IAEA-SM-199/52)
CONF-751105--4

# PHYSICAL AND CHEMICAL CHARACTERISTICS OF PLUTONIUM IN EXISTING CONTAMINATED SOILS AND SEDIMENTS*†

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## ABSTRACT

PHYSICAL AND CHEMICAL CHARACTERISTICS OF PLUTONIUM IN EXISTING CONTAMINATED SOILS AND SEDIMENTS. Plutonium from three sites has been studied to provide information necessary in understanding its behavior and fate under prevailing conditions. Plutonium in soils from the Nevada Test Site (NTS) was predominantly associated (50 - 75%) with the coarse silt (53 - 20 μm) fraction. The coarse silt fraction was further segregated by density gradient zonal centrifugation; the plutonium in the sample from a bare soil ranged from 60 - 85% in the "heavy" mineral fraction (> 2.9 g/cm³) suggesting the presence of oxide forms. The plutonium in a sandy mound taken beneath shrubbery occurred predominantly (80 - 95%) in a lighter fraction (2.5 - 2.7 g/cm³) associated with felspar. Soil extraction of NTS plutonium with 0.1 M citric acid solution showed very low solubility (≈ 1%).

The plutonium in samples from Oak Ridge National Laboratory (ORNL) and Mound Laboratory (ML) was predominantly in the clay size (< 2 μm). The solubility in citric acid was about 20 - 25% in the ORNL sample and 40 - 50% in the ML sample. Density gradient segregation of the clay size fraction of the ML sample showed the activity distribution to be directly related to the weight of the recovered fraction with enhanced contribution by the very light organic fraction. Approximately 71% was found in the 2.3 - 2.4 g/cm³ fraction which contained 65% weight percent of the clay and 16% in the < 1.8 g/cm³ fraction (organic fraction) which contained 6% of the weight fraction.

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*Research sponsored by the U. S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

†Publication No. 787, Environmental Sciences Division, ORNL.

The results obtained are discussed as they relate to the resuspension and plant uptake of plutonium. Citrate solubility of plutonium appears to be promising as a potential "soil test" solution to predict uptake of plutonium by vegetation.

## 1. INTRODUCTION

To date, accidental and deliberate releases of plutonium have been confined mainly to the local environs of plutonium-handling facilities. These contaminated environmental situations, of different origin, provide opportunities for the study of this important radionuclide in diverse environments. The physical and chemical characteristics of the plutonium as it exists in the soil and sediment matrices provide valuable information necessary in understanding its fate under prevailing conditions.

At each of the sites where contaminated soils and sediments were obtained for this study, large and comprehensive programs are in progress to assess the environmental and radiological health questions associated with plutonium. This particular phase of these programs is directed toward characterizing plutonium in terms of particle size, its relative solubilities in mineral acids and complexing agents, and its association with the mineral matter of the matrices. From these investigations, insight should be gained into its behavior, its movement into the soil, and its potential resuspension by wind action.

Initially, this investigation was concerned with the characterization of plutonium in the Nevada Test Site (NTS) as part of the program of the Nevada Applied Ecology Group (NAEG). Later investigations were undertaken of samples from the Oak Ridge National Laboratory (ORNL) and Mound Laboratory (ML) sites as part of these characterization studies. Consequently more information on the characterization of environmental plutonium has been developed at the NTS site than those from the ORNL and ML sites, and parts of the results obtained to date on NTS plutonium have been published [1,2,3]. These earlier studies report on particle size distribution of plutonium in soil samples from several locations within NTS and the effect of distance from the point of detonation on plutonium concentration. By applying treatments developed for the NTS samples on the ORNL and ML samples, comparisons of the properties of the plutonium at all three sites have been possible.

The physical characteristics of the plutonium and the environmental factors which affect the behavior of the nuclide in the given environments are discussed in this paper. These results should be considered to be preliminary in nature; only through continued efforts at characterization can a full understanding of the behavior and fate of plutonium be achieved.

## 2. SAMPLE DESCRIPTION

Plutonium was deposited in the environment under different conditions at the three sampling sites. At the Nevada Test Site (NTS) plutonium was deposited in the various Mojave and Great Basin desert environments from the "safety shot" series; subcritical nuclear devices were detonated without fission and the plutonium thereby dispersed over the immediate landscape. Subsequent to deposition, the area remained undisturbed by man for about 17 years. The land surface is covered with desert shrubs at 5 - 10% plant density; the rainfall is approximately 10 - 20 cm/yr.

The sandy-textured soil in the sampled area (referred to as Area 13 at NTS) shows two distinct types of occurrence. Most of the soil is devoid of vegetation and occurs as bare soil of alluvial origin. In the uniformly distributed vegetated area (5 - 10% plant density), the soil occurs as a sandy mound beneath the canopy. The absence of gravel particles suggests that the mound was formed by wind deposits of sand particles. Interestingly, within a given area the portable field monitor (which measures the $^{241}$Am gamma rays that correlate with plutonium content) indicates a higher plutonium content under the shrubbery than over the bare soil. Since over 90% of the plutonium is in the upper 5 cm [4], the results for the NTS samples discussed in this paper represent plutonium occurrence to this depth.

Samples from the Oak Ridge National Laboratory (ORNL) site were taken from a flood plain on the banks of White Oak Creek formerly used as a holdup pond for radionuclide retention. The earthen dike failed after about 6 months of operation in late 1944; a young flood plain forest has developed on the 2-ha site along with understory and ground vegetation representative of flood plains in the Tennessee Valley [5]. The annual rainfall in this area is approximately 125 cm. White Oak Creek occasionally floods the area. Although the texture of the soil varies, the samples used in this investigation were silty clay loam in texture. The pH of the samples ranged from 6.5 - 7.5; the samples used in this investigation had pH's of 6.70 and 7.0. Samples used to characterize the plutonium were taken at 0 - 7.5 cm depth.

The samples from Mound Laboratory (ML) in Miamisburg, Ohio, were from a sediment core taken in the old Erie Canal. The source of the contamination was a leak in the acid waste transfer line in the plant site. The contaminated soil was removed, but a small fraction eroded from the plant site and settled in the canal. The texture of the sediment samples was silty clay loam; sandy lenses were also present. The pH of the sediment ranged from 8.0 - 8.4. The material used in this investigation was taken at different depth intervals from the sediment core, which measured 47 cm.

## 3. ANALYTICAL METHODOLOGY

Samples were analyzed for total plutonium using the $HNO_3$-HF digestion technique [2] for the NTS samples and hot 8 $\underline{M}$ $HNO_3$ [6] for the ORNL and ML samples with either $^{236}$Pu or $^{242}$Pu as the internal standard. The $HNO_3$ technique was used for the ORNL and ML samples after several samples were analyzed by both methods and the results showed over 95% extraction with the hot $HNO_3$.

For total plutonium analyses of the soil sample, 10 g of < 2 mm particles were used. The amount used for total plutonium in segregated materials depended on the total amount of materials available. Thus in size segregating 100 g of soil from NTS, about 1 - 5 g of clay size particles were obtained; in these cases approximately one-half of the sample was used for total plutonium analysis.

Following anion exchange purification, plutonium was electrodeposited and counted on a 200 $mm^2$ surface barrier detector. Although counting times varied, depending on activity levels, replicate analysis showed standard deviation of 1 sigma at about ± 15%.

Samples which were extracted using selected reagents such as 0.1 M citric acid and 0.1 M sodium citrate were analyzed by a liquid scintillation technique developed by McDowell et al. [7]. Extraction of soils and sediment samples (5 ml/g) using these solutions resulted in a yellow or brown color in the extractants. In order to establish consistent recovery, the extracted solutions were treated with hydrogen peroxide in a nitric acid media, boiled down to ensure removal of peroxide, and the solutions were adjusted to 2 - 4 M in nitric acid, which is the condition necessary to extract plutonium into a tertiary amine nitrate [7].

Size segregation of particles was done normally by adding distilled water, stirring with a rubber policeman, and passing the suspension through various sand size sieves down to 53 µm. Below 53-µm diameter (270 mesh screen), the silt and clay sizes were segregated by utilizing Stoke's law of settling and 2.65 $g/cm^3$ as the density of the particles. This procedure was followed to minimize the disturbance of the possible bonding association of plutonium as it exists in the field. For selected samples, size segregation was preceded by a 5-min treatment with a Blackstone ultrasonic probe which dispersed the aggregates of the soil and sediment. Segregation then followed as outlined above.

Another technique utilized in further characterization of the plutonium was density gradient segregation of selected particle sizes. This technique segregates particles by differences in density [8]. Ethyl alcohol and tetrabromoethane were used to form the density gradient solution ranging from 1.8 $g/cm^3$ to 2.9 $g/cm^3$. This range permitted the lighter organic fraction to float at the surface and the heavier mineral fractions to segregate in the media, depending on their density, including the heaviest fraction which settled at the bottom of the centrifuge tube (> 2.9 $g/cm^3$). The analysis for plutonium in these fractions of the NTS samples was slightly modified due to the small samples. In these cases, a 5-g sample of a local uncontaminated soil was added to the fraction, thoroughly mixed, and analyzed by the $HNO_3$-HF technique. This addition permitted using the standard amount of solutions required in the normal procedure.

## 4. RESULTS AND DISCUSSION

Total plutonium samples which were used for further characterization studies are shown in Table I. The samples labeled A13 - 1A and A13 - 1B refer to two samples collected very close to each other at NTS. The 1A sample was taken from a bare area of the desert; the 1B sample was part of a sandy desert mound beneath a saltbush shrub, approximately 4 ft from 1A. The reported activity represents < 2-mm particles. As noted earlier, the

## TABLE I

## ACTIVITY, CONCENTRATION, AND SOIL-WATER pH OF SELECTED SAMPLES

| Site Location | Sample Code | Activity (dis/min . g) | Concentration** (ng/g) | pH |
|---|---|---|---|---|
| NTS | A13 - 1A | 3912 (115) | 28 | 9.2 |
| NTS | A13 - 1B | 2675 (101) | 19.5 | 9.0 |
| ML | 8C - 7-9 | 1692 (44) | 0.29 | 8.2 |
| ML | 8C - 11-13 | 1133 (44) | 0.19 | 8.3 |
| ML | 8C - 43-47 | 4920 (225) | 0.20 | 8.0 |
| ORNL | E0 - S180 | 135 (11) | 1.0 | 6.7 |
| ORNL | IRB - 1 | 374 (18) | 2.7 | 7.0 |

*Numbers in parentheses are the standard deviation.

**Both NTS and ORNL samples contain primarily $^{239-240}$Pu activity; ML samples contain approximately 2-5% $^{239-240}$Pu with the major activity contributor being $^{238}$Pu.

samples represent the 0 - 5 cm depth and were taken approximately 600 ft from Ground Zero (GZ). The higher mass concentration of plutonium in the NTS and ORNL samples relative to the radioactivity is due to $^{239-240}$Pu in the NTS and ORNL samples and to $^{238}$Pu primarily in the ML samples.

The ML samples were taken from a core near the inlet side of the canal. The numbers 7 - 9, 11 - 13, and 43 - 47 refer to depth increments of the core in centimeters. The sediment initially contained 35 - 45% water and was separated by centrifuging for 1 hr at 2250 rpm. The activity in this core is higher at the bottom of the core than at the top. The pH of the soil-water suspension is alkaline in both the ML and NTS samples: the high pH of the NTS sample suggests the presence of sodium ions; whereas the pH range for the ML samples is normal for calcium-carbonate bearing samples.

The samples taken at ORNL represent two locations of the flood plain. The IRB - 1 sample was taken near the earthen dam; the EO - S180 sample was taken about 100 m away, near the influent of the former pond. A more complete account of the plutonium distribution in the soils and concentrations in the vegetation of the flood plain is being published elsewhere [5]. The pH's of these samples are near neutral, suggesting that calcium carbonate, which may have been present, has been leached below the 0 - 7.5 cm depth in these samples.

The following sections discuss the plutonium association and behavior of the samples listed in Table I. All samples were not used in every treatment or test; however, the treatment or test given each sample was done under near identical conditions.

## 4.1. Particle size distribution and plutonium in size fractions

The particle size distribution and the plutonium distribution in segregated sizes are presented in this section. In the NTS samples, significant amounts of gravel particles were present; and the reported results include the gravel contribution. The plutonium distribution, however, excludes the gravel consistent with normal soil analysis [9]. If the gravel contribution is included in the total analysis (Table I), the activity in the NTS samples would be reduced proportionately to the gravel content reported in Table II.

### 4.1.1. Particle size distribution

The particle size distribution of the soil and sediment samples are shown in Table II. The NTS samples consist primarily of sand size particles (64 - 75%); the increase in silt and clay size particles after ultrasonic treatment implies that the finer particles had been adhering to the coarser sand particles. Note also that the soil taken in the bare area (1A) of NTS contains about 20% gravel particles, but the sample under the shrub (1B) contains only about 3%. The question of whether the sandy mound beneath the shrub represents erosion resistance or wind-deposited particles might be raised. The data on plutonium distribution and plutonium mineral association, presented later, suggest that the particles are wind deposited.

## TABLE II

## PARTICLE SIZE DISTRIBUTION OF SELECTED SAMPLES IN PERCENT FROM NTS, ML, AND ORNL WITHOUT (A) AND WITH (B) ULTRASONIC TREATMENT

| Size Range (µm) | NTS | | NTS | | ML | | ORNL | |
|---|---|---|---|---|---|---|---|---|
| | Sample Code | | | | | | | |
| | A13 - 1A | | A13 - 1B | | 8C - 43-47 | | IRB - 1 | |
| | A | B | A | B | A | B | A | B |
| > 2000 | 19.5 | 19.5 | 2.7 | 2.7 | 0 | 0 | --- | --- |
| 2000 - 840 | 7.2 | 7.2 | 3.0 | 2.9 | 0 | 1.9 | --- | --- |
| 840 - 250 | 24.3 | 22.1 | 20.2 | 19.6 | 6.9 | 4.0 | --- | --- |
| 250 - 125 | 21.1 | 18.7 | 29.6 | 24.7 | 6.0 | 2.8 | --- | --- |
| 125 - 53 | 17.6 | 16.3 | 33.6 | 28.1 | 6.4 | 3.7 | 0.7* | 1.2* |
| 53 - 20 | 5.2 | 6.3 | 8.5 | 10.1 | 28.8 | 22.2 | 23.3 | 19.8 |
| 20 - 5 | 2.4 | 3.3 | 1.1 | 3.2 | 32.2 | 28.4 | 42.9 | 38.4 |
| 5 - 2 | 1.4 | 2.7 | 0.5 | 3.0 | 9.5 | 7.2 | 10.8 | 9.8 |
| < 2 | 1.3 | 4.1 | 0.6 | 5.4 | 10.3 | 29.7 | 19.6 | 28.6 |
| Total | 100.0 | 100.2 | 99.8 | 99.7 | 100.1 | 99.9 | 97.3 | 97.8 |

*Percentage greater than 53 µm.

The ML and ORNL samples contain much higher clay content than the NTS samples. Ultrasonified samples show about six times higher clay content in the ML and ORNL samples than in the NTS samples. The higher clay content is to be expected in the more highly weathered soils of eastern United States, which serve as the parent material of the sediments.

### 4.1.2 Plutonium distribution in size fractions

The percentage contribution of each fraction to the total soil plutonium is shown in Table III. In the ORNL sample only the ultrasonified samples were analyzed for plutonium, and in the ultrasonified ML sample the sand size particles were not analyzed. The contribution of plutonium in the sand size is less than 5% if the concentration of plutonium in the nonultrasonified samples are used to calculate the contribution.

The fraction contributing the highest amount of plutonium in the NTS samples is the coarse silt (53 - 20 μm). In the bare soil (1A) about 50% is in this fraction; under the shrub over 70% is in this fraction. This finding is consistent with those obtained on other bare soil samples in the same area (Area 13). However, data obtained from another area (GMX site in Area 5), also subjected to "safety" shot tests, showed that the highest contributors to the total soil plutonium were the two finer sand sizes on both bare soil and a sandy mound samples [2]. Data in Table III show that 28.1% (bare) and 15.8% (sandy mound) of the activity were contributed by two sand sizes in the nonultrasonified samples. In the Area 5 samples, these size fractions contributed 64% (bare) and 75% (sandy mound). The difference in the size association of plutonium in these two different areas may be due to their distance from GZ; the samples from Area 13 were 600 ft from GZ, and the samples from Area 5 were approximately 250 ft from GZ. Following the detonation, the deposited plutonium was coarser or was associated with coarser particles and, thus, deposited proportionately closer to GZ in Area 5. Data by Mork [10] obtained from Yucca Flats indicate that the size association of plutonium is a function of distance from GZ.

The most obvious effect of ultrasonic treatment of plutonium distribution in the NTS samples was the decrease in the fine sand (125 - 53 μm) and the increase in the medium silt (20 - 5 μm) fraction contributions to total activity. In the bare soil the changes were due primarily to the decrease in activity in the sand and an increase in activity in the medium silt; on the other hand in the sandy mound, the changes in contribution are due to changes in both activity contribution and particle size redistribution.

In the ML and ORNL samples, the highest contributor of activity was the clay fraction. The clay fraction of ML sample contributed nearly 70% of the sediment activity; whereas the clay fraction of ORNL soil contributed 40%. A possible explanation for the more even distribution in the ORNL sample may be due to the original state of the samples. In the ORNL sample, the soil was dry and compact when sampled; the ML core sample was wet and loose on sampling. The 5-min ultrasonic treatment was probably insufficient to completely disperse the aggregates in the ORNL sample, and,

TABLE III

PLUTONIUM CONTRIBUTION (%) BY PARTICLE SIZE WITHOUT (A) AND WITH (B) ULTRASONIC TREATMENT

| Size Range (μm) | NTS | | NTS | | ML | | ORNL |
|---|---|---|---|---|---|---|---|
| | A13 - 1A | | A13 - 1B | | 8C - 43-47 | | IRB - 1 |
| | A | B | A | B | A | B | B* |
| 2000 - 840 | 0.5 | 0.3 | 0 | 0.1 | --- | --- | --- |
| 840 - 250 | 1.5 | 0.2 | 1.5 | 0.1 | 3.9 | --- | --- |
| 250 - 125 | 1.4 | 0.3 | 0.9 | 0.2 | 1.8 | --- | --- |
| 125 - 53 | 26.7 | 8.3 | 14.9 | 5.9 | 5.6 | --- | --- |
| 53 - 20 | 44.4 | 50.9 | 75.1 | 73.2 | 24.8 | 6.4 | 19.3 |
| 20 - 5 | 22.0 | 32.7 | 6.3 | 14.9 | 29.8 | 12.3 | 32.0 |
| 5 - 2 | 2.6 | 4.5 | 0.8 | 4.2 | 16.9 | 11.8 | 8.8 |
| < 2 | 1.0 | 2.9 | 0.4 | 1.5 | 17.1 | 69.5 | 39.9 |
| | 100.1 | 100.1 | 100.1 | 99.9 | 99.9 | 100.0 | 100.0 |

*The A series of ORNL sample was not analyzed.

thus, they remained as coarser particles. It is interesting to note, however, that the wet mud of the ML sample was aggregated originally since the nonultrasonified sample shows that the silt sizes were the major contributor of activity.

In applying Stoke's law for size segregation, the equation contains a term for specific gravity of the particles. In soils the value of 2.65 g/cm$^3$ is generally used, and in the segregation of these samples this value was used to calculate settling velocities. If the plutonium exists as discrete oxides, the density would be approximately 11 g/cm$^3$ and particles smaller than the designated size fractions could be present. Thus in the 53 - 20 µm fraction, plutonium oxide particles as small as 8.5 µm could be present. The importance of this would be especially significant in the NTS samples; thus, without further information, the plutonium in the coarse silt fraction of the NTS samples should not necessarily be assumed to have the diameters designated in this paper.

## 4.2. Solubility test of plutonium

Analyses of soils and sediments for plutonium have generally focused on total plutonium in the matrix. To aid in characterizing possible different forms of plutonium in these contaminated matrices, different extractants were used. Dissolution tests with 8 M $HNO_3$ at room temperature (28°C) and 1-hr contact time showed that the plutonium in selected NTS samples was least soluble (10 - 15%); the plutonium in ORNL samples was quite soluble (60 - 75%); and the plutonium in ML samples was very soluble (80 - 85%) [3]. These results suggested the use of citric acid as an extractant since this organic reagent can complex plutonium. Furthermore, Lindenbaum and Westfall [11] report that polymerized plutonium is only slowly depolymerized and complexed by agents such as citrate; hence the extraction would provide information on whether polymer existed in these samples.

Results of the citric acid extraction of selected soil and sediment samples are given in Table IV. In performing the tests, it was observed that ML samples evolved $CO_2$ during the extraction. Hence pH readings were taken of the citric acid-sediment suspensions. The results showed that the ML samples had significantly raised the pH from 2.0 for pure citric acid to about 5.5. The NTS and ORNL samples increased in pH only moderately. The high extraction of the ML sample could be interpreted as being due to either extraction of monomeric plutonium or to dissolution of plutonium carbonate matrix. The latter form is, however, unlikely to be present in the simple carbonate form in soils [12].

To eliminate calcium carbonate decomposition, the samples were extracted with sodium citrate at pH 8.5. These results are also shown in Table IV; NTS samples were not tested for plutonium extraction in these tests. The results show that an overall reduction was observed in the calcareous ML and the noncalcareous ORNL samples. The results, unfortunately, do not permit evaluating the possible influence of plutonium carbonate in the ML samples as anticipated due to differences in suspension pH. The pH of the suspensions differ in that the noncalcareous ORNL sample showed a decrease in pH; whereas the ML samples showed an increase

## TABLE IV

## EXTRACTION (%) OF PLUTONIUM FROM SELECTED SOILS AND SEDIMENTS IN 0.1 M CITRATE SOLUTIONS (pH OF CITRIC ACID = 2.0; pH OF SODIUM CITRATE = 8.5; SUSPENSION pH TAKEN 15 MIN AFTER CONTACT.)

| | | Fraction Extracted | | Suspension pH | |
|---|---|---|---|---|---|
| Site | Sample Code | Citric Acid | Sodium Citrate | Citric Acid | Sodium Citrate |
| NTS | A13 - 1A | 0.43 | --- | 2.30 | 9.6* |
| | | 0.47 | --- | | |
| | A13 - 1B | 1.5 | --- | --- | |
| ML | 8C - 7-9 | 42.8 | 8.0 | 5.7 | 9.1 |
| | 8C - 11-13 | 58.8 | 13.9 | 5.2 | 9.2 |
| | | 57.7 | 12.8 | | |
| | 8C - 43-47 | 45.5** | | | |
| ORNL | EO - S180 | 23.7** | 7.1 | 3.1 | 7.3 |
| | | 23.3 | 7.6 | 3.2 | --- |

*Only pH reading taken.

**Data from previous report [3].

in pH. However, the data do show that citrate extraction is dependent on the pH of the system. The decrease in pH observed in the ORNL sample is attributable to the buffering action of the original soil (pH = 6.7); the increase in pH in the ML and NTS samples is likely due to formation of calcium citrate and sodium carbonate.

Since the depolymerization of plutonium polymer has been reported to be an extremely slow process [11], the plutonium in the ML and ORNL samples could not have been present in these matrices in polymerized form. On the other hand, the low solubility of plutonium in the NTS sample would not rule out the possibility of polymerized plutonium.

Plant uptake studies of plutonium using NTS substrate have been reported to show discrimination factors (ratio of concentration in plant and in soil) of $10^{-4}$ to $10^{-6}$ [13]. Studies of uptake by plant species of a natural ecosystem on the flood plain reported herein show discrimination factors ranging from about $6 \times 10^{-3}$ to $10^{-4}$ [5]. The increase in uptake is consistent with the increase in solubility of plutonium in citric acid. On the basis of the data in Table IV, one might expect a slightly higher discrimination factor (greater uptake) for plants growing on ML substrate. The fraction of extractable plutonium in the ML samples is approximately twice that in the ORNL samples; hence the availability may be increased by a factor of 2 in the ML vegetation. One must keep in mind, however, that uptake by plants is also influenced by the nature of the vegetation (aquatic versus terrestrial), root characteristics (fibrous versus tap root), and other environmental factors so that predictions based on one consideration are open to question.

## 4.3. Mineral association of plutonium

Particle size segregation of the NTS samples has shown that the plutonium is associated with the coarse silt size particles; and in the ML sample, the plutonium was found primarily in the clay size particles. Chemical solubility tests have shown low solubility of the plutonium in the NTS samples and high solubility of the plutonium in the ML samples. To further investigate the nature of the plutonium, these high plutonium fractions were subjected to density gradient segregation. This technique separates minerals according to their specific gravity. X-ray diffraction analysis to identify the minerals in the recovered fractions (bands) were performed; these fractions were then analyzed for plutonium.

### 4.3.1. Plutonium distribution in density-gradient fractions

The fractions obtained after density gradient segregation are listed in the first column of Table V. The bulk of the particles in the NTS samples show specific gravities ranging from 2.5 to 2.7 g/cm$^3$. The interesting finding is in the distribution of the plutonium. In the bare soil sample, the plutonium is concentrated mainly in the "heavy" fraction (> 2.9 g/cm$^3$) with approximately 75% in the 11% weight fraction. On the other hand, under the vegetation, the "heavy" fraction contributed less than 10% of the activity with nearly the same weight of particles. The plutonium under the vegetation is associated primarily with the 2.5 - 2.7 g/cm$^3$ fraction (80 - 95%).

## TABLE V

## PLUTONIUM DISTRIBUTION OF COARSE SILT FRACTION OF NTS SAMPLES AND THE CLAY FRACTION OF ML SAMPLE

| Density Range ($g/cm^3$) | Nonvegetated Soil (A13 - 1A) |  | Vegetated Soil (A13 - 1B |  | 8C - 43-47 |  |
|---|---|---|---|---|---|---|
|  | Weight (%) | Activity* (%) | Weight (%) | Activity* (%) | Weight (%) | Activity (%) |
| < 1.8 | 0.3 | 1-3 | 1.0 | 0-1 | 5.9 | 16 |
| 1.8-1.9 | --- | --- | --- | --- | 8.5 | 6 |
| 2.0-2.2 | 2.1 | 1-2 | 0.7 | 0-1 | --- | -- |
| 2.2-2.3 | 6.2 | 1-2 | 5.0 | 0-1 | 7.9 | 6 |
| 2.3-2.4 | 9.8 | 3-4 | 7.8 | 2-3 | 64.9 | 70 |
| 2.4-2.5 | 17.2 | 4-5 | 6.5 | 0-2 | --- | -- |
| 2.5-2.7 | 45.0 | 5-15 | 61.5 | 80-95 | --- | -- |
| > 2.9 | 11.1 | 60-85 | 8.9 | 1-10 | 4.5 | 2 |
|  | 91.7 |  | 91.4 |  | 91.7 |  |

*Numbers refer to range in values for duplicate analysis.

These findings suggest that the bulk of the plutonium in the bare soil occurs as discrete particles, presumably plutonium oxide. On the other hand, the plutonium under the shrubbery is different from that found in the bare soil. One possible explanation of the difference may be that the plutonium deposited under the shrubbery is "smeared" on the surface of silicate particles which were originally in the bare soil. Further speculation is premature at this time, especially since only one sample has been analyzed thus far. More samples should be examined from different areas and distances from Ground Zero, as well as samples representing different depths of the bare soil and the vegetative mound, to further elucidate mechanisms of association and implications on vegetation uptake.

### 4.3.2. Mineralogy of plutonium-bearing fractions

X-ray diffraction analysis of the minerals was performed on the recovered bands of NTS and ML samples. Diffractograms of the significant plutonium-bearing fractions in the 2.5 - 2.7 and the > 2.9 g/cm$^3$ bands of NTS and the 2.3 - 2.4 g/cm$^3$ band of the ML sample are shown in Figure 1. For given density bands, both the bare soil and the sandy mound showed very similar mineral distribution; the selected diffractograms marked a and b are from the bare soil. The 2.5 - 2.7 g/cm$^3$ band (Fig. 1a) is conspicuous by its high concentration of felspar (Fl). Although quartz (Qr) appears to be prominent, the amount of quartz is minimal as 5% quartz would show prominently in diffraction patterns. In the "heavy" mineral band (> 2.9 g/cm$^3$ in Fig. 1b), mica (Mi) and hornblende (Ho) are dominant. Felspar is detected and the multipeak character of the felspar in this band suggests different felspars as compared with the lighter band. Although chlorite (Ch) and kaolinite (Kl) are difficult to differentiate, occurrence in the "heavy" band suggests chlorite as a component. Note also the occurrence of dolomite (Do) in the "heavy" band which proves the calcareous nature of the soil.

The near identical mineral suites found in both the bare soil and the sandy mound strongly suggests the same source term. If the plutonium in the "heavy" mineral fraction had been bonded strongly to the minerals, one would expect the "heavy" mineral fraction under the shrubbery to contain a high concentration of plutonium. The concentration of plutonium in the 2.5 - 2.7 g/cm$^3$ band of the bare soil was much lower than that in the same density fraction of the sandy mound. Since the concentration is low in the bare soil, transport of the particles to the shrubbery should not have resulted in the high concentration observed there. A possible reason for the difference may be that the sampled depth (0 - 5 cm) of the bare soil extended too far downward and included uncontaminated coarse silt particles. The wind may have transported particles from the very near surface of the bare soil which may have been more highly concentrated in plutonium. Limited data obtained on depth profile samples show about 95% of the activity in the 0 - 5 cm depth is in the 0 - 2.5 cm depth.

Figure 1c is the diffractogram of the 2.3 - 2.4 g/cm band of the clay fraction from the ML sample. This band made up about 65% by weight of the clay fraction (Table V). Although the 10.1 A peak is labeled mica (Mi), peaks more like the mica peaks shown in Fig. 1b of the NTS sample are observed in the "heavy" mineral fraction of this sample. The term "illite"

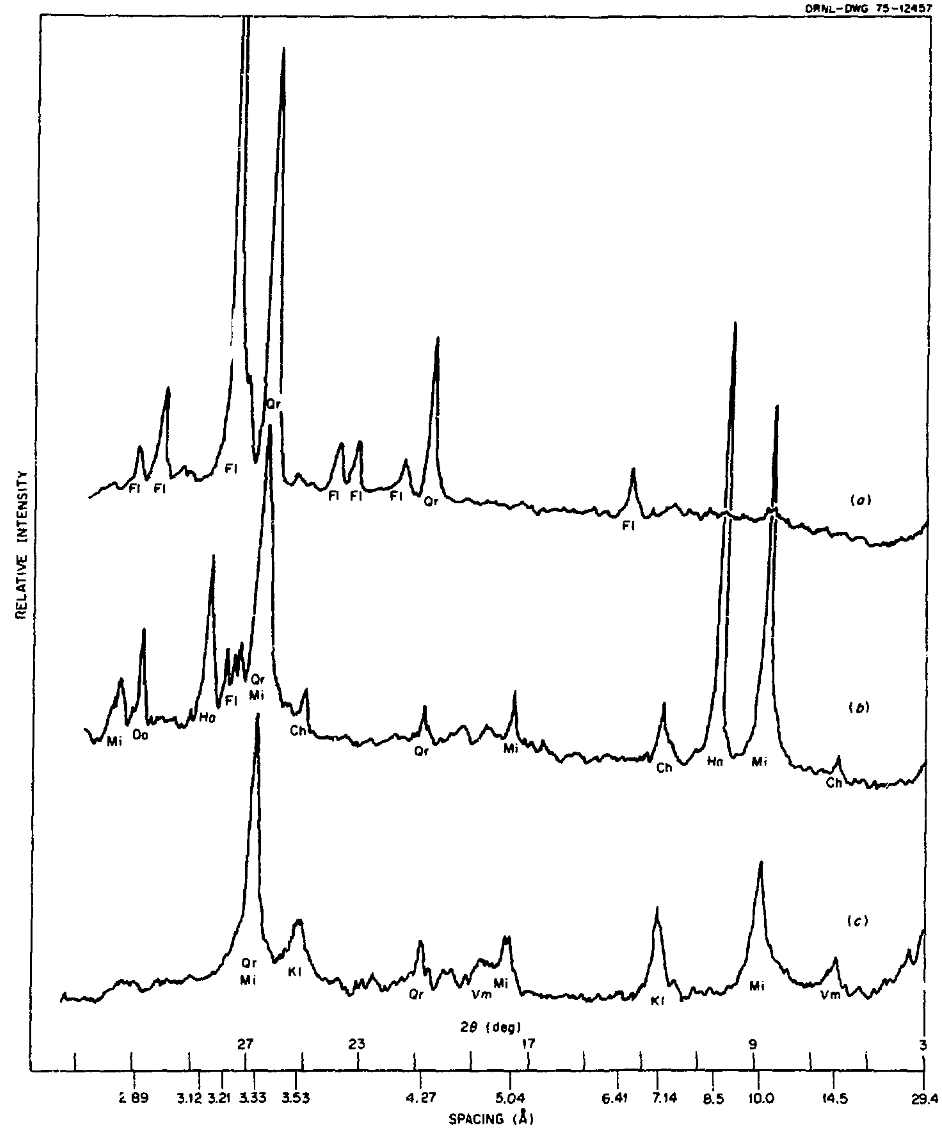

Fig. 1. X-ray diffractograms of selected density bands of the coarse silt fraction of NTS soils and the clay fraction of ML sediment. a = 2.5 - 2.7 g/cm$^3$ of NTS; b = > 2.9 g/cm$^3$ of NTS; c = 2.3 - 2.4 g/cm$^3$ of ML. (Fl = felspars; Qr - quartz; Mi = mica; Ch = chlorite; Ho = hornblende; Do = dolomite; Vm = vermiculite; Kl = kaolinite.)

is often used for this diffraction maximum. The specific gravity of 2.3 - 2.4 g/cm$^3$ suggests that kaolinite (Kl) and vermiculite (Vm) are present; however, this has not been verified.

Data in Table V show that the distribution of plutonium in the density fraction is directly related to the amount by weight of the band, the exception being the lightest fraction which includes organic material with approximately three times the concentration. The mineralogy of each band supports this type of distribution in that the diffractograms are very similar, the major difference being widening of the maxima for each mineral which may be interpreted to mean that the finer particles were more highly hydrated and thus exhibited a lower specific gravity. The exception to the mineralogy was the "heavy" band that showed the presence of dolomite, which was absent in all other fractions. If plutonium were associated with carbonates, the activity in the "heavy" fraction should show a higher concentration that that observed. Thus the evidence suggests that the plutonium is associated mainly with silicate particles and that possibly 10% is associated with the high organic matter fraction (< 1.8 g/cm$^3$). Since about 30% of the plutonium is in the silt sizes, the nature of the association with silicates cannot be due simply to the identified silicates of Fig. 1c. In trace-level reactions, small amounts of minor components can significantly affect adsorption reactions.

The results obtained to date provide an insight to understanding the behavior of plutonium as it exists under diverse environmental conditions. The amount and character of the plutonium in the NTS samples, for example, have implications for the resuspension and vegetative uptake of this nuclide in the desert. The different character of the plutonium under the shrubbery from that in the bare soil suggests that in resuspension by saltation and creep, the transport of plutonium is dependent on the contamination and movement of silicates rather than as plutonium oxide particles [14]. Furthermore, discrimination factors obtained with bare soil substrate may not truly reflect conditions of uptake by native vegetation in the desert. The concentrations of plutonium in the finer silt and clay sizes, though constituting a small fraction of the total soil plutonium, are important considerations in evaluating the higher airborne particles bearing plutonium which may be transported over longer distances [15].

Although the total concentration of plutonium in a matrix is important in assessing the potential hazard, total amounts do not necessarily indicate its potential availability to plants. Results of the citrate solubility tests appear to hold promise as a means of evaluating the available amount of plutonium. Development of a reliable "soil test" for correlating amount found in plants with amount in the soil will provide a valuable tool for assessing the hazard of plutonium accidentally released to the environment.

It should be reemphasized that the results obtained to date are exploratory in nature. They show that plutonium characteristics differ, including differences in size and association of particles and in extractability. Vigorous pursuit of these types of studies, as well as other related studies of site properties, should provide better understanding of plutonium's behavior and fate in the environment.

## 5. CONCLUSIONS

The following tentative conclusions may be drawn on the basis of the experimental results and the interpretations presented herein:

1. Plutonium in the NTS samples occurs predominantly in the silt size fraction. Dispersion of the soil prior to size segregation reduced the contribution of plutonium by the sand size particles and increased the contribution by the silt size particles.

2. In the ML samples, the predominant fraction containing plutonium is the clay fraction. The clays occur as aggregates and, in the natural state, behave as silt particles.

3. In the ORNL sample, the plutonium is more evenly distributed in the silt and clay sizes; however, the clay size is the highest contributor.

4. Citrate extractions show the highest plutonium solubility in the ML sample, followed by the ORNL sample, and least in NTS samples.

5. Citrate solubility comparison with published discrimination factors for NTS and ORNL samples shows a direct relationship which may prove useful as a technique for predicting potential uptake.

6. Density gradient segregation and x-ray diffraction studies of selected NTS sample suggest differences in the character of the plutonium in the bare soil and in the sandy mound. Movement of plutonium by wind action may be as particles which are tightly bonded to silicate particles rather than as separate plutonium oxide particles.

7. Density gradient and x-ray diffraction studies of ML sample suggest a relatively even distribution of the plutonium on clay particles; limited data further suggest that the plutonium is not incorporated or co-precipitated with carbonates.

## 6. ACKNOWLEDGMENT

To the many scientific co-workers who assisted me during the investigations, I wish to express my deep gratitude. Personnel of Reynolds Electrical and Engineering Company, Mound Laboratory, Health and Safety Laboratory, and Oak Ridge National Laboratory provided full cooperation and assistance during sampling. Special appreciation is expressed to the Nevada Applied Ecology group (NAEG) of the Nevada Operations Office who provided initial funding and encouragement to pursue these studies. I especially want to thank Mr. E. R. Eastwood of ORNL who performed the plutonium analyses and Mr. E. G. Struxness who has been a source of inspiration during pursuit of these studies.

## REFERENCES

[1] TAMURA, T., "Distribution and characterization of plutonium in soils from Nevada test site," The Dynamics of Plutonium in Desert Environments (DUNAWAY, P. B., WHITE, M. G., Eds.), USAEC Rep. NVO 142 (1974).

[2] TAMURA, T., Distribution and characterization of plutonium in soils from Nevada test site, J. Environ. Quality 4 (1975) 350.

[3] TAMURA, T., "Characterization of plutonium in surface soils from Area 13 of the Nevada test site," The Radioecology of Plutonium and Other Transuranics in Desert Environments (WHITE, M. G., DUNAWAY, P. B., Eds.), USAEC Rep. NVO 153 (1975).

[4] GILBERT, R. O., EBERHARDT, L. L., "Statistical analysis of Pu in soil at the Nevada test site--some results," The Dynamics of Plutonium in Desert Environments (DUNAWAY, P. B., WHITE, M. G., Eds.), USAEC Rep. NVO 142 (1974).

[5] DAHLMAN, R. C., TAMURA, T., Plutonium distribution in vegetation and soil of a 30-year-old contaminated flood plain, Health Physics (submitted for publication) (1975).

[6] REYNOLDS ELECTRICAL AND ENGINEEERING CO., Standard procedures of the radiological sciences department, 7 May 1968; revised 25 September 1972, Mercury, Nevada.

[7] McDOWELL, W. J., FARRAR, D. T., BILLINGS, M. R., Plutonium and uranium determination in environmental samples: combined solvent extraction-liquid scintillation method, Talanta 21 (1974) 123.

[8] FRANCIS, C. W., BONNER, W. P., TAMURA, T., An evaluation of zonal centrifugation as a research tool in soil science: I. Methodology, Soil Sci. Soc. Amer. Proc. 36 (1972) 366.

[9] DAY, P. R., "Particle fractionation and particle-size analysis," Ch. 43, Methods of Soil Analysis, Part 1 (BLACK, C. A., Ed.), Amer. Soc. Agronomy, Madison, Wisconsin (1965).

[10] MORK, H. M., Redistribution of plutonium in the environs of the Nevada test site, University of California Rep. UCLA 12-590 (1970).

[11] LINDENBAUM, A., WESTFALL, W., Colloidal properties of plutonium in dilute aqueous solution, Int. J. Appl. Rad. Isotopes 16 (1965) 545.

[12] CLEVELAND, J. M., "Carbonates and Oxalates," Ch. 13, The Chemistry of Plutonium, Gordon and Breach Science Publishers, New York (1970).

[13] ROMNEY, E. M., DAVIS, J. J., Ecological aspects of plutonium dissemination in terrestrial environments, Health Physics 22 (1972).

[14] REICHMAN, J. M., "Saltation and creep sampler," The Dynamics of Plutonium in Desert Environments (DUNAWAY, P. B., WHITE, M. G., Ed.), USAEC Rep. NVO 142 (1975).

[15] ANSPAUGH, L. R., PHELPS, P. L., "Results and data analysis: resuspension element status report," The Dynamics of Plutonium in Desert Environments (DUNAWAY, P. B., WHITE, M. G., Eds.), USAEC Rep. NVO 142 (1975).