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# The Environment Transport of Radium and Plutonium: A Review By Brice Smith and Alexandra Amonette

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**The Environmental Transport of  
Radium and Plutonium:  
A Review**

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Alexandra Amonette

Institute for Energy and Environmental Research

June 23, 2006

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June 22, 2006

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## Chapter One: Introduction

It has been estimated that since the dawn of the nuclear era more than “73 million cubic meters of soils and sediments in the U.S. alone have been contaminated with actinides and fission products by Department of Energy defense nuclear activities.”<sup>1</sup> However, with respect to the protection of human health, the most relevant question is not how much radiation is in the ground, but how much radiation will eventually reach people and damage living cells. In order to answer this question it is necessary as a first step to predict the transport of the contaminants from where they leaked or were discharged through the environment to areas where humans may be exposed to them. The second step is to then try to predict how much of that radiation people would be exposed to, and thus how big a dose they would receive. In this report we will consider only the first step in this process. There are a number of routes of exposure and transport, such as (1) resuspension of deposited radionuclides into the air, (2) uncovering of buried radionuclides due to erosion and subsequent exposure to gamma radiation, (3) migration of radionuclides into groundwater, and (4) mobilization of radionuclides by erosion into surface water. This report provides a review of the last two mentioned pathways, which impact the purity of water resources. It is further focused on two elements, radium and plutonium, that are present at many contaminated sites across the United States and in other countries as well.

Given the inhomogeneous and highly complex chemical, biological, and physical properties of soil, rocks, groundwater, and surface water, it has been found that predicting the mobility of radionuclides is far from simple. For example, when many of the sites within the U.S. nuclear weapons complex were founded, it was believed that their arid climate and thick unsaturated zones would help to protect the groundwater beneath the sites for hundreds to thousands of years. However, investigations of contaminant mobility at these sites have revealed these early assumptions to be in substantial error. For example, the travel time estimated by the DOE for radionuclides to reach the Snake River aquifer under the Idaho National Engineering and Environmental Laboratory (now the Idaho National Laboratory) has fallen from tens of thousands of years in their predictions from the mid-1960s to just a few tens of years today. This thousand fold increase in the contaminant’s estimated mobility was prompted by the discovery that plutonium had already reached the groundwater 200 meters beneath the Radioactive Waste Management Complex.<sup>2</sup>

A second example where early predictions of limited contaminant transport were later disproved by facts on the ground is the case of tritium at the waste disposal facility in Beatty, Nevada. Despite the fact that it was originally predicted that no tritium would migrate from the disposal area at all, tritium has already been found 48 meters below the site. A third example of this kind of failure was the DOE’s prediction that the low rain fall and 90 meter thick unsaturated zone below the waste disposal areas at Hanford in Washington State would prevent any contamination from reaching the groundwater. Unfortunately, some fission products and other radionuclides that have leaked from high-level waste tanks have already reached the water table below Hanford, in some areas, after just 60 years.<sup>3</sup> Finally, a fourth example of the failure of past DOE predictions can be found in its analysis

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<sup>1</sup> [Loyland Asbury, Lamont, and Clark 2001 p. 2295] Until 1974 the Atomic Energy Commission was responsible for the U.S. nuclear weapons complex. In 1974 it was split up into the Energy Research and Development Administration and the Nuclear Regulatory Commission. In 1977, the Energy Research and Development Administration became the Department of Energy. [DOE Timeline] For simplicity we will use the term Department of Energy in this report regardless of the time period.

<sup>2</sup> NAS/NRC 2001 p. 93-94 and Long and Ewing 2004 p. 391

<sup>3</sup> NAS/NRC 2001 p. 93 and Long and Ewing 2004 p. 391

of plutonium migration from the underground nuclear weapons tests conducted at the Nevada Test Site (NTS).<sup>4</sup>

In all of these examples, the conceptual models relied upon by the DOE for decision making failed to accurately predict contaminant transport, and it was only after the discovery of radionuclides spreading into the environment that these models were revised. The failure of these transport models was due in large part to the failure to adequately characterize the systems. As summarized by the National Research Council of the U.S. National Academies of Science

Simply stated, a transport model is only as good as the conceptualizations of the properties and processes that govern radionuclide transport on which it is based.<sup>5</sup>

In real systems there may be chemical and biological processes that will occur which effect the mobility of contaminants. These processes may themselves be changing over space and time which would further complicate efforts to predict radionuclide transport. There may also be more pathways by which the radionuclides can move than originally expected. For example, plutonium and other transuranics can adsorb onto very small particles known as colloids. These particles are so small that they can move with the ground or surface water thus mobilizing contaminants that would otherwise have been considered to be insoluble and tightly held by the soil or sediments. In other systems flooding or surface erosion may dominate the transport of some radionuclides. Finally, the transport model itself might be adequate, but the information on what parameters to input may not be available from experimental evidence or the information available may not be adequate to properly represent the characteristics of the site.

In this report we will provide a brief review of the environmental transport of two specific radionuclides. In Chapter Two we will consider the mobility of radium. This naturally occurring radionuclide is part of the uranium and thorium decay series, and is thus a potential concern in many areas where these elements have been mined or processed. In addition to the large number of sites with radium bearing waste, we chose to focus on this radionuclide in part due to the high concentrations of radium-226, and its thorium-230 parent, in the raffinate waste from the former Fernald Feed Material Production Plant in Ohio. In Chapter Three we will discuss the mobility of plutonium, and to some extent other transuranic elements. Contamination with these anthropogenic radionuclides has been discovered at a number of DOE sites and, due to the long half lives of many of these elements, they are a potential concern for long-term management.

For both radium and plutonium we have found that there are a number of important site-specific properties that can either enhance or retard the mobility of these radionuclides. In addition, to discussing the chemical, biological, and physical processes that can affect the mobility of these radionuclides, we have also provided a discussion of the main transport model used today in determining regulatory compliance as well as its strengths and weaknesses. As a result of this review, our primary conclusion is that detailed, site-specific analyses are essential when attempting to accurately predict the transport of radium or plutonium through the environment. Performance assessments which are predicated on simplified models and default values should not be accepted as an adequate basis for demonstrating compliance with regulatory limits. Site-specific measurements of important model parameters should include an adequate number of samples to ensure that the results are truly representative of the entire site and the chemical state of the contamination. In addition, the measurement methodology used should be carefully chosen to most closely approximate the

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<sup>4</sup> [Kersting et al. 1999] This example is discussed in greater detail in Section 3.3.

<sup>5</sup> NAS/NRC 2001 p. 92

conditions at the site. Finally, transport modelers should learn from past surprises and unexpected behavior of radionuclides and seek to be realistically conservative in their treatment of potential transport pathways and in the parameters they use. This is particularly true for radium and many of the transuranic elements, given the long half lives of many of these radionuclides and their parents.

## Chapter Two: Radium Mobility in the Environment

Radium is a naturally occurring radionuclide that is part of the uranium and thorium decay series. Only four radium isotopes are known to exist in nature, and all four are radioactive.<sup>6</sup>

Isotope	Half life	Primary Decay Mode	Decay Series
Radium-228	5.75 years	beta	Thorium-232
Radium-226	1,600 years	alpha, gamma	Uranium-238
Radium-224	3.66 days	alpha, gamma	Thorium-232
Radium-223	11.44 days	alpha, gamma	Uranium-235

In addition to their own radiological properties, three of these radium isotopes present additional environmental and health concerns due to the fact that they decay into radon. Radon is a gas at room temperature and is thus more mobile in the environment. The National Research Council noted that radon-222 “was the first occupational respiratory carcinogen to be identified” and that “[r]adon has now been classified as a human carcinogen by the International Agency for Research on Cancer.”<sup>7</sup> The three radon isotopes created by the decay of radium are:

Radon Isotope	Half life	Parent Isotope
Radon-222	3.8 days	Radium-226
Radon-220	56 seconds	Radium-224
Radon-219	4.0 seconds	Radium-223

Generally, the most important radium isotope is radium-226 given the relative abundance of uranium-238 in the environment, the long half life of radium-226, and the fact that it decays into radon-222.

The most recent information on radium’s mobility in the environment was reviewed in 2004 as part of a study by the U.S. Environmental Protection Agency entitled *Understanding the Variation in Partition Coefficient,  $K_d$ , Values: Volume III: Review of Geochemistry and Available  $K_d$  Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium*. The majority of the information presented in this appendix is drawn from Section 5.7 “Radium Geochemistry and  $K_d$  Values.”<sup>8</sup>

Radium belongs to the group of alkaline earth metals, and its chemical properties are, therefore, most similar to those of barium. In the body, radium is a calcium analog, and goes primarily to the bone. Over a wide range of pH values from acidic (pH 3) to basic (pH 10), “the dominant aqueous species for dissolved radium” is believed to be the +2 oxidation state. While dissolved radium generally does not form aqueous complexes, the following complexes have been identified in experimental settings; “ $\text{RaOH}^+$ ,  $\text{RaCl}^+$ ,  $\text{RaCO}_3^0$  (aq), and  $\text{RaSO}_4^0$  (aq).”<sup>9</sup>

Radium dissolved as  $\text{Ra}^{+2}$  can adsorb onto soil through ion exchange. The strength of this interaction for a given set of chemical conditions and soil properties can be quantified in terms of the partition coefficient ( $K_d$ ). The partition coefficient is an equilibrium property that relates the concentration of a contaminant adsorbed onto the solid phase to that dissolved in the liquid phase.<sup>10</sup> This definition

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<sup>6</sup> EPA 2004 p. 5.64

<sup>7</sup> NAS/NRC 1999 p. 20

<sup>8</sup> EPA 2004 p. 5.63-5.72

<sup>9</sup> EPA 2004 p. 5.64

<sup>10</sup> EPA 1999 p. 2.16 to 2.18



results in the partition coefficient having the somewhat unusual units of liters per kilogram (L/kg) or, equivalently, milliliters per gram (ml/gm).

$$K_d = \text{concentration in the solid phase (pCi/kg)} / \text{concentration in the liquid phase (pCi/L)}$$

A large value of the partition coefficient, therefore, implies that the contaminant is tightly bound to the soil and will migrate slowly, while a small value implies the opposite. Due to its relative simplicity, the constant  $K_d$  approach is one of the most important transport models used today.<sup>11</sup> For example, ResRad, the computer program developed at Argonne National Laboratory for use in determining compliance with DOE and NRC regulations, uses this type of transport model.<sup>12</sup>

Despite the presence of radium-226 in uranium bearing ores, there have been only a relatively modest number of studies conducted on the mobility of radium in the environment. The 2004 EPA review includes the following table summarizing the available data:

Table 2.1. Measurements of the partition coefficient for radium for various soil types. The wide range over which the results are spread is noteworthy given the relatively limited number of observations.<sup>13</sup>

Soil Type	$K_d$ Values (ml/g)		
	Geometric Mean	Number of Observations	Range
Sand	500	3	57 - 21,000
Silt	36,000	3	1,262 - 530,000
Clay	9,100	8	696 - 56,000
Organic	2,400	1	N.A.

The EPA notes that these data are drawn from a “minimal number of adsorption studies” and that, therefore, the effect of soil and water chemistry on the mobility of radium is not well known. The authors go on to note that,

However, as an alkaline earth element, the adsorption behavior of radium will be similar and somewhat greater to that of strontium for which extensive studies and data exist. For screening calculations of radium migration in soils, the  $K_d$  lookup table listed in Volume II [of *Understanding the Variation in Partition Coefficient,  $K_d$ , Values*] can be used as general guidance for radium.<sup>14</sup>

This recommendation notwithstanding, the EPA concludes that

Given the absence of definitive maximum and minimum  $K_d$  values for radium as a function of the key geochemical parameters, such as pH, EPA suggests that  $K_d$  values measured for radium at site-specific conditions are thus *essential* for site-specific contaminant transport calculations and conceptual models.<sup>15</sup>

This conclusion is supported by an earlier review of radium mobility conducted by the Agency for Toxic Substances and Disease Registry (ATSDR). In its 1990 review, the ATSDR noted that

<sup>11</sup> EPA 1999 p. iii

<sup>12</sup> Yu et al. 2001

<sup>13</sup> EPA 2004 p. 5.72

<sup>14</sup> EPA 2004 p. 5.67

<sup>15</sup> EPA 2004 p. 5.67 (emphasis added)

Adsorption constants [ $K_d$ ] for inorganic ions such as  $Ra^{2+}$  cannot be predicted a priori because they depend on the type of adsorbent, the pH of the water, and the presence of other ions in solution.<sup>16</sup>

In this chapter, we will first summarize the information available regarding the adsorption/desorption behavior of radium. Second, in light of the EPA's recommendation that it is "essential" that site-specific measurements of the partition coefficient be made, we will examine some of the difficulties that are encountered in making such measurements. Finally, we will conclude by reviewing the limitations of the constant  $K_d$  transport model for predicting the environmental mobility of contaminants like radium.

## Section 2.1 – Adsorption/Desorption Studies

Radium is known to be "readily adsorbed to clays and mineral oxides present in soils, especially near neutral and alkaline pH conditions."<sup>17</sup> In addition, studies of adsorption and desorption "indicate that radium is essentially completely reversibly adsorbed."<sup>18</sup> In a study of uranium mill tailings, Landa and Gray found that "alkaline earth sulfate and hydrous ferric oxide solids are important sorption phases" for radium.<sup>19</sup> Similar results have been found in relation to radium's mobility in groundwater. For example, Turekian found that the retardation of radium was "high in oxidizing ground waters because of the scavenging of radium by manganese and iron oxide surfaces."<sup>20</sup> These results are important to consider in connection to the Fernald raffinate waste given the presence of high concentrations of sulfates and lead oxide in the silos compared to the concentration of radium.<sup>21</sup>

In addition to the presence of alkaline earth sulfates and metal oxides which influence the sorption of radium, there are a number of other factors that can affect the sorption of materials in general. For example, the affinity of an element for ion exchange relative to other members of its chemical group increases with increasing atomic weight. Therefore, the sorption of radium is the strongest of all the alkaline earth metals.<sup>22</sup> Second, given that the number of sites at which ions may be adsorbed are limited, the adsorption of any particular species decreases as the concentration of competing ions increases. In the specific case of radium, its adsorption "has been shown to be strongly dependent on ionic strength and concentrations of other competing ions."<sup>23</sup> Third, the pH of the system also has a strong effect on the adsorption of cationic species like radium. When an ion is adsorbed onto soil it typically releases a hydrogen ion ( $H^+$ ). This release is favored under alkaline conditions and inhibited under acidic conditions. Thus, radium will become increasingly mobile in acidic soils and waters. This effect has been found to be particularly strong when the decrease in pH is due to the presence of organic acids.<sup>24</sup>

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<sup>16</sup> ATSDR 1990 p. 49 (emphasis in the original)

<sup>17</sup> EPA 2004 p. 5.67

<sup>18</sup> EPA 2004 p. 69

<sup>19</sup> EPA 2004 p. 5.66 and 5.68

<sup>20</sup> Turekian Abstract 1997 p. 2

<sup>21</sup> The average radium concentration of the raffinate waste in Silos 1 and 2 at Fernald (prior to addition of bentonite clay) was approximately 300 parts per billion. The sulfate concentration, on the other hand, was 90,000 times higher than the concentration of radium while the lead oxide concentration was 327,000 times higher than that of radium. [Fioravanti and Makhijani 1997 p. 224, 237, and 239]

<sup>22</sup> EPA 2004 p. 5.67

<sup>23</sup> EPA 2004 p. 5.67

<sup>24</sup> IAEA 1990 p. 331 and EPA 2004 p. 5.67

As a result of the “minimal number of adsorption studies” that have been carried out, there remain important outstanding questions about the adsorption of radium to materials other than clays, mineral oxides, and alkaline earth sulfates. Some studies have suggested that “radium may be strongly adsorbed by organic material in soils,” while others have been less conclusive.<sup>25</sup> For example, Nathwani and Phillips found that “the adsorption of radium on organic matter is ten times as high as on clay” and “therefore conclude that the affinity of radium for organic exchangeable places is somewhat larger than for average ions.”<sup>26</sup> However, in a study of “highly weathered and sandy soils,” Willet and Bond found “no clear relationship between <sup>226</sup>Ra sorption and the concentrations of organic matter and clay in the soils.”<sup>27</sup> These results strengthen the conclusion that site-specific measurements of radium’s mobility are essential when conducting site-specific performance assessments.

Finally, we note that the adsorption of radium on crushed rock and numerous pure mineral phases has also been studied.<sup>28</sup> However, the EPA concluded that these results “are not necessarily relevant to the mobility and sorption of radium in soils” given the complexity of typical soil systems and the strong dependence of the partition coefficient on local physical and chemical conditions.<sup>29</sup> In addition, many of the studies on crushed rock were conducted as part of efforts to study the geologic disposal of spent nuclear fuel. As such, they “were conducted over a range [of] temperatures above ambient to determine the extent of radionuclide adsorption as a function of temperature and with respect to changes in groundwater chemistry (e.g., pH and Eh) and mineralogy that will occur with increasing temperature.”<sup>30</sup> This further limits their value in estimating radium mobility at typical soil temperatures.

## Section 2.2 – Measuring the Partition Coefficient

One of the most significant difficulties that is encountered in trying to accurately measure the partition coefficient for radium or any other element is that the value of  $K_d$  is strongly dependent on the local chemical properties of the system.<sup>31</sup> Therefore, it is very important to collect a suitably wide range of samples in order to ensure that the samples being studied are truly representative of the site.

There are currently five methods for measuring the partition function in general use. These include the “laboratory batch method, *in-situ* batch method, laboratory flow-through (or column) method, field modeling method, and  $K_{oc}$  method.”<sup>32</sup> As summarized by the EPA

Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating  $K_d$  values from experimental data. Consequently, it is not only common, but expected that  $K_d$  values measured by different methods will produce different values.<sup>33</sup>

One significant disadvantage of these techniques is that “[e]ssentially all of the assumptions associated with the thermodynamically defined  $K_d$  value... are violated in the common protocols used to measure

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<sup>25</sup> EPA 2004 p. 5.67 to 5.68

<sup>26</sup> IAEA 1990 p. 329

<sup>27</sup> EPA 2004 p. 5.68

<sup>28</sup> EPA 2004 p. 5.72 and H.2 to H.5

<sup>29</sup> EPA 1999 p. 2.1 and EPA 2004 p. 5.72

<sup>30</sup> EPA 2004 p. H.4

<sup>31</sup> EPA 1999 p. 2.1

<sup>32</sup> EPA 1999 p. 3.1

<sup>33</sup> EPA 1999 p. 3.1

$K_d$  values for use in contaminant transport codes.”<sup>34</sup> As a result, partition coefficients measured for the same system using different methodologies “commonly” differ by “over an order of magnitude.”<sup>35</sup>

In the case of radium, additional measurement uncertainties arise due to the potential for precipitation or co-precipitation of radium with other alkaline earth metals. It is known that in moderate to high sulfate containing waters, “precipitation and redissolution of calcium (Ca), strontium (Sr), and barium (Ba) sulfates, rather than adsorption/desorption, could control the concentrations of dissolved radium in the soil environment.”<sup>36</sup> The direct precipitation of radium sulfate ( $\text{RaSO}_4$ ) is not the controlling solid phase. Generally the most important co-precipitate is  $(\text{Ba,Ra})\text{SO}_4$  given that co-precipitation with barium is the preferred method “for the removal of dissolved  $^{226}\text{Ra}$  from effluents from uranium mining and milling operations” and that it “has also been shown to be [an] important process in controlling the solubility of radium in natural waters.”<sup>37</sup> In general, co-precipitation with alkaline earth metals is likely to be important in tailings which have high concentrations of sulfuric acid and in the Fernald raffinate waste which is known to have a high concentration of sulfates.

As a result of the potential for radium to co-precipitate with other alkaline earth metals, the EPA “cautioned that any data that indicates very high adsorption of radium on geological materials should be suspect due to the possibility that  $(\text{Ba,Ra})\text{SO}_4$  co-precipitation may have occurred during the measurement.”<sup>38</sup> A specific example of where this may have occurred in reported results was the work of Nathwani and Phillips. The EPA noted that their results were “unusually large, and orders of magnitude greater than those reported by most researchers,” and that this fact “suggests that precipitation of radium may have occurred during the course of these measurements.”<sup>39</sup> In their overall summary of studies on radium, the EPA concluded that

It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the  $K_d$  values used for each compilation. The compilations do not typically consider important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large  $K_d$  values are listed, there is a risk that the original  $K_d$  measurement may have included precipitated components.<sup>40</sup>

Care should be taken in conducting site-specific assessments to ensure that co-precipitation does not lead to the reporting of erroneously large values for the partition coefficient.

### **Section 2.3 – Limitations of the $K_d$ Approach**

While the use of a constant partition coefficient is the most common transport model used in determining regulatory compliance, it has a number of limitations that hinder its usefulness in some real world situations. As summarized by the EPA in 1999

Clearly, the greatest limitation of using  $K_d$  values to calculate retardation terms... is that it describes solute partitioning between the aqueous and solid phases for only 1 set of

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<sup>34</sup> EPA 1999 p. 2.16

<sup>35</sup> EPA 1999 p. 3.2

<sup>36</sup> EPA 2004 p. 5.63

<sup>37</sup> EPA 2004 p. 5.65 to 5.66

<sup>38</sup> EPA 2004 p. 5.66 to 5.67

<sup>39</sup> EPA 2004 p. 5.69

<sup>40</sup> EPA 2004 p. 5.71

environmental conditions. Such homogeneity does not exist in nature and therefore greatly compromises the usefulness of the constant.<sup>41</sup>

In a review of the use of the  $K_d$  transport model, Bethke and Brady note that

$K_d$  theory works best for trace amounts of nonionized hydrophobic organic molecules, but is too simplistic to accurately represent sorption of ionic species within soils and sediments. The  $K_d$  coefficient measured for an ionic species is not meaningful in the general sense but is specific to the sediment and fluid tested. The  $K_d$  value for a metal typically varies over many orders of magnitude, depending on fluid pH and composition as well as the nature of the sediment.<sup>42</sup>

As noted, radium exists in solution as a +2 cation and it is therefore not surprising that its partition coefficient is strongly dependent on the local aqueous and solid phase chemistry as well as being dependent on the other properties of the soil.

In addition to these general limitation of the  $K_d$  approach given the heterogeneity of the partition coefficient across a site, there are additional limitations to the use of this model. Specifically, the constant  $K_d$  model does not include a constraint for the total number of adsorption sites available to the contaminants. Without such a constraint there is no way for the  $K_d$  models to account for the competition for adsorption sites among chemically similar elements; nor is there a way for the models to account for saturation effects at higher contaminant concentrations. In addition, the constant  $K_d$  approach does not take into account the impact of electrostatic effects which arise due to the surface charge induced by adsorbed ions such as radium.<sup>43</sup>

As noted above, determining an appropriate  $K_d$  value can be complicated, and a number of samples are required to ensure that the results are representative of the site. Adding a more detailed analysis requires additional information to the knowns about the site which increases both the complexity and the cost of performing these kinds of site evaluations. As a result, in many cases a suitable value can be chosen such that the constant  $K_d$  model is adequate for demonstrating compliance with the performance objectives. However, examples can be found where the use of the  $K_d$  model results in inaccurate predictions about the migration of contaminants.<sup>44</sup> The use of more complex transport models may be required in some cases of radium contamination such as for uranium mine and mill tailings. As summarized by Zhu,

In the situation of active or abandoned mining sites with acid mine drainage problems, the shortcomings of the  $K_d$  approach become more severe because mining impacted groundwater systems are reactive, involving multiple components that interact with each other, and are chemically heterogeneous. Multiple, sharp reaction fronts are involved, and these fronts evolve through space and time.<sup>45</sup>

In the case of the Fernald raffinate waste, it may also be required to consider more sophisticated transport models for some disposal sites, given the low pH resulting from the addition of grout to the waste, which would tend to increase the mobility of radium, and the presence of high concentrations of sulfates, which may tend to retard the mobility of radium.

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<sup>41</sup> EPA 1999 p. 2.19

<sup>42</sup> Bethke and Brady 2000 p. 437

<sup>43</sup> Bethke and Brady 2000 p. 438

<sup>44</sup> For an example involving lead contamination see Bethke and Brady 2000 and for an example involving sulfate contamination at a uranium mine see Zhu, Hu, and Burden 2001, Zhu, Anderson, and Burden 2002, and Zhu 2003.

<sup>45</sup> Zhu 2003 p. 352

## Section 2.4 – Biota Effects Impacts on Radium Mobility

In addition to the general limitations of the  $K_d$  approach, there are additional complications that may arise as a result of the influence of bacteria, plants, and animals on the mobility of radium. Of particular importance is the fact that the barium-radium co-precipitate that can control radium's solubility is not thermodynamically stable under all reducing conditions. As such, "[s]ulfate-reducing bacteria can produce rapid dissolution of (Ba, Ra)SO<sub>4</sub> sludge under suitable reducing conditions and appropriate carbon sources."<sup>46</sup> For example, Pardue and Guo found that radium in soil "was remobilized under anaerobic sulfate-reducing conditions" and Landa found that radium mobility "was greatly enhanced in the presence of sulfate-reducing bacteria" under anaerobic conditions.<sup>47</sup>

In addition to the dissolution of sulfate precipitates, plants and animals may have additional impacts on soil chemistry or properties that can affect the mobility of radium near the surface. In their 1990 review, the International Atomic Energy Agency summarized these impacts as follows

For the surface layer of soil there exists still another migration mechanism, the mixing due to the activity of soil micro and macro fauna.... It is even very probable that in the upper 20 cm of the soil 'bioturbation', as it is called, surpasses physicochemical transport. An important transfer mechanism is the movement of small animals, but microorganisms also play a role. They produce complexing agents in rather large quantities, just as do the roots of plants. Owing to this complexation, the solubility of radium becomes significantly enhanced. The problems associated with a quantitative description of the impact of this complexation are rather large and are outside the scope of this chapter.<sup>48</sup>

As noted above, radium does not generally form complexes when free in solution, but a number of complexes have been identified experimentally.<sup>49</sup>

Finally, the ATSDR notes that, given its chemical similarity to calcium, radium "may be bioconcentrated and bioaccumulated by plants and animals, and it is transferred in food chains from lower trophic levels to humans."<sup>50</sup> In support of this conclusion, they note specific examples of where radium in the soil has been transferred to plants, particularly in areas where radium or uranium was mined or processed.<sup>51</sup> In their review on radium mobility, however, the IAEA notes that

Soil to plant transfer factors ( $B_v$ 's) are also influenced by various interrelated soil properties, including texture, clay content, dominant clay mineral, cation exchange capacity, exchange cations, pH and organic matter content. Uptake varies with the chemical and physical forms of the nuclides, plant species, plant part and stage of growth, as well as with experimental conditions and the manner in which the isotope is introduced into the soil. As a result, the  $B_v$ 's exhibit much more variability than transfer coefficients for animal products. Generic transfer factors for soil to plant can vary by up to 3 orders of magnitude.<sup>52</sup>

Thus, in cases where the transfer of radium to plants and animals is expected to play an important role in the radionuclide's transport, site-specific measurements of plant transfer functions will also be required as part of conducting site-specific performance assessments.

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<sup>46</sup> EPA 2004 p. 5.66

<sup>47</sup> Landa 1996 p. 22 and EPA 2004 p. 5.66

<sup>48</sup> IAEA 1990 p. 328

<sup>49</sup> EPA 2004 p. 5.64

<sup>50</sup> ATSDR 1990 p. 48

<sup>51</sup> ATSDR 1990 p. 50

<sup>52</sup> IAEA 1990b pp. 355-356

## Section 2.5 – Conclusions

As summarized by the Environmental Protection Agency in 1999

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different  $K_d$  methods and perhaps more importantly the underlying assumption of the methods in order to properly select  $K_d$  values from the literature. The  $K_d$  values reported in the literature for any given contaminant may vary by as much as *6 orders of magnitude*. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate  $K_d$  value(s) for contaminant transport modeling.<sup>53</sup>

While they do report a summary table for radium with geometric mean values reported, the EPA explicitly cautioned against the use of such values in conducting performance assessments. Specifically, the authors of the EPA report emphasized that

The range for the  $K_d$  values used to calculate the “geometric mean” cover several orders of magnitude. Readers are cautioned against using “geometric mean” values or any other form of averaged  $K_d$  values as “default”  $K_d$  values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed... the variation observed in the literature for  $K_d$  values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.<sup>54</sup>

Even for the “minimal” amount of data available for radium, the distribution in results can be significant. For example, the  $K_d$  values for radium measured in sandy soils vary by nearly 370 between the largest and smallest values while the range for silty soils is more than 420.<sup>55</sup>

As a result of the lack of information and the site-specific nature of studies on radium’s mobility, the ATSDR concluded that

Studies of releases of radium that result from uranium mining and processing would be helpful to fully assess the total amount and environmental fate of radium released to the environment. Field data on the mobility of radium in groundwater would also be helpful in attempts to predict its potential for occurrence in sources of drinking water at remote sites.<sup>56</sup>

This conclusion was reinforced by the EPA in 1999 when they noted that “[s]oil geochemists knowledgeable of sorption processes in natural environments have long known that generic or default  $K_d$  values can result in significant error when used to predict the absolute impacts of contaminant migration or site-remediation options.”<sup>57</sup> Finally, in the specific case of radium, the EPA reiterated this conclusion in 2004 and stated that “one of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.”<sup>58</sup>

Performance assessments where radium is an important driver of risk, either directly or indirectly as a source of radon gas, which are predicated on default values of the partition coefficient should not be accepted for regulatory purposes given the EPA’s clear and unequivocal conclusion regarding the need

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<sup>53</sup> EPA 1999 pp. 3.28 to 3.29 (emphasis in the original)

<sup>54</sup> EPA 2004 p. 5.71

<sup>55</sup> EPA 2004 p. 5.72

<sup>56</sup> ATSDR 1990 p. 56

<sup>57</sup> EPA 1999 p. 1.1

<sup>58</sup> EPA 2004 p. 5.67 (emphasis in the original)

for site-specific measurements in order to conduct site-specific analyses. The site-specific measurements of the partition coefficient should include adequate sampling to ensure that the results are truly representative of the site. In addition, the measurement methodology should be carefully chosen to best represent the conditions at the site and to avoid artifacts such as sulfate co-precipitation. In many cases a suitably conservative  $K_d$  value can be arrived at to adequately model the impacts of the contamination, but at sites with highly concentrated and reactive wastes, consideration should be given to the use of more complex transport models in light of the well known limitations of the  $K_d$  approach.



### Chapter Three: Plutonium Mobility in the Environment

Plutonium is essentially an anthropogenic radionuclide that is produced in nuclear reactors from naturally occurring radionuclides by neutron capture.<sup>59</sup> Plutonium belongs to the actinide chemical family and inside the body preferentially goes to the bone. While 15 plutonium isotopes are known to exist, there are only four that are generally considered to be of potential concern in the context of environmental radioactivity:

Isotope	Half life	Specific Activity	Primary Decay Mode	Comments
Plutonium-238	87.7 years	17.3 Ci/gm	alpha	Used to make radioisotope thermoelectric generators
Plutonium-239	24,100 years	0.063 Ci/gm	alpha	Fissile material used in nuclear weapons and mixed-oxide reactor fuel
Plutonium-240	6,540 years	0.23 Ci/gm	alpha	Sometimes decays by spontaneous fission releasing neutrons
Plutonium-241	14.4 years	104 Ci/gm	beta	Decays into americium-241 which is a strong gamma emitter (half life = 432 years)

In addition to plutonium, there are other transuranic elements (i.e., elements with an atomic number greater than uranium) that have been produced by the nuclear complex which may also be of a concern in the environment. These radionuclides include neptunium (Np), americium (Am), and curium (Cm).

As a result of an early belief that transuranic elements would be essentially immobile in the soil,

Prior to 1970, wastes contaminated with such materials were not subject to any special regulations other than very weak ones pertaining to low-level radioactive waste. As a result, they were commonly disposed of along with low-level waste and chemical waste in a variety of ways, including burial in pits and trenches and, in the case of liquid wastes, direct dumping on the ground and injection into wells.<sup>60</sup>

The contamination of soil and water with transuranic elements can pose a significant long-term risk in some cases. As summarized by Fioravanti and Makhijani

Transuranic radionuclides pose special risks. First, the half-lives of some of the most important ones are very long. For example, plutonium-239 has a half-life of over 24,000 years and neptunium-237 has a half-life of over two million years. Despite this, the radioactivity per unit of weight (the “specific activity”) for these radionuclides is high enough for tiny quantities of the material to be dangerous. For instance, plutonium-239 is about 100,000 times more radioactive than natural uranium (which consists of a mixture of uranium-238, uranium-235 and a trace of uranium-234). One-millionth of an ounce (about 30 micrograms) of plutonium-239 deposited in small particles in the lung is very likely to induce cancer. Further, alpha radiation is far more damaging per unit of energy deposited in the body relative to gamma and beta radiation. The high concentrations of long-lived radionuclides in TRU waste require this

<sup>59</sup> Trace quantities of plutonium are generated naturally, but essentially all plutonium in the environment today has been produced by humans.

<sup>60</sup> Fioravanti and Makhijani 1997 p. 50

waste to be disposed of in a geologic repository under Environmental Protection Agency rules similar to those for high-level waste (codified in 40 CFR 191).<sup>61</sup>

Already plutonium from the DOE nuclear weapons production and testing program can be found in the surface waters and groundwater at a number of sites.<sup>62</sup> In fact, plutonium contamination has been specifically identified at nine of the Superfund National Priorities List sites.<sup>63</sup>

Like many contaminants, plutonium dissolved in groundwater or surface water can adsorb onto soil through ion exchange. As it is for radium, the strength of this interaction for a given set of chemical conditions and soil properties can be quantified in terms of the partition coefficient ( $K_d$ ). The partition coefficient is an equilibrium property that relates the concentration of a contaminant adsorbed onto the solid phase to that dissolved in the liquid phase.<sup>64</sup> This definition results in the partition coefficient having the somewhat unusual units of liters per kilogram (L/kg) or, equivalently, milliliters per gram (ml/gm).

$$K_d = \text{concentration in the solid phase (pCi/kg)} / \text{concentration in the liquid phase (pCi/L)}$$

A large value of the partition coefficient, therefore, implies that the contaminant is tightly bound to the soil and will migrate slowly, while a small value implies the opposite.

The measured values of  $K_d$  for plutonium have shown a wide range “from low to extremely high affinities.”<sup>65</sup> Typical values range from 11 L/kg to as much as 300,000 L/kg. Over a wider range of pH values, the values of  $K_d$  measured just at the Hanford site alone have shown variation over more than three orders of magnitude.<sup>66</sup> These variations in  $K_d$  for plutonium are not unexpected given the sensitivity to the local chemical and physical properties of the soil and the other limitations inherent with the constant  $K_d$  model with respect to the transport behavior of heavy metal contamination (see Section 2.3 for a further discussion of these issues). In addition to adsorption, a number of other physical and chemical processes are known to be important for plutonium in many cases. These include such things as the changes in the oxidative state of the plutonium through redox transformations, the transport of plutonium on colloidal particles, the formation of chemical complexes with greater mobility, and the precipitation or co-precipitation of solid contaminant phases.<sup>67</sup> Despite the significant effort that has been expended on studying the migration of plutonium, there remain significant areas of uncertainty. As summarized by Duff in 2001 “sorption, co-precipitation and oxidation state speciation behavior of Pu on geologic materials is poorly understood.”<sup>68</sup>

Finally, when dealing with sites that are contaminated with other transuranic elements, it is important to consider decay and ingrowth of elements which may have significantly different mobility or half lives. For example, the beta decay of plutonium-241 (half life 14.3 years) into americium-241 (half life 432 years) which in turn decays via alpha emission into neptunium-237 (half life 2.14 million

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<sup>61</sup> Fioravanti and Makhijani 1997 p. 57

<sup>62</sup> Fioravanti and Makhijani 1997 p. 50-147, Choppin and Morgenstern 2001 p. 92-93, and Hinton and Pinder 2001 p. 415-418

<sup>63</sup> EPA 1999b p. 5.35

<sup>64</sup> EPA 1999 p. 2.16 to 2.18

<sup>65</sup> EPA 1999b p. 5.34

<sup>66</sup> EPA 1999b p. 5.34 and Cantrell, Serne, and Last 2003 p. 28-30

<sup>67</sup> Rai and Serne 1977 p. 94-95, Fjeld et al. 2003, and Kaplan et al. 2004

<sup>68</sup> Duff 2001 p. 153

years) has been found to be an important series to consider in an assessment at the Nevada Test Site.<sup>69</sup> Another example is the alpha decay of curium-244 (half life 18.1 years) into plutonium-240 (half life 6,540 years). The decay of curium into plutonium has, in fact, already been found to have had a measurable impact on the transport of contaminants at the Savannah River Site.

We will first review the oxidation states for plutonium and what environmental conditions can affect it. Second, we examine the formation of plutonium complexes with organic and inorganic compounds which can increase the mobility of plutonium. Third, we will review the evidence surrounding the transport of plutonium and other transuranics on colloidal particles. Fourth, we will examine the mobilization of sediment bound plutonium via erosion and flooding at Los Alamos National Laboratory. Fifth, and finally, we will briefly discuss the impacts biota can have on the mobility of plutonium.

### Section 3.1 – Oxidation States of Plutonium

Under typical environmental conditions, plutonium is known to exist in four different oxidation states (i.e. +3, +4, +5, and +6). Under reducing conditions, the +3 and +4 oxidation states would be the most stable with the +3 state dominating at pH values below 8.5 and +4 state dominating at pH values above 8.5. Under oxidizing conditions the +4, +5, and +6 oxidation states exist at pH values above 4.0. The EPA reports that “[a] number of investigators believe that under oxidizing conditions, the +5 state to be [sic] the dominant redox state.”<sup>70</sup> Choppin and Morgenstern conclude that “[i]n most natural systems” plutonium is found in the +4 and +5 oxidation states. They go on to note that, while dissolved plutonium can be in either the +4 or +5 redox state, “most adsorbed plutonium” is found to be in the +4 redox state.<sup>71</sup>

The oxidation state of plutonium can have a significant impact on the mobility of the contaminant. This is particularly true given the range of redox states that are possible for plutonium in the environment.<sup>72</sup> In fact, Choppin and Morgenstern conclude that

The most important property of plutonium with respect to its environmental behavior is its oxidation state because solubility, hydrolysis, complexation, sorption and colloid formation reactions differ significantly from one oxidation state to another.<sup>73</sup>

The +5 and +6 oxidation states are typically more mobile in groundwater than the +3 or +4 redox states.<sup>74</sup> For example, an 11 year study at the Savannah River Site found that, if the oxidation of plutonium in the environment was not considered, the mobility of the radionuclide would be underestimated by approximately three and half times.<sup>75</sup> In addition, studies of plutonium in Lake Michigan and in Gull Pond, Massachusetts, have concluded that the influence of iron-magnesium redox reactions in deep anoxic waters significantly increased the amount of dissolved plutonium during certain times of the year.<sup>76</sup> However, investigations in contaminated ponds on the Savannah River Site found no such increase in plutonium concentrations that could be associated with redox reactions, and instead Hinton and Pinder believe that the observed increase at SRS during the summer

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<sup>69</sup> Hu et al. 2003 p. 44

<sup>70</sup> EPA 1999b p. 5.35

<sup>71</sup> Choppin and Morgenstern 2001 p. 102

<sup>72</sup> Skipperud, Oughton, and Salbu 2000 p. 82-83 and NABIR 2003 p. 23

<sup>73</sup> Choppin and Morgenstern 2001 p. 93

<sup>74</sup> Ohnuki et al. 2003

<sup>75</sup> Kaplan et al. 2004

<sup>76</sup> Sholkovitz 1983 p. 144-145 and Hinton and Pinder 2001 p. 427 and 433

was due to a redistribution of the plutonium that was already dissolved in the ponds, and not to an increase in contaminant mobility from the sediments.<sup>77</sup> As summarized by Duff in 2001, “[w]ithout site-specific information on Pu speciation behavior in the geologic environment, it is difficult to assess the mobility and dynamics of Pu in nature.”<sup>78</sup>

Given the importance of plutonium’s oxidation state to its mobility, it is necessary for risk assessment to carefully consider all of the factors that may influence it at a given site. This task is complicated by the fact that the oxidation state of plutonium depends both on how the contaminant was originally formed and released to the environment as well as on the environmental conditions that it is exposed to following placement. Factors that are known to affect the redox state of plutonium include the ambient temperature, the presence of organic matter and other complexants, the alkalinity and pH of the water, the presence of certain types of bacteria, and the impacts of radiolysis.<sup>79</sup> The influence of environmental conditions on the redox state of plutonium can result in contamination becoming either more or less mobile over time. Therefore, as noted by Duff, “a once highly stable form of Pu contamination may eventually become a very active source-term to the surrounding environment.”<sup>80</sup> The interplay between plutonium’s oxidation state and the environmental conditions it encounters are important to keep in mind throughout the discussion in the following two sections in which the impact of complexing agents and colloids on plutonium transport is reviewed.

### **Section 3.2 – Complexing Agents**

Plutonium is known to form a number of complexes with organic and inorganic agents. As summarized by the Environmental Protection Agency

Dissolved plutonium forms complexes with various inorganic ligands such as hydroxyl, carbonate, nitrate, sulfate, phosphate, chloride, bromide, and fluoride; with many naturally occurring organic ligands such as acetate, citrate, formate, fulvate, humate, lactate, oxalate, and tartrate; and with synthetic organic ligands such as EDTA and 8-hydroxyquinoline derivatives.<sup>81</sup>

The presence of these complexing agents in the environment can also alter the oxidation state of plutonium and thus can have multiple impacts on its mobility.

Choppin and Morgenstern note that “[a] significant fraction of the total amount of plutonium that has been released in terrestrial and aquatic environments appears to be associated with humic substances.”<sup>82</sup> These organic materials can reduce plutonium from higher oxidation states to lower states. In “anoxic waters under strongly reducing conditions” complexes of plutonium in the +3 oxidation state with the humic material may also play a significant role in determining the speciation of the contaminants.<sup>83</sup> In addition, “microbially produced complexing ligands such as citric acid” may also affect the mobility of plutonium in the environment.<sup>84</sup> In fact, the EPA concluded that, when the pH is low (i.e. at pH values below about 5 or 6), and when there are “high concentrations of dissolved

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<sup>77</sup> Hinton and Pinder 2001 p. 427 and 433

<sup>78</sup> Duff 2001 p. 154

<sup>79</sup> Sholkovitz 1983 p. 100-101 and 106, EPA 1999b p. 5.35, and Ohnuki et al. 2003

<sup>80</sup> Duff 2001 p. 141

<sup>81</sup> EPA 1999b p. 5.35

<sup>82</sup> Choppin and Morgenstern 2001 p. 98

<sup>83</sup> Choppin and Morgenstern 2001 p. 98 and 102

<sup>84</sup> NABIR p. 23

organic carbon, it appears that plutonium-organic complexes may be control [sic] adsorption and mobility of plutonium in the environment.”<sup>85</sup>

In cases where organic ligands were initially disposed of along with plutonium bearing wastes, it may be important to consider the degradation of these organic materials over time given the long half lives of plutonium-239 and plutonium-240. The degradation of organic agents in the waste will change the environmental chemistry of plutonium resulting in inhomogeneous migration over time.<sup>86</sup> For example, while the transport mechanisms are not yet fully understood, in discussions of contamination found at disposal sites near the Plutonium Finishing Plant at Hanford, it was noted as a possibility that “transuranics could be adsorbed by the soil column after degradation of the organic complexing agents.”<sup>87</sup>

At pH values above 7, the EPA notes that the mobility of plutonium can be influenced by “concentrations of dissolved carbonate and hydroxyl ions” and that the “hydroxy-carbonate mixed ligand complexes” are “[a]mong the strongest complexes of plutonium” known to exist in the environment.<sup>88</sup> These complexes can inhibit the adsorption of plutonium, and thus increase its mobility in the +4 and +5 oxidation states. In addition, “[p]henomenon similar to the reduction and suppression of plutonium adsorption in the presence of carbonate ions have also been observed for other actinides which also form strong hydroxy-carbonate mixed ligand aqueous species.”<sup>89</sup> In summary, the EPA concluded that “[t]hese data suggest that plutonium would be most mobile in high pH carbonate-rich groundwaters.”<sup>90</sup>

Finally, in some waste streams, such as at Hanford, there are synthetic chemicals that were added to the waste which act to enhance the mobility of plutonium. Specifically, ethylenediaminetetraacetate (EDTA), “a synthetic chelator that was used during the production and processing of plutonium” and which is “widely present in the mixed wastes at the Hanford site” is known to reduce the adsorption of plutonium onto soil when present at high concentrations.<sup>91</sup> Care must be taken to consider the concentration of EDTA remaining in the waste given that the EPA noted that it is “unlikely that such concentrations of these synthetic ligands [including EDTA at one millimole per liter] would exist in soils.”<sup>92</sup> The impact of EDTA on plutonium mobility relates both to its ability to form stable complexes with the contaminant as well as its ability to adsorb onto the soil itself, thus reducing the number of surface sites available for plutonium adsorption.<sup>93</sup> The inability of the constant  $K_d$  model to treat the competition of different materials for the same surface adsorption sites and the model’s inability to treat saturation effects are known to be important limitations of this approach (see Section 2.3).

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<sup>85</sup> EPA 1999b p. 5.34 and 5.36

<sup>86</sup> Rai, Serne, and Moore 1980

<sup>87</sup> Dirkes, Hanf, Poston 1999 p. 6.90

<sup>88</sup> EPA 1999b p. 5.34 and 5.36

<sup>89</sup> EPA 1999b p. 5.40

<sup>90</sup> EPA 1999b p. 5.40

<sup>91</sup> NABIR p. 23 and Hakem, Allen, and Sylwester 1999 p. 1

<sup>92</sup> EPA 1999b p. 5.42

<sup>93</sup> Hakem, Allen, and Sylwester 1999 p. 8 and 10

### Section 3.3 – Colloid Mediated Transport

In addition to the formation of complexes, one of the other important processes that can affect the transport of plutonium and other transuranic elements is their ability to adsorb to colloidal particles. Colloids are small particles that occur naturally and are easily suspended in ground and surface water. These particles can be “either inorganic (mineral fragments and secondary minerals of the host rock), or organic material.”<sup>94</sup> Actinides that are in the oxide or hydroxide phase can also aggregate to form “intrinsic colloid” of pure material.<sup>95</sup> Typically the upper size limit for colloids is considered to be one micron, but the definition is sometimes restricted to particles that are smaller than clay (i.e. approximately 0.24 microns).<sup>96</sup> Choppin and Morgenstern note that “[d]epending on their size and charge relative to the surrounding solid phase, colloids can move more slowly or more rapidly than the average groundwater flow,” and thus, the adsorption of transuranic elements onto the surface of colloids may either enhance or retard their mobility.<sup>97</sup>

The potential for colloidal transport to affect the mobility of contaminants like plutonium was recognized more than 50 years ago.<sup>98</sup> While the colloid transport pathway has been known for some time, the interest of researchers in the ability for colloids to enhance the mobility of plutonium in the environment was heightened by the discovery that plutonium from at least one nuclear weapons test at the Nevada Test Site had migrated as much as 1.3 kilometers in approximately 30 years. Kersting et al., the researchers who reported this discovery, concluded that “[m]odels that either predict limited transport or do not allow for colloid-facilitated transport may thus significantly underestimate the extent of radionuclide migration.”<sup>99</sup> Additional experiments have affirmed the conclusion that the mobility of plutonium and other transuranic element could, under certain conditions, be much higher than earlier models would have predicted due to adsorption on colloids.<sup>100</sup>

Depending on the environmental conditions, plutonium is capable of adsorbing to a wide variety of organic and inorganic colloids.<sup>101</sup> Like its ability to form chemical complexes, the absorption of plutonium onto colloids is affected by its oxidative state. Choppin and Morgenstern note that “[t]he mechanism of the formation of actinide associative colloids has been shown to be closely related to the hydrolysis of the actinide ions” and the “strong tendency” of plutonium in the +4 oxidation state “to undergo hydrolysis thus favors its sorption onto colloidal particles.”<sup>102</sup> In this light, it is important to note that the oxidation state of dissolved plutonium has itself been found to be depend “on the colloidal organic carbon content in the system.”<sup>103</sup> The interplay of the redox state of the plutonium and the presence of colloidal material should therefore be carefully considered. In addition to its impact on the redox state of plutonium, Santschi et al. note that “[o]rganic matter can modify the surface charge and characteristics of particle and colloid aggregates” and that, therefore, “[d]epending on the type of natural organic matter, particles and colloids can aggregate (‘coagulate’) or

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<sup>94</sup> Kersting et al. 1998 p. 76

<sup>95</sup> Choppin and Morgenstern 2001 p. 98-99, EPA 1999 p. 2.39, and Kersting et al. 1998 p. 76

<sup>96</sup> Choppin and Morgenstern 2001 p. 98, EPA 1999 p. 2.37, and Kersting et al. 1998 p. 76

<sup>97</sup> Choppin and Morgenstern 2001 p. 98

<sup>98</sup> Gephart 2003 p. 5.33

<sup>99</sup> Kersting et al. 1999 p. 59

<sup>100</sup> See for example Runde et al. 2002 p. 837 and 849-850, Toulhoat 2002 p. 978 and 980-981, Schäfer et al. 2003 p. 1528 and 1533, and Lu et al. 2003 p. 713 and 719.

<sup>101</sup> Buesseler et al. 2003 p. 3-6, Santschi, Roberts, and Guo 2001, Contardi, Turner, and Ahn 2001, EPA 1999b, p. 5.35 and 5.41-42, and Choppin and Morgenstern 2001 p. 98-99

<sup>102</sup> Choppin and Morgenstern 2001 p. 99

<sup>103</sup> EPA 1999b p. 5.41-42

disaggregate” affecting their ability to remain suspended, and thus affecting their ability to be transported through the environment.<sup>104</sup>

While the primary focus of research has been on plutonium, it is also known that other transuranic elements can adsorb to colloids under certain conditions. The difference in these elements preference for binding to colloids can, therefore, lead to different types of mobility for different transuranics. For example, it was found at Los Alamos that “plutonium was associated with the largest size class of colloids, while most americium was either in solution or associated with very small colloids.”<sup>105</sup> As a result, the “uncharged colloid is slowly removed from solution, accounting for the greater removal of plutonium relative to americium.”<sup>106</sup> Thus, the weaker adsorption of americium on the types of colloids present in this case could further increase its mobility relative to plutonium.

Given the highly site-specific nature of the colloidal transport pathway, we will consider the evidence for and against colloid mediated transport at a five DOE facilities. In addition, a discussion of plutonium migration at the Idaho National Laboratory (formerly the Idaho National Engineering and Environmental Laboratory) can be found in the IEER report *Poison in the Vadose Zone*.<sup>107</sup> Despite the significant increase in knowledge that has been gained over the past decade, there remain significant uncertainties at many sites as to how plutonium is migrating. As noted by Contardi et al., “[e]ven in situations where plutonium transport has been documented it is often difficult to determine what mechanism was responsible.”<sup>108</sup>

As highlighted above, Kersting et al. reported in 1999 that plutonium from an underground nuclear weapon test at the Nevada Test Site had migrated much further than originally expected. These researchers found “[t]ritium, and low concentrations of cobalt, cesium, europium and plutonium isotopes” in sample taken from “two aquifers downgradient from an underground nuclear event.”<sup>109</sup> After filtering the samples to select particles of various sizes, Kersting et al. found that, “[e]xcept for tritium, greater than 95% of the measured radioactivity was associated with particulate and colloidal fractions consisting of predominately clays [illite and smectite] and zeolites [mordenite and clinoptilolite/heulandite].”<sup>110</sup> As a result, the researchers concluded that “[t]his finding and the previously reported results of Pu sorption experiments are most consistent with Pu migrating as colloidal material and not as a dissolved phase” and “that modeling radionuclide transport based solely on solubility arguments will severely underestimate the transport of radionuclides associated with colloids.”<sup>111</sup>

However, as noted by Honeyman,

... three conditions must be met for defensible evidence that colloids have transported contaminants: first, colloids must be present; second, contaminants must associate with them; and third, the colloid-contaminant combination must move through the aquifer. The results of Kersting et al. qualitatively meet the first two conditions. But, as the authors point out, the possibility of sampling artifacts meant that they could not quantify some of the parameters

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<sup>104</sup> Santschi, Roberts, and Guo 2001 p. 3

<sup>105</sup> Nelson and Orlandini 1986 p. 3-10

<sup>106</sup> Nelson and Orlandini 1986 p. 3-12

<sup>107</sup> Makhijani and Boyd p. 92-102

<sup>108</sup> Contardi, Turner, and Ahn 2001 p. 324

<sup>109</sup> Kersting et al. 1998 p. 76

<sup>110</sup> Kersting et al. 1998 p. 76 and 80

<sup>111</sup> Kersting et al. 1998 p. 83

needed for supporting the detailed assessment of colloid-facilitated Pu transport in their study. That is, the third condition has not been rigorously met.<sup>112</sup>

Despite this caution, Honeyman does go on to note that, “[n]evertheless, their work clearly shows that a low-solubility contaminant traveled some way from the source, perhaps at or near the local groundwater flow velocity.”<sup>113</sup>

The findings of Kersting et al. have particular significance for the proposed Yucca Mountain repository, which sits on the Nevada Test Site. As noted by Duff, “waste-form glasses can potentially release Pu-containing colloids, a process that could result in enhanced Pu mobility via colloid transport in the subsurface.”<sup>114</sup> This could be important given the evidence of colloidal transport at the Nevada Test Site and the plans to dispose of vitrified high-level waste at Yucca Mountain. While there remains a debate over the significance of colloidal transport of plutonium, the models used by the DOE in their performance assessment of Yucca Mountain do include some consideration of colloid mediated transport. However, despite the fact that multiple colloidal phases have been found in the groundwater at the Nevada Test Site, including some that are known to have a particularly high capacity for incorporating actinides, the performance assessment for Yucca Mountain restricted its analysis to only two types of colloids.<sup>115</sup>

In addition to the findings of Kersting et al. at the Nevada Test Site, Santschi et al. found that, at Rocky Flats, “most of the <sup>239,240</sup>Pu and <sup>241</sup>Am transported from contaminated soils to streams occurred in the particulate (> 0.45 μm, 40-90%) and colloidal (3kDa [kilodaltons] - 0.45 μm, 10-60%) phases.”<sup>116</sup> They went on to conclude that “colloidal Pu formation can become one of the most important vectors for enhancing Pu dispersion at Rocky Flats.”<sup>117</sup> At this site, Santschi et al. found that the mobile plutonium was “mostly associated with organic (humic or fulvics) rather than with the more abundant inorganic (iron oxide and clay) colloids” and that the “remobilization of colloid-bound Pu during soil erosion events can be enhanced by humic and fulvic acids.”<sup>118</sup>

While the colloidal transport of plutonium at Los Alamos National Laboratory was believed to be important by Penrose et al. in a study published in 1990 as part of the DOE’s Subsurface Science Program, a 1997 study by Marty et al. has disputed the significance of colloids for long distance contaminant transport. Penrose et al. found plutonium and americium in samples drawn from wells as far as 3.39 kilometers down gradient from the point at which waste was discharged into Mortandad Canyon.<sup>119</sup> The authors found that “the plutonium and part of the americium are tightly or irreversibly associated with colloidal material between 25 and 450 nm in size” and that “[t]he mobile forms of these actinides defeat the forces that normally act to retard their movement through groundwater systems.”<sup>120</sup> While the authors considered the possibility that flooding caused by storms could be responsible for the transport of these radionuclides, they concluded that “the tritium oxide transit time measurements suggest that the majority of water movement takes place in the subsurface.”<sup>121</sup>

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<sup>112</sup> Honeyman 1999

<sup>113</sup> Honeyman 1999

<sup>114</sup> Duff 2001 p. 144

<sup>115</sup> Long and Ewing 2004 p. 381

<sup>116</sup> Santschi, Roberts, and Guo 2001 p. 2

<sup>117</sup> Santschi, Roberts, and Guo 2001 p. 2

<sup>118</sup> Santschi, Roberts, and Guo 2001 p. 2

<sup>119</sup> Penrose et al. 1990 p. 228

<sup>120</sup> Penrose et al. 1990 p. 228

<sup>121</sup> Penrose et al. 1990 p. 228



Reanalyzing the data in 1997, Marty et al. acknowledged that “plutonium has been detected in groundwater as far as 3.4 km from the effluent outfall” and that they cannot conclusively determine the transport mechanism.<sup>122</sup> However, Marty et al. noted that

<sup>239</sup>Pu entering the canyon increased sharply in the early 1980s. Routine monitoring during this period shows that isotopically distinct plutonium appeared in one downgradient well before it appeared in wells closer to the source. If this is ignored, plutonium moved at least twice as fast as groundwater flow and easily outdistance a tritium peak. Isotopically heavy plutonium arrived simultaneously in surface alluvium and groundwater, and the isotopic composition of plutonium in alluvium and groundwater are identical.<sup>123</sup>

From these observations, the authors concluded that “[p]lutonium clearly did not move down-canyon via groundwater” and that “[t]he potential for plutonium movement through groundwater on colloids may be overstated at this and other sites.<sup>124</sup> While they acknowledge that “colloidal transport of plutonium over short distances (meters or tens of meters) in the canyon cannot be discounted by the current discussion” they believe that “plutonium must have moved across the surface before entering the monitoring wells.”<sup>125</sup> In support of this conclusion they note the significance of flooding following storms to contaminant transport in the canyons at Los Alamos.<sup>126</sup>

Determining the mechanisms that have led to such rapid migration of plutonium in the canyons at Los Alamos is particularly important given the large discrepancy that has been discovered in LANL’s estimates of how much plutonium has been discharged to waste. A recent analysis by IEER has concluded that approximately 300 kilograms of plutonium is unaccounted for at Los Alamos when the information in the Nuclear Materials Management and Safeguards System is compared to all available information on plutonium in waste at Los Alamos, including that which is retrievably stored, dispersed by hydronuclear tests, or buried at shallow or intermediate depths.<sup>127</sup> If a significant fraction of this unaccounted for plutonium is actually buried onsite, then it would pose a significant health and environmental hazard.

Finally, at both Hanford and the Savannah River Site, it is not currently believed that colloidal transport of plutonium has played a major role in contaminant mobility. At Hanford, plutonium is among the radionuclides that have leaked from the waste tanks in the 200 Area and plutonium has been found in the groundwater beneath this site.<sup>128</sup> Plutonium has also been detected at “extremely low” levels beneath the 100-K area at Hanford where the KE and KW reactors were operated.<sup>129</sup> In addition, sediments from along the Columbia River and behind the McNary Dam have also shown evidence of contamination with plutonium and other radionuclides from the Hanford facility.<sup>130</sup> Despite this evidence of migrating contamination, however, Dai et al. noted that “[s]ize fractionation data from two wells [in the 100-K area] suggest that 7-29% of the Pu is associated with colloids.”<sup>131</sup> From this the authors concluded that “neither the low fraction of colloidal Pu, nor the decreased

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<sup>122</sup> Marty, Bennett, and Thullen 1997 p. 2021

<sup>123</sup> Marty, Bennett, and Thullen 1997 p. 2020

<sup>124</sup> Marty, Bennett, and Thullen 1997 p. 2020

<sup>125</sup> Marty, Bennett, and Thullen 1997 p. 2026

<sup>126</sup> Marty, Bennett, and Thullen 1997 p. 2020-2021

<sup>127</sup> Makhijani and Smith 2006

<sup>128</sup> Gephart 2003 p. 5.34-5.40

<sup>129</sup> Dai, Buesseler, and Pike 2004 p. 2

<sup>130</sup> Gephart 2003 p. 5.43-5.44

<sup>131</sup> Dai, Buesseler, and Pike 2004 p. 2

concentration of Pu in the downstream well supports enhanced transport of groundwater Pu colloids at this site.”<sup>132</sup>

At the Savannah River Site, there have been observations of plutonium-238 associated with colloidal material.<sup>133</sup> However, the plutonium-239/240 contamination studied has shown little evidence of being transported by colloids. For example, Dai et al. found “that < 4% of the <sup>239</sup>Pu or <sup>240</sup>Pu is found in the colloidal fraction.”<sup>134</sup> As such Dai et al. noted that “[t]he observation of a low abundance of colloid-associated Pu in SRS groundwater cannot be extrapolated to all sites, but is in contrast to the conclusions of prior groundwater Pu studies at the SRS and elsewhere.”<sup>135</sup>

One of the main reasons for the lack of adsorption to colloids at SRS is the fact that, unlike Hanford where much of the plutonium is in a reduced chemical state, the vast majority of plutonium detected near the seepage basins at Savannah River Site was oxidized.<sup>136</sup> The difference in the plutonium oxidation state between SRS and Hanford is not due solely to the differences in their environmental chemistries. At SRS it has been discovered that the decay of curium-244 (half life 18.1 years) into plutonium-240 after the curium has been transported away from the seepage ponds is an important contributor to the apparent rapid migration of plutonium at the site. As noted by Dai et al., “because  $\alpha$  spectrometric methods measure combined <sup>239</sup>Pu and <sup>240</sup>Pu activity... all <sup>239,240</sup>Pu was mistakenly presumed to derive from Pu seepage basin discharges.”<sup>137</sup> The importance of curium migration and decay is consistent with the observation of the higher oxidation state for plutonium.<sup>138</sup> Thus, as Dai et al. summarize, “looking for geochemical reasons to explain groundwater Pu speciation variability between SRS and Hanford Site is complicated by this <sup>244</sup>Cm source of oxidized <sup>240</sup>Pu at SRS.”<sup>139</sup>

If these results from SRS hold true more generally, it may have a significant impact on the evaluation of long-term environmental risk at some sites. While the magnitude of the discharges of curium was typically far smaller than plutonium, and thus often not considered to be as significant a risk, the discharges of curium-244 could be important if it is more mobile in the environment given its decay into a long-lived plutonium daughter.<sup>140</sup>

### Section 3.4 – Erosion and Surface Water Transport

Plutonium adsorbed onto sediment at the bottom of rivers or lakes may become mobilized by resuspension. For example, a study of the Rhone River in Europe found that “after a resuspension event, the plutonium activity increased by a factor of 2 to 3 both in its particulate and dissolved phases” which indicates “the existence of a plutonium desorption process during resuspension events.”<sup>141</sup> In their study of plutonium behavior in the lakes on the Savannah River Site, Hinton and Pinder concluded that “[t]he timing of the winter remobilization suggests that resuspension of plutonium-bearing sediment particles by bottom currents or wave action in near-shore sediments may

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<sup>132</sup> Dai, Buesseler, and Pike 2004 p. 18

<sup>133</sup> Loyland Asbury, Lamont, and Clark 2001 p. 2299-2300

<sup>134</sup> Dai, Kelley, and Buesseler 2002 p. 3690

<sup>135</sup> Dai, Kelley, and Buesseler 2002 p. 3690

<sup>136</sup> Dai, Buesseler, and Pike 2004 p. 2-3

<sup>137</sup> Dai, Kelley, and Buesseler 2002 p. 3698

<sup>138</sup> Dai, Kelley, and Buesseler 2002 p. 3690-3691 and Dai, Buesseler, and Pike 2004 p. 3 and 18

<sup>139</sup> Dai, Buesseler, and Pike 2004 p. 17

<sup>140</sup> Buesseler et al. 2003 p. 6 and 26-27

<sup>141</sup> Lansard et al. 2003 p. 99-100

be important.”<sup>142</sup> Further, Santschi et al. concluded that “aggregation and disaggregation processes” occurring during soil erosion are important factors in the migration of plutonium via surface water at Rocky Flats.<sup>143</sup>

One of the areas where the transport of plutonium via surface water is known to be a particularly important pathway is the Los Alamos National Laboratory (LANL). Canyons surrounding the Los Alamos laboratory were contaminated with plutonium due to the early waste management practices of the lab. In his 1994 book entitled *Plutonium and the Rio Grande*, Graf concluded that

Sediments in Los Alamos Canyon impregnated with plutonium move down the canyon system in a stepwise fashion, with each step taken as a few meters to a few kilometers during each flood event. Each flood stores the sediments as channel or flood-plain deposits, and each subsequent flood remobilizes them until they reach the Rio Grande.<sup>144</sup>

and later that

Surface water is the main driving force behind the movement of plutonium through the surface system of northern New Mexico. The energy represented by the water is expended partly by the moving sediments and associated plutonium from one place to another and partly by the mixing and dispersion of contaminants.<sup>145</sup>

To give a sense of scale to the importance of this pathway, Graf notes that “[i]n just one storm at Los Alamos, surface water run off transported 1 to 2 percent of the entire sediment-bound inventory of plutonium.”<sup>146</sup> In this context, it is important to note that the sorting processes that redeposit the sediments of different grain sizes in different locations can result in a spatially inhomogeneous distribution of plutonium that should be taken into account when remediation efforts are undertaken.<sup>147</sup> In addition to its influence on redeposition, the grain size of the sediments to which the plutonium is adsorbed at Los Alamos can be used to help identify whether the contamination is from the laboratory or is a result of nuclear weapons testing. Based on the fact that fallout plutonium is “mostly associated with fine-grained materials and suspended sediments, whereas the inputs from Los Alamos are mostly associated with coarse particles and bedload,” Graf estimates that plutonium from LANL accounts for only about 10 percent of the total amount in the “basin upstream from the confluence of the Rio Grande and Los Alamos Canyon,” but that this contamination is a concern because it “is concentrated in only a few places.”<sup>148</sup>

The significance of the surface water transport pathway has increased since May 2000 when the Cerro Grande fire burned approximately 43,000 acres in and around Los Alamos laboratory. During this fire, nearly 80 percent of the watershed feeding Pueblo Canyon was “subjected to a high intensity burn.”<sup>149</sup> This loss of vegetation has led to increased erosion in the areas around the canyon, particularly during the flooding that follows storm events. The increased erosion has led to a corresponding increase in the transport of contaminants located near the surface.<sup>150</sup> Measurable quantities of plutonium have been detected being swept out of Pueblo Canyon by storm runoff following the Cerro Grande fire. As might be expected, the amount of plutonium activity resuspended

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<sup>142</sup> Hinton and Pinder 2001 p. 426

<sup>143</sup> Santschi, Roberts, and Guo 2001 p. 3

<sup>144</sup> Graf 1994 p. 127

<sup>145</sup> Graf 1994 p. 235

<sup>146</sup> Graf 1994 p. 10

<sup>147</sup> Graf 1994 p. 12

<sup>148</sup> Graf 1994 p. 64-65, 149-150, and 235

<sup>149</sup> Englert, Ford-Schmid, and Bransford 2003 p. 2

<sup>150</sup> Englert, Ford-Schmid, and Bransford 2003 p. 2, 12-13, and 30

by the flooding generally increases with increasing rates of water flow.<sup>151</sup> The rate of plutonium migration during storms was found to be highly inhomogeneous. For example, in one 10 hour storm event in June 2002, 97 percent of the plutonium was estimated to have been washed away within the first five hours.<sup>152</sup>

One of the most significant floods with respect to plutonium migration at LANL occurred on July 2, 2001. During this flood, the laboratory's automated sampling system did not function properly and was therefore not able to estimate the amount of plutonium being washed down Pueblo Canyon. The New Mexico Environment Department, however, did take a grab sample and was able to make an estimate. The plutonium-239/240 activity measured in the grab sample was 250 picocuries per liter. This was nearly 16.7 times higher than the gross alpha limit for drinking water and nearly 1,670 times higher than the surface water standard set by the State of Colorado for areas around Rocky Flats.<sup>153</sup> A LANL report concluded that "[t]he recent floods seen since the Cerro Grande fire contribute pulses of plutonium into the Rio Grande, likely not seen since the 1960s."<sup>154</sup> All told, the amount of contaminants measured in the storm runoff for the year 2001 were "the highest ever recorded for plutonium-239, -240" and the increase was attributed "to increased storm runoff after the Cerro Grande fire."<sup>155</sup>

### Section 3.5 – Biota Impacts

Finally, as is typical of heavy metals, the amount of plutonium that is taken up into plants is several orders of magnitude less than the amount present in the soil. As such, transfer to vegetation is not likely to play a significant role in the transport of plutonium.<sup>156</sup> Despite this, however, there are other biota effects that can impact the migration of plutonium. The roots of plants as well as microbes and funguses can introduce agents that enhance the formation of complexes which inhibit the adsorption of plutonium onto soil and thus enhance its mobility.<sup>157</sup> In addition, some types of bacteria can have multiple impacts on the adsorption of plutonium. For example, in experiments with the bacteria *Bacillus subtilis*, it was found that between 80 and 90 percent of the plutonium was adsorbed by the bacteria at the end of the first day. In addition, it was observed that the plutonium was converted from the +6 oxidation state to the +5 state "within 2 hours" and that roughly four-fifths of the sorbed plutonium was in the +4 oxidation state after 48 hours.<sup>158</sup> The enhanced mobility of plutonium in the presence of bacteria has been attributed to the production of "extracellular metabolic products, organic acids, such as citric acid, and sequestering agents, such as siderophores."<sup>159</sup> The impact of bacteria in the environment is complicated by the fact that, in some instances, the reduction of plutonium to lower redox states may inhibit its mobility, and by the possibility that living bacteria may act as colloids themselves upon which the plutonium may adsorb, thus increasing its mobility.<sup>160</sup> A detailed examination is beyond the scope of this report.

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<sup>151</sup> Englert, Ford-Schmid, and Bransford 2003 p. 15

<sup>152</sup> Englert, Ford-Schmid, and Bransford 2003 p. 15 and 17

<sup>153</sup> [LANL 2002 p. 189, 40 CFR 141 p. 441-443, and Colorado Reg. 31, 2005] IEER has recommended that the EPA adopt a 0.15 picocuries per year limit as the new drinking water standard for alpha emitting transuranic radionuclides during its 2006 review of the Safe Drinking Water Act standards. [Makhijani 2005]

<sup>154</sup> LANL 2002 p. 189

<sup>155</sup> LANL 2002 p. 190

<sup>156</sup> Graf 1994 p. 107

<sup>157</sup> Negri and Orlandini 1995 p. 5

<sup>158</sup> Ohnuki et al. 2003

<sup>159</sup> Francis 2001 p. 201

<sup>160</sup> Francis 2001 p. 206-211 and 216-217

### Section 3.6 – Conclusions

Discussing the difficulties encountered when developing models for the performance of a high-level waste repository, the National Research Council concluded that “[s]imply stated, a transport model is only as good as the conceptualizations of the properties and processes that govern radionuclide transport on which it is based.<sup>161</sup> This sentiment holds true for assessments of plutonium migration through the environment as well. The Environmental Protection Agency has acknowledged that

Soil geochemists knowledgeable of sorption processes in natural environments have long known that generic or default  $K_d$  values can result in significant error when used to predict the absolute impacts of contaminant migration or site-remediation options.<sup>162</sup>

Beyond the general limitations of the constant  $K_d$  approach, the importance of redox transformations, complex formation, colloidal transport, and surface erosion and sediment transport combine to make determinations of plutonium migration a difficult and highly site-specific challenge.

Given the very wide range of  $K_d$  values found, even across a single site like Hanford, any performance assessment where plutonium or other transuranic elements are an important driver of risk which is predicated on default values of the partition coefficient should not be accepted for regulatory purposes. At a minimum, an effort should be undertaken to determine a well founded site-specific value for  $K_d$ . The site-specific measurements of the partition coefficient should include adequate sampling to ensure that the results are truly representative of the site and the redox state of the contamination. In addition, the measurement methodology should be carefully chosen to best represent the conditions at the site.

In cases where erosion and surface water transport or colloid-mediated transport are potentially important or where there are high concentrations of complexing agents present that may change over space and time, it is not likely that a realistic  $K_d$  value can be arrived at to adequately model the migration of the contamination. At such sites, a more complex transport model should be used that takes these other pathways into account, particularly in light of the well known limitations of the  $K_d$  approach and the relatively rapid migration of plutonium that has already been observed at some sites. Finally, these models should seek to be conservative in their treatment of potential transport pathways and in the parameters they use given the long half lives of many of the important transuranic radionuclides and the fact that we still cannot fully explain the mechanisms by which plutonium has already been observed to migrate at all sites.

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<sup>161</sup> NAS/NRC 2001 p. 92

<sup>162</sup> EPA 1999 p. 1.1

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