming off the oxide as Pu(VI) I don't know. I might mention on this one that these oxides had previously been in pH 2 solution for a year and a half before they were taken out and washed and this experiment started. It's possible that sitting at that pH there could have been some disproportionation at the surface. I don't know. We're going to take some oxide that has had no contact with water and check the same thing. But we know that the minute you put these in water the PuO_2, which was made by the Sol-Gel process, there is quite a bit of activity that comes off of them. It appears to be soluble.

Holcomb: When you say "quite a lot" would you quantify that?

Bondietti: No, I can't. All I'm saying is that it's more than if you were to wash them and do it again. What I wanted to present today was mainly the valence work and give you an idea of some of the things that we've found, and how we are trying to understand the oxidation states in the solution. Because I somehow feel that we should understand that, both in terms of the phase diagram calculations and experimentally. We are developing methods to do it, and it's very hard to describe some of the systems that we try to set up, equilibriums and distribution coefficients. I sometimes wonder, when we study rates or distribution coefficients, if we really aren't measuring distribution coefficients of alpha particles rather than distribution coefficients of species. Somehow we have to know what the species in solution are. Obviously that's terribly difficult.

Holdomb: Were these done in glass?

Bondietti: Polypropylene.

Nyhan: Ernie, are there large amounts of nitrate possibly coming out of some of these burial grounds too? I was trying to think of a way to explain the movement of the plutonium-238 from the burial grounds in the water samples that you talked about.

Bondietti: This is a solid waste burial ground. What is in there, heaven knows.

Nyhan: Couldn't the nitrates present in the leach water with the plutonium account for more oxidizing conditions? I don't know, but in looking at the slide that you presented it looks like there could also be reduction under certain types of conditions and possibly even formation of plutonium (III).

Bondietti: Pu(III) formation would require acid, anaerobic conditions. The leachates are alkaline.

Nyhan: There is another school of thought that states that under natural conditions of a stream or in a lake that the oxidation/reduction potential is more reducing (due to the biological activity in the sediments) than a lot of the solutions you used in the laboratory for testing out similar types of equilibrium relationships.

Bondietti: I think the Kd would be even higher than maybe Pu(IV). I don't know what Dr. Polzer thinks, but some of the data I have seen on Pu(III) absorption, the soils the Kd goes higher than with Pu(IV). On Pu(IV) you don't know if they had disproportionation . . . Anyhow, we see Pu(VI) in some systems. How stable it is in the environment is the question when it starts to get into sediments and more reducing conditions. Some previous work of mine has shown that many organics can reduce Pu(VI). How significant these things are in the real world is of course another question. And whether or not in the seepage solution there really is Pu(VI) or whether that's an artifact that occurred in the bottle in the laboratory. But at least I think we have identified Pu(VI) in the system. Again, I've done most of these analyses myself and I myself am satisfied that what we're measuring is Pu(VI) and not something else.

Rai: Thermodynamic calculations indicate that under an oxidizing environment, the PuO_2^+ and PuO_2^{+2} would be predominant whereas Pu^{4+} would be present in negligible amounts.

Bondietti: The only reason I presented this was because Dr. Polzer and I have talked about it a number of times. You want to remember the concentration of plutonium for example in this trench is 10^4 dpm/liter and we're measuring in the solution coming out 50-60 dpm/liter. We're not talking about very much plutonium, but the question is why is it coming out. Most of it is Pu(VI), and I think we're going to have to recognize that although we focus on the mobile plutonium most of it is not moving. What is moving is of interest to understand why it is moving.

Serne: Ernie, in your time experiments of 3 weeks up to a year, with your 71% absorption "blank", were you using polypropylene there also?

Bondietti: Yes. It's interesting if you remember there was less estimated Pu(VI), and that was about 25%. Of course there was more total plutonium, about 30% of the plutonium was still in the aqueous phase. I can't resolve the problem whether or not my removal of the organic matter from the clay resulted in an oxidized surface and affected the formation of plutonium (VI), but if that is not the case, then I would suggest that the clay scavenged some of the Pu(IV) that originated from the disproportionation. So that 50% of the plutonium in the aqueous phase was Pu(VI) and presence of clay, but only 25% of Pu(VI) did not have clay there. So Pu(IV) scavenged a lot more.

Holcomb: Did you try any experiments where you equilibrate your soil or clay with the organic matter present, then take your clay and remove the organic matter and again equilibrate, and then remove the iron and then equilibrate?

Bondietti: That's what I did . . .

Holcomb: I thought it was successive.

Bondietti: No, I took part of it and removed the organic matter, took part of that and removed the iron. These all were then run simultaneously. The results are somewhat disappointing because I really still don't know quite what happened, but it did intrigue me about the oxidation states, so we did perceive that problem. I think that was more important also, and I wanted to bring it up because of the variability I've run across in some literature work. It was mentioned yesterday, that with the same soil run five times, there is tremendous variability. I just wonder sometimes if this isn't due to how fast you neutralize it, how fast it sorbs the soil, or how fast polymer is formed, etc. You think you are doing it exactly the same and it's frustrating when this variability occurs. It may be just slight differences in the acidification that you do.

Rogers: Maybe a slight difference in the particule size?

Nyhan: Maybe differences in microbial activity along the lines of some of the work that Ray Wildung has done looking at increased plutonium solubility with increased microbial activity rates.

Bondietti: It could be. The problem is defining what you end up with. The best reproducibility we had is when we didn't do anything to the clay. But the minute we started to manipulate the clay, reproducibility became much poorer.

FUTURE WORK

FUTURE WORK

E. A. BONDIETTI

The oxide work is being done by another fellow and I'm going to be working with him on that. Hopefully he can describe the system in terms of kinetics, etc. I can't do that; I'm not a physical chemist. My main work in soils has focused on soils contaminated in 1943 with plutonium at Oak Ridge. We have been doing some work on species in the soils, how much is associated with the organic matter and species that are easily transferrable to resins and things like that. I'm curious as to what would happen if we took, I don't know about the Oak Ridge soil, but if we took Nevada test site soils with a higher pH soil, extracted with carbonate, and then try some of these valence procedures to see if you could extract hexavalent plutonium. You have to get a contaminated soil, and some of these soils from the Nevada test site have a lot of PuO_2. Obviously one has to worry about whether or not you would change an oxidate state. I think if you added different isotopes in known oxidation stages you might be able to try it, and this is something that I am thinking about trying. We want to understand what are the species that are absorbed in the soil. Most of it I think will be Pu(IV). Maybe all of the plutonium that plants take up might be Pu(IV). Or it might be a chelate species. I think those are the two things we need to resolve. How stable is Pu(IV) and whether or not the chelation problems of Pu(IV) would be important. As far as mobility or leaching in the environment, all of these Kd's are so high that plutonium just doesn't move very fast.

Rogers: Ernie, when you are saying Pu(VI), you really mean possibly both Pu(V) and Pu(VI), do you not?

Bondietti: Yes. As I said, it is sort of fascinating to read the Manhattan literature. At that time they talk about an oxidized plutonium species . . . They didn't even know Pu(III) was present and Pu(V) was never identified by the chemical method that they had been using. Only when they went to spectophotometry was Pu(V) determined. But I don't know if we could ever distinguish Pu(V). First of all, I don't know if we could ever get any Pu(V) to test.

W. L. POLZER/P. A. GLOVER

Our main purpose was to obtain enough data so that we might eventually be able to postulate a mechanism for the movement of plutonium and americium in the soil. Because of the information obtained from the regression analysis, we feel it is more correct to use the phrase "postulate a process or processes" rather than mechanism since it's possible that several processes are involved in plutonium movement.

To complete our study, we will continue our column elution studies using soluble and insoluble plutonium and americium. Four additional soils with more diverse physical and chemical characteristics have been selected to complete the study. The soils chosen have varied cation exchange capacities, pH's, sand, silt and clay content.

Along with the elution studies we would like to identify the plutonium species in the eluate. Identification of the plutonium species will be useful when postulating processes for the movement of plutonium in the soil. I'd like to find out more about techniques used by Bondietti to determine the species of plutonium when it is present in trace quantities.

H. P. HOLCOMB

We are going to continue looking at some of the equipment that is buried at Savannah River. We have about 100,000 cubic feet of equipment whose transuranium content is unknown--not only plutonium but also other transuranics. Also, our supervisor, Bill Reinig, Elmer Wilhite, and I have just formulated a research proposal to ERDA for funding for fiscal year 1977 and 1978 to the extent of about half a million dollars to study the long-term effects of leaving the pre-1965 unencapsulated solid alpha waste buried as is at the Savannah River burial ground. This particular research proposal covers a multitude of investigations. We are going to do extensive sampling to determine actual migration. We want to dig up some of the waste and do some analytical testing like Ernie has mentioned to see what is there now, several years later. I am not a botanist, but we want to look at the uptake of the transuranics by plants and what would possibly happen, say, if one of our nice long-leaf pines happened to root over a waste trench. What would happen if the plutonium were still there and by some mechanism the pine tree gets hold of it? We want to investigate uptake, resuspension, redeposition and the consequences--things of this sort. It will require an extensive research program and it is something that we hopefully will get funded and get involved in within the next fiscal year, then continue. Our proposal only covers the next two fiscal years, but we envision it lasting longer than that.

J. W. NYHAN

About half of my job is really involved in doing a soil survey of Los Alamos County, hand in hand with the radionuclide work that we are doing. We feel that if we can better understand what's out in the environment, we can better understand the radionuclide behavior in soils in that same system.

In conjunction with this work, we are doing a lot of work with transuranics and cesium-137. For example, we're looking at different soil sampling techniques, both at Los Alamos and Trinity Site. We are investigating coring and trenching techniques relative to the accuracy of sampling the soils in the field, and looking at the effects of mass of sample collected versus aliquoting errors.

In addition, we have had a chemist helping us out for the last year on developing an americium procedure for soils. We are pretty close to having an americium procedure for looking at femtocurie to picocurie levels of americium in soils. Eventually we would like to use the americium procedure and the information we will get from looking at different methods of sampling soils to get improved inventories of transuranics at Los Alamos. We're specifically looking at americium and plutonium in the stream bank soils as well as the stream channel soils there.

We're also getting into looking at radionuclide transport mechanisms. We're trying to evaluate what the levels of water soluble plutonium are, for example, in the stream channels, in situ. These measurements will be correlated with the biological and chemical properties of alluvium. The treatment plant effluents contain large amounts of nitrates and nutrients which help algae grow better at Los Alamos. We've identified that there's about 10-fold higher concentrations of plutonium in algae than in the underlying soils in the field. Thus, we will be looking at the biological activity of the sediments as related to fluctuations in water soluble levels of plutonium in the field.

We also did an experiment at Trinity Site, where we applied about 2 year's worth of rain on some of the soil profiles that I discussed on the Chupadera Mesa, seeing if we could effect a change in the vertical distribution of plutonium. Variables that we are looking at there are differential rates of application of the water. Also at Trinity Site we're looking at resuspension of plutonium in soil that is resuspended at two of our four intensive study sites.

Again, I'm involved in a multidisciplinary effort, and the other people want to know the answers to: how much soil could possibly be on my vegetation? Why is there plutonium concentration on the hide and in the lungs of my small mammal samples that I am taking out there at some sites and not the other sites? We are also trying to identify the Trinity Site source terms a little better and get a better idea of what the distribution of plutonium particles are as superimposed on the distribution of soil particles.

R. W. ATCHER

We're going to continue with our lab study on the migration in the tuff, and we're going to see if we can push the deposit rate up to a point where we see plutonium physically forced down, and see if we can see the kinetic limits of the process. And we have no idea whether we can--we haven't yet. We also would like to find a radionuclide not absorbed by the same mechanism and see if we can define better this question of saturated versus unsaturated flow. We're doing some standard Kd studies on some limestone samples as a function of salt concentrations; the plutonium was initially in a saltwater. And we're going to be doing a little bit more work on a computer model and see if we can reproduce the behavior that we have seen in our lab scale model.

We're getting some core samples from the unused disposal site at Los Alamos probably some time in April. We'll take a look and see if we can predict where the plutonium is going to be found and we're negotiating with Chalk River and also Hanford to look at some core samples from there. We have a couple other proposals in, one of which is going to be a study of actinide burnup in fast-flux reactors; I think we have some competition on that one. The other one is to study storage of long-lived waste in clays that will be injected in underground caverns.

Ames: These samples you are going to get from Hanford, Bob, are basalts? Or what are they?

Atcher: I think they are going to be sand samples.

L. L. AMES

I'm intrigued with the plutonium that I know is there in the altered areas of this glassy basalt. You can't get at it; you can't extract it to find out what the speciation is or anything else without changing the speciation. We're trying to find some way of looking at it without changing the associations and speciation as it is now. One way we're going to investigate it is with the use of ESCA (electron spectroscopy for chemical analysis), an instrument that's supposed to be able to determine the oxidation state. Another thing we're going to look at is using the ion microprobe. We should be able to get to lower weight percent oxide than is possible with the electron microprobe. Jeff Serne is going to be doing some leaching studies also, looking into particulate movement, and hopefully some speciation as well of the leachate.

Some of the contaminated sediments are rather high in actinide concentration. They're going to be quite a bit warmer than most of the things we've been talking about here in the last day and a half. Most of the drilling is up to Sue, and I don't know where we stand with that. I believe that Sue is drilling at Z-12 trench now, that has received waste with a pH of about 10. We hopefully will be able to determine or characterize the soil and determine where the plutonium and americium is in relation to the soil and soil minerals, and compare these with the acid waste and with some future sites that will be drilled on neutral waste disposal. This should give us a good start on natural sediment occurrences. We really don't know enough to do any modeling yet. We're not anywhere near that far along. Until we can determine even where the americium is in relation to the plutonium and soil minerals and identify oxidation states, we won't know anywhere near enough to go into the laboratory and try to reproduce any of the occurrences.

J. E. MENDEL

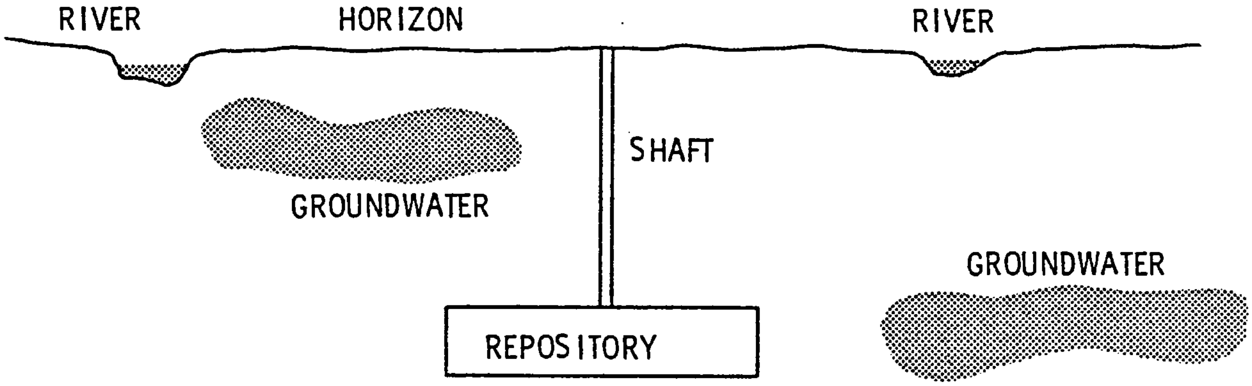
Our main project is evaluating glasses for immobilization of the high-level waste and our primary goal to date has been to determine more or less the internal factors, like what thermal effects do to the glasses, what the contained radiation does to the glasses and so forth. And we haven't worried as much about how the glasses might interact with geologic storage sites, but we are now beginning to make some small glass specimens in the hot cell from actual power reactor fuel waste, some of the first that have ever been made. We have some fuel that was irradiated to over 50,000 mwd per ton and it's less than 2 years old. We're making glass specimens of about 100 g each from waste made from this fuel. We will cut these into wafers and plan to expose these to different types of candidate waters from various locations such as salt-brine, seawater, different kinds of soil water, and probably just some water of varying pH's. We will take the equilibrated water and use it as a source water for some Kd measurements with various candidate materials from proposed geologic disposal sites. The goal is a deep geologic disposal site, so there will probably be more things like granite, limestone, and so forth, rather than surface soils.

HYPOTHETICAL PROBLEM ON TERMINAL WASTE STORAGE

HYPOTHETICAL PROBLEM ON TERMINAL WASTE STORAGE

H. C. BURKHOLDER

Yesterday, I showed you an outline of the U.S. Geologic Final Storage Program, and I indicated some questions that needed to be answered. I want to address those questions by drawing a scenario.



Given this sort of scenario, a knowledge of the geology and the hydrology, and $5 million dollars, how would you describe how the waste might get from its containment in the repository back to the biosphere? What experiments would you perform, what samples would you take, etc.?

Nyhan: What sort of information do we have on the source term?

Burkholder: Assume you know the waste inventory and assume that John Mendel describes for you the waste form characteristics. Using the Carlsbad site as an example, how would you characterize the nuclide retention properties of that site?

Nyhan: Since you used the Carlsbad Site as an example and I am from New Mexico, I will volunteer to start the discussion. I don't think there are any better experts about the Carlsbad area than the poeple that live in New Mexico, so I wouldn't start, by asking Oak Ridge personnel what the geology in New Mexico is like.

I think I'd want to be sure that I had some way of monitoring water movement around that container, and an ample supply of experts in hydrology. I'd also like to look at the physical and chemical properties of geologic materials in the area, and make sure I had detailed stratographic cross sections of the whole area. If there is anything left out of the $5 million you gave me, I would then do a few field experiments to measure distribution coefficients. You might also want to take into account the kinetics of these reactions in the field and not just the static "equilibria" situation such as reported as Kd's in many of the papers presented yesterday.

Burkholder: Is Kd the thing to measure?

Nyhan: I don't know. That's a good question. I would rather look at the kinetics of the reactions in the field.

Ames: One of the problems probably is this. Whatever you come up with for an evaluation, it's got to be legally defensible. Somebody's going to take you to court.

Lini: How many different kinds of sites are you talking about? You mentioned Carlsbad, and you mentioned basalt as at Hanford, you also mentioned several others. Another factor to consider is that water is going to be the medium in which the radioactive species will migrate from the storage site. At the other extreme, you could visualize a situation in which the wastes get so hot and vaporize up the monitoring wells or some unlikely thing, like that. Again, it's a matter of probabilities. First you need water movement into the storage vault and then leaching out of radioactive species from the glasses through a sealed container. Additionally, you would have to consider the nature of the leachate, what is the nature of water, and what geological formations is this water migrating through. In a basalt the water migrates through fissures, cracks, pores, whereas in a clay migration is through particles.

Burkholder: Would you approach the problem by investigating the most likely path back to the biosphere in great depth or would you investigate many pathways in less depth.

Lini: You have $5 million to do it with. That sounds like a lot of money and it is, but. That's why I asked you how many different formations you are talking about placing the storage vault in.

Burkholder: The plan is to choose six. I'm suggesting $5 million for each of the six.

Lini: I think you have to go back to some sort of fault-tree type of approach, and start determining what are the pathways and, I don't know how to do it, but also try to assign some probability factors so that you can come up with some plausible distribution or ranking.

Burkholder: Let's make a comparison. The probability that a meteorite hits the site is probably about 10^{-13}/yr and so if we integrate that over 10^6 years, the integrated probability is still much less than 1. On the other hand the probability the groundwater intrudes the site might be 10^6/yr. If we integrate that probability over 10^6 years, the integral probably approaches 1. Thus groundwater intrusion may well occur in the time span of our interest.

Lini: Some meteor from outer space. You begin to do that and your program becomes unmanageable. You would be on a firmer basis to start with water migration at a particular site and expand the program from there.

Burkholder: What would you do at Hanford?

Lini: Begin to look at a combination of things; at the chemicals dissolved in the water, and the leachate, because that's the material that's going to be doing the moving and the leaching. First you've got to have the liquid, and then consider the physical movement through the strata and chemical interaction of the liquid with the strata.

Rai: If the chemical and physical properties, hydrology of the geologic media, and the form and properties of the waste are known, one needs to evaluate the interaction of the waste with the geologic media. Reactions such as dissolution, precipitation, coprecipitation, adsorption and filtration of the moving radionuclides need to be evaluated.

Burkholder: I'm concerned about what happens deep in the geologic formation. Perhaps measurements made with sediment are not applicable to the final storage problem.

Rai: If you already know what's there (properties of the geologic media) and the properties of the waste, the interactions can be easily evaluated.

Burkholder: We have some knowledge of what's there in a generic sense, but very little knowledge at specific sites.

Rai: You are saying then that you don't know all the properties of the system.

Burkholder: We would probably know from site reconnaissance where the water is at present and have some information about the geology.

Rai: Not general geology; I'm not talking about that. I think you have to know detailed characteristics of the media such as pH, Eh, mineralogy, porosity, pore size distribution, rate, amount and direction of water movement.

Burkholder: Let's assume we didn't know that. What sample would you take, how would you take those samples, where would you take the samples, and what would you do with the samples after you had them.

Rai: If the disposal site is already selected, then it should be thoroughly characterized. If the site is not selected then various kinds of geologic media samples can be tested for their potential to immobilize the radioactive materials. On the basis of these types of investigations, one can then select the ideal disposal site.

Lini: You've got to do some characterization to make sure that the mine or whatever you call it, is compatible with the geological formation at the site. The area might not be a suitable storage site.

Bruns: Presumably you've done a lot of geological work and hydrology work or they wouldn't select these sites.

Rai: The compatibility of the waste form with the geologic media should not be neglected. For example, disposal of acidic liquid waste to the calcium carbonate media may be undesirable because of the possible high CO_2 pressures that may be created by the action of acid on calcium carbonate.

Bruns: I agree with you, Dhan. You have to look at all the chemical potential reactions, explosion-type reactions, etc.

Glover: There are so many things that you don't know and there would have to be so much research done that it would probably use up your $5 million dollars.

Ames: You've got to know the kinetics and the thermodynamics characteristic of each site.

Burkholder: Which nuclides should we look at? I'll list them as you name them. Americium, plutonium, neptunium, curium, strontium, cesium, iodine. We're missing possibly two of the most important ones, technicium and radium.

Rai: There goes our $5 million.

Glover: They might have to settle for some very haphazard data. You could probably do it with $5 million dollars, but as far as the worth of your data is concerned, I don't know. We've all done experiments with just plutonium and americium and we actually have physical and chemical characteristics, we've got physical data on all of those, and there's still so much more than we do not know about it, that it's a matter of the risk that you're willing to take upon accepting that data as is. If they only have $5 million for you to do this, they will probably take a big risk. We could probably come up with something.

Polzer: Let's go back to what Dr. Ames said. You've got to legally defend yourself.

Rai: Another possibility is spreading that $5 million into a lot more workable units.

Burkholder: But we would have a great lack of control over that kind of research.

Ames: I don't know if I would have much faith in what came out of that.

Lini: You might just have to manage the program yourself. Spend most of your time and money planning the programs, and contracting out the work to specific investigators indicating that this is the way you think you want them to carry out the work and get the answer back to you in a form you can use it.

Garland: That's assuming you can ask the question.

Nyhan: Of course past experience with similar large programs would indicate that it would be better not to maximize subcontracting large amounts of money to a large group of people. It might be better to direct the total effort from one central organization that would maintain close supervision over farming out several parts of the question.

Polzer: Are you referring to the work that is being done at the Nevada test site?

Burkholder: That site would be an example.

Polzer: I mean type of work. A group of people, many of whom are from different National Laboratories, work on specific problems in a given discipline of research.

Nyhan: People tend to do things they are interested in, and I'm saying that probably the most efficient way to farm out this program would be to take small pieces of the problem and expect a definite answer within a defined period of time.

Burkholder: Then you think the program needs to be very well planned out before it starts?

Polzer: You have to know what pieces of information you want.

Nyhan: How many pieces of information should I have for $5 million?

Bondietti: Are there leaching characteristics of these nuclides now from the primary matrix, the glass?

Burkholder: It would be reasonable to assume that high-level waste would be in a glass matrix.

Garland: How much of the iodine gets in the glass?

Lini: Does it volatilize on heating?

Burkholder: Iodine volatilizes at the reprocessing operation but current plans call for trapping and solidifying it. We will likely put the iodine in the repository with the high-level waste so it is reasonable to consider them as being together.

Lini: It's the same with helium. It won't be there at time zero. What about other gases, once water gets in there hydrogen and oxygen could be formed.

Burkholder: Is that going to crack the glass?

Nyhan: It will probably crack the containment vessel over time.

Lini: Again, you've got to have migration of water into the storage site. If you have too much heat, water movement will be away from the site, unless you get flooding. This would be the case for the short run while the site is geologically young.

Ames: What is the evidence for that, Harry? Is it away or toward?

Nyhan: Salt is toward.

Burkholder: One of the concerns about salt disposal is that if some interstitial water is present in the salt it may move up the thermal gradient and surround the canister. Now the canister is movable and it seems possible, although improbable for several of these move together and overheat. If nuclides are volatilized they could be transported by molecular diffusion.

Nyhan: It could be that a relatively large percentage of the water that's moved in extremely dry situations, which I assume is what you're going to pick here, is moved due to temperature gradients and movement of water in the vapor phase. The same thing was true of radionuclide movement, then, we might have an unpredictable situation.

Serne: That may be true for the leading edge, but you'd have to assume with caverns flooded that you've got saturated conditions in the vicinity of your source term and that'll cut down your vapor diffusion significantly.

Burkholder: I have trouble envisioning saturated conditions. I envision the nuclides being leached from the glass very slowly so that the concentration of the nuclides in the contaminated groundwater is very low.

Serne: I'm talking about saturation with water.

Polzer: But if water is present, you still have a saturated solution.

Serne: I'm talking about saturated physical flow in the pores. If the pores are filled with water the soil is saturated, not chemically saturated with chemical constituents, and that has a very big effect on transport by vapor.

Polzer: I think the biggest problem that we'll encounter is describing the water flow. The first approach is don't even mess around with the chemistry. Figure out the travel times of the water to determine whether the water is going to travel far enough. If not, you don't have to worry about Kd's. So your hydrologist has got the biggest chore.

Serne: You'll never really get the answer because of the fissure and crack situation. The only way you're going to get to that is to punch holes all over the place and then you're going to end up destroying the site.

Polzer: I think that's where the chemical composition of your water, which includes waste, becomes important. You don't know how rapid the water will move. The chemical characteristics of the water should give some insight to the fate of the waste, regardless of how rapid the water moves.

Serne: You still need to have some sort of an estimate of the fissures or cracks and how much surface area is available for sorption.

Burkholder: By the way, how do we take a sample of the medium without destroying its characteristics in the sampling process?

Glover: Get a small drill.

Burkholder: I envision a large drill so that the sample in the middle of the core is untouched.

Holcomb: Let me be a little bit sophomoric and ask you, has it been definitely decided that you're going to put this stuff underneath the ground?

Burkholder: Yes.

Glover: You haven't thought of trying to reprocess your waste, or remove as much of the long-lived radioisotopes from the high-level waste in process as practicable.

Burkholder: Remove what?

Glover: Your actinides.

Burkholder: Transmutation?

Glover: Yes, or something similar.

Burkholder: We have done a study which concludes that there is no incentive to partition nuclear waste.

Glover: I brought that up mainly because there has been talk at Rocky Flats from time to time that we're trying to cut down on our waste as much as possible because in the near future we are looking at retrieving our waste and reprocessing it, and that's an awful lot of waste.

Burkholder: How is that waste disposed of?

Glover: It's just buried. They're actually thinking of retrieving that waste and removing as much of the activity as possible to get it down to low level.

Polzer: Volume reduction is what you're talking about.

Glover: Yes.

Rai: Are these going to be retrievable systems?

Burkholder: These systems would be retrievable until the public decided that they no longer wanted it to be retrievable.

Bondietti: Or when someone forgot where they were buried.

Nyhan: It seems like we need some long-term experiments, too.

Burkholder: How long?

Bondietti: As long as Congress will fund them I guess.

Nyhan: You (Burkholder) mentioned some time periods initially that might not be practical.

Burkholder: The dates or the experiments?

Nyhan: You're talking in terms of time like a million years--maybe the experiments that should be done should be concluded in a million years.

Rai: If you can watch it for a million years then you don't have any problem.

Nyhan: Well, you were talking about something that's going to be legally defensible. I wonder if anybody here would care to temporarily extrapolate outside of their own set of data to a million years later to predict what some of these radionuclide reactions will be. I wouldn't want to.

Burkholder: So what do we do?

Rogers: Well how do the hydrologists decide how the water is going to move in this area when there is no water there now? That's along about the same line we're talking about here.

Because obviously if you have a system with water there you could suggest a whole group of trace experiments and things that could be run with injection down into that area and find out how these isotopes move, but if there is no water there and you're predicting a situation where there is a probability of 10^{-5} or 10^{-6} per year that someday you may have water at this location, then you've got to decide how that water would behave at the time you are talking about. In that length this whole geology may have changed a great deal. So the problems are rather formidable.

Burkholder: And the problem takes on a sort of science-fiction character.

Rogers: Ernie had a suggestion: Why don't you wait until the water gets there and then find out.

Rai: That's probably not a too far out suggestion. Instruments to check the changes in water movement could be inserted all around the disposal site. In case of an undesirable change, pumps could be used to withdraw the water.

Rogers: You mean a collective guardian system where you actually insert instruments into the ground and alarms go off when migration reaches some stage?

Burkholder: We will wish to monitor the disposal site, but it's hard to believe that we will watch the site forever.

Rai: It's such an important thing to watch. I would think it would have to be watched until the desired safety level is achieved.

Rogers: Don't you think there's a real possibility too that they won't have to be watched forever? The fact is that we will be "smarter" in, say, 200 years?

Burkholder: For example, perhaps we can "prove" that even if water contacted the waste as soon as it was put underground, the dissolved nuclides would not get back to the biosphere before the length of time necessary for decay. There are a large number of parameters to this problem and they are all interrelated. Sorption on the geologic medium is just one part of problem.

Rai: The sorption is not independent of what's in the water. They both are related.

Rogers: Well, until proven otherwise, you would have to assume that anything that left the immediate area is headed toward someplace you wouldn't like it to go.

Burkholder: You're getting at a kind of worst-case analysis, aren't you?

Rogers: I'm sure that your critics will be doing that.

Burkholder: Then what is a reasonable worst case to consider?

Rogers: That's a matter of probability. I think you can sort those out.

Ames: There is a problem with geologic probability. Geologists will extrapolate to 100 years or 10 million, but are reluctant to do so between. A million year extrapolation is an indecent suggestion as far as it concerns the probabilities of climate changes and topographical changes. Geologists just won't put any firm probability on it, and with good reasons.

Nyhan: Once you ultimately move out of the geosphere and into the biosphere and consider the present radioecological knowledge that we have today, we've got another situation to evaluate.

Burkholder: That's another part of the program.

Nyhan: You're talking about cycling of plutonium over very long periods of time in whatever happens to be the specific ecosystem components at the site. Right now you could make guesses as to what these cycling rates are in some places, but probably not in more than one or two of the 30 potential sites.

Rogers: You have to make some specific measurements, don't you think? I think we have enough information now on some of the processes that go on and with a few specific measurements taken at a specific location, we could isolate this somewhat better than we have been able to do by trying to generalize worldwide or countrywide?

Nyhan: I'm referring more to things that change with time. For example, in Trinity soils we currently found the plutonium continuing its migration into the soil, an observation which we would not have predicted on the basis of the data collected in the 50's. Who is to say what's going to happen in 200 years versus 20 years? What's going to be the most important redistribution process? It is going to be wind-blown material that will eventually equilibrate with all the soil on the earth? Is it going to be leaching of plutonium to some unknown depth? At the Nevada test site, they are looking at things like plant uptake of plutonium by the foliage in natural ecosystems. Whether the plutonium is in or on the plant part may not be important if animals eating that foliage make the plutonium more mobile as time goes on. However, how long does it take for a cow population to ingest all the plutonium on the range and make it more mobile? There are really a lot of unknowns even in the basic ecology of the ecosystems.

Rogers: I'm not sure that any answer you would come up with today would be an answer that would stand for a million years. I think you could come up with answers today that would stand for the reasonable length of time that we can foresee. I think you may have to reevaluate periodically. This may be a continuing problem that may have to be studied as time goes on and changes made. I don't know if you want to wait a million years before you solve the whole problem for all time.

Burkholder: Well if we wait that long we won't have a problem any more.

Rogers: Well, we don't, that's for sure.

Lini: The definition of the problem might have changed, that's all. What concerns us today will not be something that possibly will concern us in a thousand years.

Rogers: I see what you're saying and I agree. But I think we have a tendency to dwell more on uncertainties than on the things we know. That's the nature of the beast here.

Nyhan: On the other hand, the most difficult questions to answer are often the ones that are the most basic.

Rogers: On mechanistic answers? The processes and rate data? Of course, but we need not solve all of this before we can answer the major questions regarding mobility of the actinides in the environment.

CONCLUDING REMARKS

CONCLUDING REMARKS

L. L. AMES

This is about the end of the working meeting. I want to thank everybody. I really enjoyed this meeting, and I learned a lot. I hope to see all you people again in the future.

Rai: Lloyd, I have a small comment about the use of Kd values which I would like to make.

Ames: Go ahead.

Rai: My comment concerns the Kd, the distribution coefficient, that supposedly determines the ability of soils to sorb actinides and other elements. I question the use of Kd values and its usefulness. Kd is supposed to be constant for a given soil and solution when the micro or trace concentrations of the element are used. What is a trace or micro concentration? Nobody knows. In this meeting, Polzer presented data that showed that the change in plutonium concentration from 10^{-7} to 10^{-8} moles/liter changed the Kd values by a factor of approximately 2.5. On the other hand, Roger's data showed that the Kd values were constant for 10^{-7} to 10^{-14} moles/liter of plutonium. Kd values have many limitations such as: 1) solution and soil specificity, 2) several determinations are needed to find Kd values that are independent of solution concentration, 3) dependence on solid to solution ratios, 4) does not identify mechanisms of adsorption, and 5) changes with the variations in relative concentration of the element with respect to other solution ions, such that extrapolation to other solutions and geologic sorbing media are difficult. Therefore, the use of Kd values and the percent adsorbed from solution should be discontinued. Until a better understanding of the mechanisms of sorption is available, it would be more meaningful to report the equilibrium concentration and the amount adsorbed instead of Kd and percent adsorbed.

Ames: Anybody have any comment on that?

Glover: When we started out, we knew we were not measuring true distribution coefficients, and that is why we report our data in Kd(m), and not as a true distribution coefficient. In our papers we put the reasoning down, which is the same, and I guess it's more a matter of tradition that most people report distribution coefficients for the distribution of an ion in a mixture, and it probably takes something like this where people are now realizing that it is not a distribution coefficient per se that we are measuring. Many people have mentioned, "this is a distribution ratio, and not a distribution coefficient," and eventually, in the soils work related to actinide elements, distribution coefficient will become less important and less dependent on them. In our work we actually define equilibrium sorption as percent sorbed rather than true Kd's because in most of the work that everybody has presented, they do not rely mainly on distribution coefficient for defining characteristics or defining sorption. We measured distribution coefficients. We'll use them, but these numbers were not used to say, "This is what's actually happening." Because they changed so drastically as I had measured them. If I had done all the runs over again, I might have had all different distribution coefficients.

Rai: Most of the researchers report Kd's and percent adsorbed. Percent adsorbed doesn't mean anything unless initial and final solution concentrations are reported.

Rogers: That's true of Kd, and that's true of all of the things that we have done. What everybody had performed is a very gross experiment because we don't know how to sort out the speciation that's in either one of the phases. So you're still stuck. No matter how you report the data, reporting conditions under which the data were taken is critical. And I don't see anything particularly wrong with that as long as the data are used with some amount of judgment. It might be advisable since we have contact with most of the people that are making these kinds of measurements and we establish that there is certain information that has to accompany one of the Kd's so that cross-evaluation between values can be performed.

Rai: The Kd value changes with the solution composition and the amount of the element in the solution. Most all the researchers don't have the same kind of concentration or the same nature of the solution to determine Kd under. So you really can't compare different soils with Kd value.

Bondietti: I think in some cases there are certain numbers that always pop up with respect to plutonium in most soils, 10^4 and 10^5, I think are the numbers. The modelers like Kd's but I don't care if it's 10^4 or 10^5, a modeler's computer would run a long time before he gets plutonium moving very far in the soil. I'm not quite sure if you're asking for precision that is necessary in a Kd number, I don't know. You want a Kd number or a measurement of distribution precise enough maybe to apply to some speciation model.

Rogers: You want a thermodynamic Kd, and we just aren't there, I don't think. But avoiding taking any measurements at all is clearly not the answer.

Rai: I am not suggesting discontinuation of measurements. However, I am suggesting that until better data become available, the initial and final concentrations should be reported.

Rogers: Sure.

Wildung: I think by definition a Kd is supposed to be at a trace concentration level that's independent of concentration.

If you get into a situation where it's concentration dependent, it no longer fits the Kd definition. I think the main reason that it was used early on is because it comes out in units useful in terms of estimating sorption capacity and predicting movement down the soil profile. And so your point is well taken. If you are going to use it, you have to redefine Kd *per se*.

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