The measurements of the oxidation states of fallout plutonium in rainwater collected at Monaco indicate that plutonium exists predominantly in the higher oxidation states (Pu(V) and Pu(VI)). The results obtained show that the percentage of the higher valency fraction of plutonium ranges from 38 to 89% of the total soluble plutonium in rain. The percentage tends to be lower when the storage time before the chemical treatment becomes longer. A thermodynamical computation supports these findings.

The occurrence of plutonium in the higher oxidation states in rain is considered to be one of the major causes of the characteristic geochemical stability of fallout plutonium observed in the Mediterranean Sea.

**INTRODUCTION**

Plutonium has been intensively studied in the aquatic environment and numerous published works dealing specifically with its geochemistry have been critically reviewed recently by Sholkovitz (1983). According to this author significant advances include the observations by Bowen et al. (1980), Nelson and Lovett (1978, 1979, 1981), Nelson and Orlandini (1979), Wahlgren et al. (1977a, b) and Santschi et al. (1979, 1980). Owing to many unknowns which still exist in the behaviour of plutonium in the aquatic environment, Sholkovitz (1983) proposed that future studies should focus on pore waters and the overlying water column as well as on the oxidation state distribution of dissolved plutonium within these solutions. However, he did not refer to the extensive literature dealing with the Mediterranean (cf. Fukai et al., 1979; Holm et al., 1980; Fukai et al., 1982). Laboratory studies on the interaction of plutonium with sediment particles (Murray and Fukai, 1975), or with chelating substances in soil and natural waters (Silver, 1972, 1983; Bondietti et al., 1976; Nelson and Lovett, 1978; Bondietti and Trabaluka, 1980; Rai et al., 1980; Aston, 1980; Edgington, 1981), as well as on the ingestion of plutonium by marine organisms (Fowler and Guary, 1977; Fisher et al., 1983) suggest that the oxidation states of plutonium substantially influence its behaviour in the aquatic environment. There is still no definitive agreement among various authors about the oxidation state of plutonium in the freshwater and marine environments.

Sholkovitz et al. (1983) have performed laboratory experiments to study the diagenetic chemistry of plutonium. From estimated diffusive fluxes in the pore water they concluded that plutonium does not show significant chemical mobility in coastal sediments of Buzzard Bay, Mass., U.S.A. Recently, Sholkovitz and Mann (1984) have developed sampling and extraction methods to collect large volumes of pore water and have made the first study of pore water chemistry of plutonium in the marine sediments collected from Buzzards Bay.

Plutonium in rain was studied much less extensively. Thein et al. (1980) measured total
$^{238}$Pu, $^{239+240}$Pu and $^{241}$Am, and Ballestra et al. (1984) reported their measurements of $^{241}$Pu in the rain of Monaco. Based on their $^{241}$Pu measurements it was possible to estimate the origin and age of the deposition which occurred during the period of their investigation. The atmospheric mean residence time was estimated to be 6-10 months. They have concluded that among all nuclear atmospheric tests only the 21st Chinese thermonuclear test with 4 MT yield in November 1976 (Carter, 1979) could have had some influence on the wet and dry fallout deposition in Monaco in 1979. Since more than 90% of fallout plutonium is known to be brought down by rain to the earth’s surface (Miyake et al., 1962; Gavani, 1978; Thein et al., 1980), its oxidation states should be one of the important factors influencing the geochemical behaviour of plutonium in the environment. To out knowledge no information is available until now on oxidation states of plutonium in rain water, except a short note published by us (Fukai et al., 1981), which does not contain experimental and calculation details. Sill (1975) only assumed that after the nuclear detonations plutonium had been injected to the atmosphere in the lower oxidation states, but he did not measure the state in which it was delivered to the earth’s surface with rain water. Plutonium specification in marine system was recently discussed by Morse and Choppin (1986).

The purpose of this paper is to present the results of measurements of different oxidation states of fallout plutonium in rain collected at Monaco in 1979, and to compare the data with the results of the simplified thermodynamical model calculation.

**Experimental**

Rain samples were collected in a 5 m$^2$ stainless steel collector placed on the Mussee Oceanographique building (~35 m high) at Monaco (43°45’N, 07°25’E) and seawater samples were taken from stations approximately 5 km off the Monaco coast. While rain water was filtered through 0.45 µm filters immediately before the chemical treatment, seawater samples were not filtered. The method employed for differentiating the oxidation states of plutonium is similar to that used by Nelson and Lovett (1978) for Irish seawater. Some modifications were necessary, however, to adapt the method to much larger samples, since the concentration of plutonium in Mediterranean rain is lower by a factor of $10^2-10^3$ than in seawater samples collected from the radioactive waste discharge area in the Irish Sea. Briefly, plutonium in the lower valency states (Pu(III) and Pu(IV)) was first coprecipitated with LaF$_3$ from 30–100 m$^3$ water samples after the oxidation of Pu(III) to Pu(IV) and Pu(V) to Pu(VI) with Cr$_2$O$_7^{2-}$ in an acid medium; plutonium in the higher valency states which remained soluble during the coprecipitation was reduced to Pu(IV) with Fe$^{2+}$ and coprecipitated with LaF$_3$. Thus, the first LaF$_3$ precipitate contains the fraction of plutonium occurring in the samples as Pu(III) and Pu(IV), while the second LaF$_3$ precipitate collects higher valency plutonium, Pu(V) and Pu(VI). Each plutonium fraction was then purified from interfering radionuclides by anion-exchange procedures and the plutonium $^{239+240}$Pu in each fraction was determined by $\alpha$-spectrometry. In order to verify the effectiveness of the valency differentiation as well as to determine the radiochemical yield of the ion-exchange separation, two different plutonium tracers in different chemical forms $^{239}$Pu (Pu(IV), major $\alpha$-energy 5.76 MeV) and $^{242}$Pu (Pu(VI), major $\alpha$-energy 4.90 MeV), were added to the samples prior to the coprecipitation treatment. The chemical forms of each tracer was tested from time to time during the study period and found to be stable. Examples of the $\alpha$-spectra obtained for the lower valency fraction (Pu(III) + Pu(IV)) and for the higher valency fraction (Pu(V) + Pu(VI)) in a rain sample (19–20 May 1979) are given respectively in Fig. 1 (A) and (B). The figure shows that the cross-contamination either by $^{242}$Pu(VI) in the lower valency fraction or by $^{239}$Pu(IV) in the
higher valency fraction did not exceed a few percent of the respective tracers recovered, indicating that the procedures adopted are sufficiently effective in differentiating desired chemical states of plutonium. The method has also been established for large environmental water samples by its originators (Nelson and Orlandini, 1979), and subsequently used by Leskinen et al. (1986) in the Baltic. The latter authors mention that it may be used for filtered waters or for waters containing particulates. The method is rather well established and now generally accepted.

**RESULTS AND DISCUSSION**

The results of the determination of soluble $^{239+240}$Pu in different oxidation states in rain are presented in Table 1 along with the dates of rainfalls, precipitation in millimeters and the length of the storage before the chemical treatment. The percentage of the higher valency plutonium (Pu (V) and Pu (VI)) in total soluble plutonium and the concentrations of insoluble $^{239+240}$Pu retained by the filters (0.45μm pore size) are also given. The determination of insoluble plutonium was made without differentiating the oxidation states, since the suspended matter contained in rain consists mostly of particles resuspended from soil by wind

**Table 1. Occurrence of different oxidation states of plutonium in Mediterranean rain and sea water**

<table>
<thead>
<tr>
<th>Date of collection</th>
<th>Precipitation (mm)</th>
<th>Storage time (days)</th>
<th>Pu (III+IV) (fCi 1⁻¹)</th>
<th>Pu (V+VI) (fCi 1⁻¹)</th>
<th>Total soluble (fCi 1⁻¹)</th>
<th>Pu(V+VI) fraction (%)</th>
<th>Insoluble $^{239+240}$Pu concentration (fCi 1⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26–27 April, 1979</td>
<td>2.4</td>
<td>17.5</td>
<td>0.6 ± 0.3</td>
<td>0.6 ± 0.2</td>
<td>1.2 ± 0.4</td>
<td>50 ± 24</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>19–20 May, 1979</td>
<td>6.3</td>
<td>1.5</td>
<td>7.8 ± 0.9</td>
<td>32 ± 6</td>
<td>40 ± 6</td>
<td>80 ± 19</td>
<td>35 ± 3</td>
</tr>
<tr>
<td>6 June, 1979</td>
<td>1.2</td>
<td>1.0</td>
<td>3.9 ± 0.8</td>
<td>33 ± 3</td>
<td>37 ± 3</td>
<td>89 ± 11</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>13–18 June, 1979</td>
<td>23</td>
<td>6.5</td>
<td>2.8 ± 0.5</td>
<td>1.7 ± 0.2</td>
<td>4.5 ± 0.5</td>
<td>38 ± 6</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>1 July, 1979</td>
<td>7.6</td>
<td>1.0</td>
<td>2.3 ± 0.4</td>
<td>5.7 ± 0.7</td>
<td>8.0 ± 0.8</td>
<td>71 ± 11</td>
<td>4.0 ± 0.6</td>
</tr>
<tr>
<td>20–21 Sept., 1979</td>
<td>43</td>
<td>3.5</td>
<td>0.33 ± 0.07</td>
<td>0.67 ± 0.08</td>
<td>1.0 ± 0.1</td>
<td>67 ± 10</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td>Sea water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26 July, 1979</td>
<td>–</td>
<td>0.5</td>
<td>0.7 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>53 ± 8</td>
<td>–</td>
</tr>
<tr>
<td>26 July, 1979</td>
<td>–</td>
<td>0.5</td>
<td>0.34 ± 0.06</td>
<td>0.50 ± 0.08</td>
<td>0.8 ± 0.1</td>
<td>63 ± 13</td>
<td>–</td>
</tr>
</tbody>
</table>
actions and does not represent fallout material originating primarily from the atmosphere. The contribution of the resuspended materials to the concentration of the soluble plutonium fraction has previously been estimated on rain samples collected similarly at Monaco by comparing the $^{239+240}$Pu/$^{232}$Th activity ratios between rain water and soil samples and was found to be less than 1% of soluble plutonium measured in rain water (Thein et al., 1980). Thus the data for the soluble plutonium given in Table 1 are considered to include only a negligible fraction of $^{239+240}$Pu originating from resuspended materials. The results show that rain water collected contains usually comparable quantities of soluble and insoluble plutonium, although in cleaner rains the insoluble fraction is much reduced. The concentration of the total soluble plutonium in rain water varies over a wide range of 1–40 fCi dm$^{-3}$. It is noted, however, that significant fractions of the higher valency plutonium (Pu V and/or Pu VI) always exist in rain, in spite of the general supposition that plutonium is in the lower oxidation states after the nuclear detonations (Sill, 1975). The percentage of the higher valency fraction ranges from 38 to 89% of the total soluble plutonium in rain, tending to be lower when the storage time before the chemical treatment becomes longer. As Table 1 shows that in several rain water samples particulate fraction as is large as 50% of the total plutonium concentrations, one should be aware that some fallout plutonium could be associated with suspended matter.

In Table 1 the results of a few similar measurements on Mediterranean surface waters are also given. The results do not include the fraction of plutonium associated with suspended matter. The reason is that the unfiltered water was used as it has been established that the particulate fraction of plutonium in Mediterranean surface waters rarely exceeds 5% except for those under heavy land run-off (Holm et al., 1980). As the seawater samples measured were collected during the dry season (July, 1979), the effects of the particulate fraction on the results presented are considered to be within the error of the measurements. The data suggest that the percentage of the higher valency fraction of plutonium in Mediterranean surface water is in a range of 50 to 60%.

The simplified thermodynamical model calculation on the plutonium oxidation state in rain water was based on the following assumptions: oxido-reduction reactions of any ions in an aqueous solution should be solely dependant on the electron activity and the hydrogen ion concentration of the medium and other types of reactions, such as complex formation, heterogeneous surface reactions, etc. can be ignored. In this sense, rain water is an ideal medium among the natural aquatic systems to apply thermodynamical predictions, since the ionic strength of rain water is much lower than that of other types of natural waters. The concentrations of other inorganic and organic ions are usually low. The electron activity of an aqueous solution is governed by the dissolved oxygen content and the pH of the solution. As rain water is well aerated and its pH value measured at Monaco is around 5.5 showing little variation, the electron activity $p = \log e^-$ in Monaco rain is estimated to be 15.1.

The following equation was used:

$$\frac{1}{2} O_2 (g) + 2 H^+ + 2 e^- = H_2O$$

(1)

and the value for equilibrium constant $\log K_1 = 41.55$. The partial pressure of oxygen in rain was considered to be equal to that in the atmosphere, $pO_2 = 0.21$ atm. Ignoring complex formation, we express the oxido-reduction equilibria of various oxidation states of plutonium in an aqueous solution as follows, taking into account the stability constants compiled by Sillen and Martell (1964):

$$PuO_2^{2+} + e^- = PuO_2^+ \quad \log K_2 = 15.7$$

(2)

$$PuO_2^{2+} + 4 H^+ + 2 e^- = Pu^{4+} + 2 H_2O \quad \log k_3 = 35.2$$

(3)
\[
Pu^{4+} + e^- = Pu^{3+} \quad \log K_4 = 16.38 \quad (4)
\]

The total concentration of soluble plutonium can be expressed as:

\[
\text{[Pu]}_{\text{tot}} = \text{PuO}_2^{2+} + \text{PuO}_2^{+} + \text{Pu}^{4+} + \text{Pu}^{3+} \quad (5)
\]

Since \( e^- \), \( H^+ \) and \( \text{[Pu]}_{\text{tot}} \) have known values, equations (2–5) form a system of four equations with four unknowns, \( \text{PuO}_2^{2+} \), \( \text{PuO}_2^{+} \), \( \text{Pu}^{4+} \) and \( \text{Pu}^{3+} \). By solving this system of equations one obtains 79.55% \( \text{PuO}_2^{2+} \) and 20.45% \( \text{PuO}_2^{+} \), with negligible contributions of \( \text{Pu}^{4+} \) and \( \text{Pu}^{3+} \). These equilibria are pH sensitive and partition would be slightly different if the rain water is more acid. If this model is a good approximate, the measurements of the oxidation state of plutonium in Monaco rain should show only the presence of the higher valency plutonium. Although the percentage of the higher valency fraction of plutonium in rain obtained on the basis of the real data is variable (Table 1), the decreasing tendency of the percentage with increasing length of storage suggests that the reduction of the higher valency plutonium has taken place chiefly after the arrival of rain at the earth’s surface (Fukai et al., 1981).

The mechanisms of the reduction from the higher to the lower oxidation states of plutonium in the rain samples cannot be deduced from the available data. However, it is known that \( \text{Pu} \) (V) disproportionates relatively quickly in solutions of pH above 5, forming equal amounts of \( \text{Pu} \) (IV) and \( \text{Pu} \) (VI) (Cleaveland, 1970). If this disproportionation reaction could proceed with reasonable speed in an extremely diluted solution of \( 10^{-15} \text{M Pu} \) (V), the rain water would contain theoretically ~40% \( \text{Pu} \) (IV) and ~60% \( \text{Pu} \) VI after the complete disproportionation of \( \text{Pu} \) (V), on the basis of the values predicted above. Although the reduction of extremely diluted plutonium in rain water may also be attributed to the presence of reductants such as pollen, organic dusts, soil particles, etc., the possible disproportionation of \( \text{Pu} \) (V) cannot be completely dismissed.

As shown in Table 1 the percentage of the higher valency plutonium in Mediterranean surface waters is in a range of 50–60%, although more extensive measurements are needed to generalize this range to other parts of the Mediterranean. The results presented demonstrate that the major fraction of fallout plutonium in Mediterranean rain as well as in surface seawater occurs initially in the higher oxidation states, although the equilibrium of the partition afterwards depends very much on redox conditions of the medium.

The lower \( ^{241}\text{Am/}^{239+240}\text{Pu} \) activity ratio in Mediterranean surface waters relative to that in the integrated fallout delivery (0.05 versus 0.22) (Fukai et al., 1976) as well as the different vertical distribution patterns between \( ^{239+240}\text{Pu} \) and \( ^{241}\text{Am} \) in the water column (Fukai et al., 1979, 1982) suggests that fallout plutonium is more stable in the Mediterranean water column relative to americium, tending to remain in solution for a longer time. The upper limit of the mean residence time of plutonium in the Mediterranean mixed layer has been estimated to be 12.3 years against that of 2.9 years for americium (Thein et al., 1980). This substantial difference in reactivity of these two elements in the seawater medium is now likely to be attributed to the difference in the \textit{in situ} oxidation states of the two actinides. While a major fraction of plutonium occurs in the higher oxidation states, as has been demonstrated, the chemistry of americium excludes the occurrence of this actinide in higher oxidation states under natural conditions (Schulz, 1976). Since the affinity of \( \text{Pu} \) (VI) for carbonate is very high, \( \text{Pu} \) (VI) in surface seawater, either brought down with rain or formed \textit{in situ}, is expected to be complexed with carbonate and remain in solution for a long time.

On the other hand, \( \text{Pu} \) (IV) would be easily hydrolyzed, associated with negatively-charged sinking particles and transported downwards with these particles. Qualitatively, this is considered to be one of the reasons why the behaviour of plutonium and americium in the
upper layers of the Mediterranean differ from each other. The detailed calculation for the oxidation states of plutonium and americium in sea water will be published elsewhere.

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Oxidation states of fallout plutonium

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