

Seasonal Variations in Interstitial Water Transuranium Element Concentrations

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The porewater concentrations of the transuranium elements Np, Pu, and Am have been measured over time at a salt marsh in west Cumbria, U.K., and all three show seasonal variations. Pu follows the pattern previously observed at this site very closely, with concentrations reaching a maximum of 32 mBq L⁻¹ and a minimum of 0.8 mBq L⁻¹ in 1996, compared with 35 mBq L⁻¹ and 1.1 mBq L⁻¹, respectively, in 1994. However, no relationship with dissolved Fe and Mn concentrations was observed in this study. Plutonium and Am concentrations follow similar patterns from April to September, but there are fluctuations in the Am concentration in February which are not observed for Pu. Neptunium concentrations, measured by accelerator mass spectrometry, follow a less clear pattern, although they are at a marked maximum of 0.56 mBq L⁻¹ in February. Changes in Pu and Am concentrations between April and September can be related to changes in the microbial community and suggest that these elements are taken up in biosorption processes. When biomass is low, no relationship is observed between Pu and Am concentrations. There is no correlation between the microbiological data and Np concentrations at any time of year.

Introduction

The BNFL Sellafield nuclear fuel reprocessing plant has been releasing low-level liquid radioactive waste directly into the Irish Sea since 1952. The activity of the transuranic elements released peaked in the mid-nineteen seventies and has now fallen to a small fraction of that level (1). The transuranium elements have a high affinity for natural solid phases and so associate rapidly with particulate matter upon release into the Irish Sea (2, 3). Only a very small proportion of the Pu and Am is transported in the solution phase, and it has been estimated that 95% of Pu released has been retained within a radius of 30 km of the release point (4). Np is known to be more soluble than Pu or Am, but it is still associated with particulate material to a significant extent (5). Transport of the transuranium elements therefore occurs mostly through

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contaminated particles being scoured from the seabed by tidal motion and carried to low-energy regions where they are deposited. This redistribution of the particles can be observed, for example, in the salt marshes of the Esk Estuary, 10 km from Sellafield, where the activity profiles of Pu in the sediment show a close correlation with Sellafield releases (6, 7). The relatively high solid phase concentrations in these sediments sustain measurable quantities of Pu in the solution phase, typically 10 mBq L⁻¹. These are around 6 orders of magnitude lower than in the solid phase, so measuring changes in solution concentrations is a sensitive probe for changes at the solid/solution interface.

There is still some controversy regarding the factors which are most important in deciding the fate of Pu and the other transuranium elements in the natural environment. Plutonium has been the most extensively studied, and one of the major points of debate is the relationship between Pu and Fe. Nelson and Lovett (2) showed that there were subsurface maxima in porewater Fe and Pu concentrations in several sediment cores in the northeastern part of the Irish Sea, which Sholkovitz (8) interpreted as evidence for a diagenetic reaction. Sholkovitz et al. (9) simulated diagenetic reactions in coastal sediments and compared the porewater chemistry of the major reactive species with that of three radionuclides, including Pu. Although subsurface maxima in aqueous phase Fe were always observed and the diagenetic markers were in agreement with field data, aqueous phase Pu did not correlate with any of the reactive species.

This study is strongly supported by the field data of Malcolm et al. (10), who demonstrated that a similar pattern exists in the Fe porewater profile in Irish Sea seabed sediments. Neither study suggested that Pu was involved in any diagenetic processes. Indeed, Malcolm et al. (10) showed that Pu and Am concentrations were not related to those of Fe or Mn in either the solid or solution phase. However, redox cycling in freshwaters may affect the solution concentrations of Pu through coprecipitation/release mechanisms (8). The Fe- and Mn-rich, oxygen-depleted bottom waters of Gull Pond, Massachusetts, were found to contain five times more Pu than the oxygenated top waters (11).

Conversely, a study investigating seasonal variations in Pu interstitial water concentrations at a salt marsh in the Esk Estuary, Northwest England, demonstrated the opposite relationship (12). Pu concentrations displayed a marked minimum in the summer months, which was closely related to increasing Fe and Mn solution concentrations. It was suggested that a shift in the redox status of the system caused solubilization of Fe and Mn while reducing Pu(V) to Pu(IV), decreasing Pu solution concentrations. Similar summer minima in aqueous phase Pu concentrations have been observed in a deep lake, Lake Michigan (13) and were attributed to bioaccumulation of Pu by a phytoplankton bloom.

Morris et al. (12) proposed that her data were consistent with microbially driven changes in the redox potential of the system. However, Pu(V) equally could be used as an electron acceptor in microbial respiration in a similar way to that demonstrated for U(VI) by Lovley et al. (14), so its reduction and loss from solution could be directly related to microbial activity. Alternatively, the increase in microbial biomass during the summer could provide a sink for the Pu, which could then be released in a more mobile form as the cells degrade in the winter (15). In this study we investigate the cycling of Pu further, broadening the scope of the study to include the two other major transuranium elements, Np and Am. We have also assessed changes in the microbial

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community over the same time period (16) in an effort to relate changes in community structure or size to solubilization/retardation of the transuranium elements

Methods

Field Site The field site used in this study was an inter-tidal salt marsh in the Esk Estuary West Cumbria (U K National Grid Reference SD 089947). The sedimentological and hydrological processes at the marsh have been studied extensively by Carr and Blackely (17). Briefly, the sediments are composed mainly of silt and fine sand (2–125 μm in diameter, 89%) and clay (<2 μm in diameter, 7%) on a gravel bed. The sediment is covered in relatively salt-tolerant vegetation dominated by *Plantago maritima* and *Armeria maritima* in the upper zone, *Halimione portulacoides* in the middle zone and *Puccinellia maritima* with *Salicornia* spp in the lower (18). The samplers are positioned at a 30–35 cm depth in the middle zone of the marsh, as defined by the vegetation. Hydrostatic pressure drives an upward movement of seawater through the sediment at each high tide, so although the marsh is only inundated during spring tides, it is regularly rewetted with oxic seawater. The constant volume and salinity of the samples show that our sampling procedure is not subject to significant variations caused by these hydrological processes or rainfall in any month. The concentrations of the redox-sensitive stable elements Fe, Mn, and S are constant down the sediment profile, and the associated porewaters also have constant concentrations, with the exception of Mn which decreases with depth (19). The Eh (250 \pm 10 mV) and pH (pH 8.5 \pm 0.2) are also effectively constant down the profile (19).

Field Sampling The porewater samples were collected using in situ ceramic porous cup samplers (20). The samplers consist of a ceramic porous cup (Soil Moisture Corp., Santa Barbara, CA) cemented to a piece of plastic pipe 30 cm in length. The sampler is sealed with a neoprene rubber bung, through which two pieces of rigid plastic tubing pass, and positioned in the sediment so that the porous cup is at a depth of 30–35 cm. This arrangement allows samples to be withdrawn from the sampler without removing the sampler from the sediment. One long plastic tube reaches the bottom of the sampler, so that the sample can be pumped out. The other short plastic tube only reaches the upper part of the sampler and is used to evacuate the sampler with a pump. Both tubes are sealed with spring clips over a flexible rubber attachment and stoppered at the top. Thus, interstitial water samples can be collected repeatedly from the same sediment zone.

The ceramic cups clearly act as a filter and, although the exact degree of filtration is not known, samples have been analyzed for Pu before and after filtration through a 0.45 μm filter, and no difference was observed in the solution activity (20). Adsorption to the sampler has also been assessed (20), and it was found to result in maximum losses of 3% for saline samples. It is important to note that colloidal particles, which may include humic material, are important in controlling actinide speciation (21, 22) and will pass through the samplers if they are present.

The samplers had been in position in the salt marsh (U K National Grid Reference SD 089947) for over 2 years prior to this study, and so were fully equilibrated with the sediment. They were pumped down to a vacuum of 70 centibars of soil suction, and left each month to allow the interstitial waters of the sediment to migrate in slowly. The samples were collected around the midpoint of each month from January to October 1996 inclusive, after which the samplers were damaged by grazing animals. They were removed and repaired, but the transuranium element and Fe and Mn data collected after this suggested the samplers were cracked and

the data were not used. However, Eh, pH and temperature values were recorded until July 1997.

The porewater samples (typically 800–900 mL) were drawn out of the samplers into a collecting vessel using the hand held pump. The vacuum was then reapplied to the sampler, and the tubing sealed with the clips. The pH, Eh and temperature of the water were recorded immediately (Hanna water test meter). The sample was acidified to pH <1 with AnalaR 16 M HNO₃. The sample volume was determined by weighing. Fifty milliliter aliquots of each sample were retained for stable element analysis. Iron, Mn, and Na were determined in these by ICP-OES and DOC by UV absorption.

Sample Preparation The samples were wet ashed with nitric acid, then Np, Pu, and Am separated using conventional radiochemical procedures (12, 23–26) in a sequential sequence. Pu and Am were determined by α spectrometry and ²³⁷Np by accelerator mass spectrometry (AMS) using the 14UD accelerator at the Australian National University, Canberra, and the procedures described in Fifield et al. (27). 1 σ errors were calculated for all three elements using the peak integrals from α spectrometry or AMS, so that

$$\sigma_{ab} = \sqrt{1/I_a + 1/I_b}$$

where $I_{a,b}$ are the peak integrals of the isotope of interest and the internal standard.

The reproducibility of the analytical methods for Pu and Am were assessed within this study as $\pm 3.0\%$ for ^{239,240}Pu and 3.8% for ²⁴¹Am. Np reproducibility was assessed in this study as $\pm 2.7\%$ using ICP-MS and has previously been determined to be 1.2% using AMS (27).

Results

Transuranium Elements The transuranic element results obtained in this study are presented in Figure 1. Between December and March, the ^{239,240}Pu activity ranges between 2.28 and 2.84 mBq L⁻¹. The highest concentration observed occurred in April (3.21 mBq L⁻¹), and this was followed by a decrease to a minimum of 0.84 mBq L⁻¹ in August. The activity concentrations then began to increase again in September.

Americium displays a seasonal pattern in aqueous phase concentration which, from April to September, mimics the Pu pattern. The ratio of maximum to minimum concentrations is 5 for Am, comparable to the value of 6 found for Pu. In the early part of the year, Am shows greater fluctuations in its solution concentrations than Pu, and in particular decreases substantially in February while Pu concentrations stay reasonably high and constant.

In the early part of the year Np activities fluctuate, with Np aqueous phase concentrations at a maximum in February. The Np concentration decreases rapidly from February to March and then, from April, follows an irregular, slightly decreasing trend to a minimum in September. The ratio of maximum to minimum concentrations is 9 for Np.

Fe and Mn The aqueous phase Fe concentrations stayed low throughout the study, fluctuating rapidly between 0.02 and 0.30 mg L⁻¹ and showing no evidence of a seasonal cycle. Aqueous phase Mn concentrations decreased from 0.64 mg L⁻¹ in December to 0.03 mg L⁻¹ in March, then rose very gradually to 0.14 mg L⁻¹ in May, before increasing rapidly up to a maximum of 2.67 mg L⁻¹ in September, the final month in the series.

Field Data. The Eh, pH, and temperature measurements taken in the field are shown in Table 1. While absolute Eh measurements are difficult (28) especially in the field, these data are useful as a relative measurement of the redox status of the sediments over time, and show that the marsh is always mildly oxic, but slightly less so in May/June. The pH is very

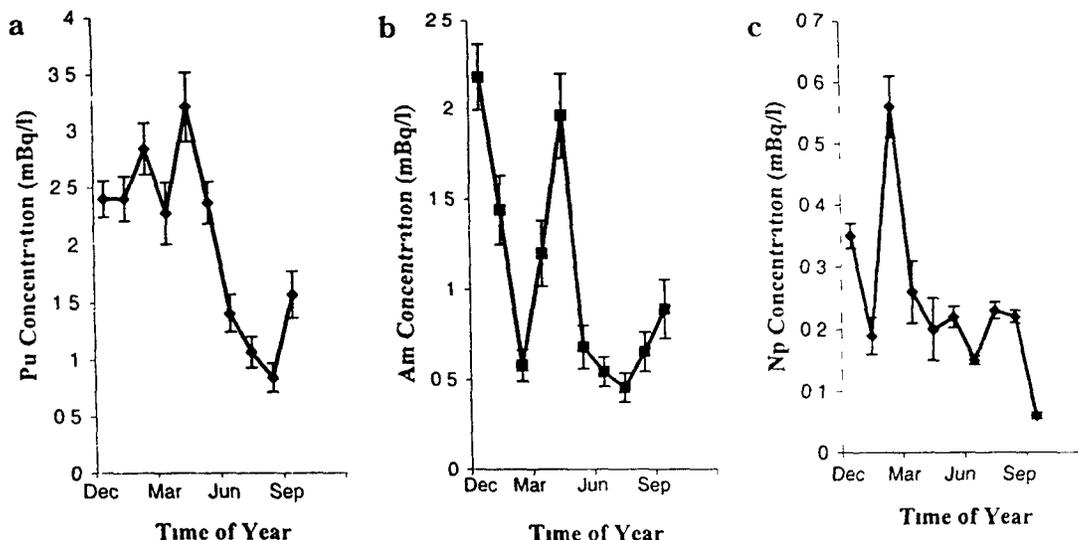


FIGURE 1 Seasonal variations of Np, Pu and Am activities in salt marsh porewaters (a) Pu, (b) Am (c) Np

TABLE 1 Eh, pH, and Temperature Measurements, December 1995–July 1997

month	Eh	pH	temp (°C)	aqueous phase Fe* (mg L ⁻¹)	aqueous-phase Mn* (mg L ⁻¹)
December	nm ^b	6.6	nm	0.16 ± 0.02	0.64 ± 0.06
January	nm	6.6	nm	0.03 ± 0.003	0.21 ± 0.02
February	nm	6.7	5.0	0.20 ± 0.02	0.06 ± 0.006
March	nm	6.5	4.0	0.03 ± 0.003	0.03 ± 0.003
April	nm	6.5	8.5	0.30 ± 0.03	0.05 ± 0.005
May	nm	6.6	nm	0.13 ± 0.01	0.14 ± 0.01
June	180	6.5	15.0	0.02 ± 0.002	0.56 ± 0.06
July	225	6.4	17.0	0.02 ± 0.002	1.1 ± 0.11
August	217	6.4	17.5	0.06 ± 0.006	2.2 ± 0.22
September	270	6.4	15.0	0.04 ± 0.004	2.7 ± 0.27
November	283	6.4	9.0	nm	nm
December	284	6.8	9.0	nm	nm
January	280	6.3	8.0	nm	nm
February	275	6.5	7.5	nm	nm
March	230	6.7	10.5	nm	nm
April	252	6.5	11.5	nm	nm
May	145	6.5	16.5	nm	nm
June	150	6.3	17.5	nm	nm
July	210	6.3	19.0	nm	nm

* The errors quoted for Fe and Mn are derived from propagation of random errors through the analytical procedures. Accuracy of the water test meter ± 5 mV ± 0.2 pH units and ± 1 °C for Eh, pH and temperature respectively (manufacturer's data) ^b nm = not measured

stable, and the only real variation over time is in the temperature. The temperature is at its lowest from February to March, when it remains around 4–5 °C, then it increases to a maximum of 17.5 °C in August. These values were assessed for a further 9 months, while the microbial data were completed, and so the conditions at the site are recorded for a longer period than the transuranium element porewater activities were measured. The Na concentration (an indicator of salinity) remained relatively constant over the sampling time (8700 ± 800 mg L⁻¹), and the DOC was below detection limit (10 mg L⁻¹) throughout. The relatively constant salinity suggests a similar degree of mixing of the fresh- and seawater each month.

Discussion

The speciation of the actinide elements in these samples is difficult to assess. They are known to associate strongly with colloidal particles including humic material (21, 22), and such particles may pass into the porous cup samplers. Thus, changes in aqueous-phase concentrations may reflect changes

in simple ionic species, or in colloidal particulate binding. However, in the Eh/pH conditions found in these sediments Am is expected to be trivalent and Np to be a pentavalent neptunyl species (29). Plutonium speciation is less predictable particularly since it may exist as a mixture of reduced (III, IV) and 'oxidized' (V, VI) species (2), but our data are consistent with Pu predominately being Pu (IV). These oxidation states provide a useful working hypothesis for the interpretation of the results.

The year can be divided into two parts: the first during winter and spring where the three transuranic elements show very different patterns, and the second from April to September, where Pu and Am respond in a very similar manner. This exemplifies the complexity of the system since there appear to be occasions when these elements behave in very different ways and others when they behave in a similar way.

The samplers used in this study had previously been used to obtain Pu porewater data in 1994 (12). Comparison of the two data sets therefore allows us to assess the similarity of Pu behavior from year to year in one precise location, so the Pu data from both studies are shown in Figure 2. The similarity between the data sets is striking, with both the trends and the actual concentrations being reproduced except for the small increase in aqueous phase Pu activity in February which was not observed by Morris et al. (12).

The similarities in the changing solution activities of Pu and Am in the second period suggest that one process is responsible for the late summer minima in the aqueous phase concentrations of both elements. Morris et al. (12) suggested that the late summer minimum in Pu solution concentrations was a result of redox changes in the marsh leading to increased reduction of Pu(V) and decreased solubility. However, the minimum solution concentrations observed at the same time for Am, which has access only to the +3 oxidation state, contradicts this argument. The Eh/pH data do not support this either because although the Eh is at a minimum in May and June it is only slightly lower than at other times of the year and the Eh rises again months before Pu and Am porewater concentrations rise. In addition the ratio of the maximum to minimum concentrations is comparable for Pu and Am. Direct redox change therefore seems unlikely to be responsible.

Morris et al. (12) found an inverse relationship between aqueous phase Fe and Mn concentrations and those of Pu and interpreted this as evidence for the coupling of Pu reduction with microbially driven Fe and Mn cycling. By contrast the Fe and Mn concentrations found in this study

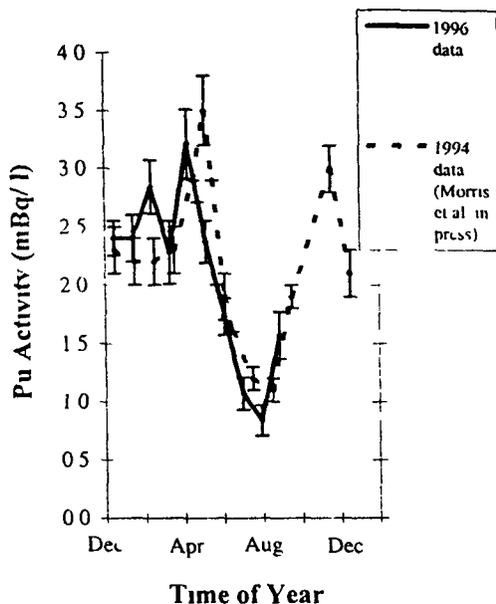


FIGURE 2 Pu porewater concentrations over 2 years at the salt marsh N B The data from Morris et al (12) have been replotted so that they coincide with the approach used in this study of plotting against the beginning of the sample collection time rather than the end

are not obviously related to the Pu pattern, suggesting that the Pu cycle and those of Fe and Mn are not related. Indeed the data in this study suggest that the seasonal pattern in Fe and Mn found by Morris et al (12) is not reproduced from year to year whereas the pattern in Pu is

Neptunium is brought out of solution earlier than Pu and Am, which suggests that it is either affected differently by a process which controls all the transuranium elements or influenced by different processes. This is consistent with the suggestion that it alone, exists predominantly in a high oxidation state.

The most prominent features in the early part of the year are the fluctuations in the concentrations of Am and Np, which are both at their most extreme in February. This suggests that some process is operating which decreases the solution concentrations of the "reduced" actinide species (i.e., Am(III)) and increases that of the "oxidized" species (i.e., Np(V)O₂⁺). Plutonium, being present in both forms to some extent would be expected to show intermediate behavior, and a slight increase in February is indeed observed.

The most marked seasonal effect, the decrease in Pu and Am aqueous phase concentrations throughout the summer, is brought about by a change to the system that results in the same response from both elements. The data suggest that this is not due to entrainment of Pu and Am in Fe and Mn cycling since there are different correlations in different years. Our data are thus in agreement with the work of Sholkovitz et al (9) and Malcolm et al (10) in marine sediments, which suggested that there is no evidence of postdepositional redox-induced diagenetic change.

Correlation of the Transuranic Data with Microbiological Data This study was carried out simultaneously with an assessment of the changes occurring within the microbial community of the salt marsh. The microbial community was estimated through phospholipid fatty acid (PLFA) analysis of the sediment at each porewater sampling, and this part of the study is discussed in detail by Keith-Roach et al (16). The overall results of the microbial analysis are shown in Figure 3 with the changes in estimated aerobic, anaerobic, fungal, and total activity plotted against the times of year that represent clusters of samples with statistically alike PLFA

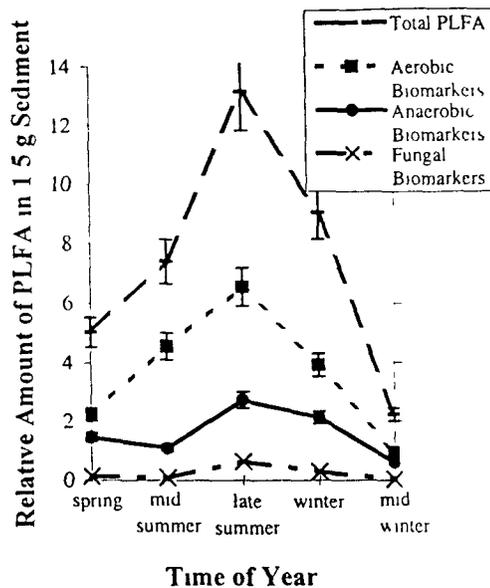


FIGURE 3 Seasonal variations in the sediment concentrations of PLFA biomarkers

profiles. Briefly, the microbial community structure was reasonably constant over the year, with aerobic species dominating at all times. Aerobic activity increased earlier in the year and to a greater extent than anaerobic activity, so aerobic organisms were particularly dominant in the summer. Fungal activity remained low at all times but showed a brief late summer peak. The major change in the microbial community over time was in overall biomass, with total PLFA concentrations varying 6 fold between the minimum in mid winter and the maximum in late summer.

When the actinide data are compared to the total PLFA concentrations, the minimum Pu and Am porewater concentrations correspond to the maximum biomass. This is consistent with the relationship observed between actinide concentrations and temperature, where the interstitial water temperature was found to be at a maximum as the actinide concentrations were at a minimum. In the early summer months, the aerobic bacterial biomass was increasing while the other groups were relatively inactive. In this period, the Pu and Am aqueous-phase concentrations were falling, which might suggest that it is aerobic activity which causes these elements to be scavenged from the porewater. Neptunium has a less obvious relationship with the changes in microbial biomass and will be discussed separately.

Wildung and Garland (30) outlined possible mechanisms through which microbes could affect transuranic aqueous phase concentrations as "(1) direct mechanisms such as alteration in valence state or alkylation, (2) indirect mechanisms, such as interactions with normal metabolites or microbial alterations of the physicochemical environment and (3) cycling mechanisms, such as uptake during cell growth and release on cell decomposition."

The first two possibilities are not consistent with the data from this study, as demonstrated by the porewater Fe and Mn concentrations and Eh data. The concentrations of microbial metabolites would be highest when biomass is at a maximum, and the metabolites would be expected to increase the aqueous phase concentrations of Pu and Am. The minimum in porewater concentrations of Pu and Am in the late summer is therefore also contrary to this mechanism. The third possibility is consistent with our Pu and Am data. Such scavenging may occur simply because as cells multiply there is an increased cell wall area and microbial cell walls have negatively charged sites for binding. The total microbial biomass increases as the Pu and Am concentrations fall and

then, as microbial activity decreases and the cells decompose, Pu and Am concentrations increase. Cell decomposition may also increase the concentrations of small molecules which could aid the solubilization of the transuranics (30). This process could account for the similarity in behavior of Pu and Am from April to September and explain why there are substantial differences from December to March, since biomass is low and may not then be a controlling factor.

The increasing level of biological activity from April to August which appears to retard the aqueous-phase concentrations of Pu and Am comparably, is therefore consistent with a bioaccumulation mechanism. This is in agreement with Mahara and Kudo (15), who suggested that Pu was retained by living bacterial cells in sediment environments. The transuranic aqueous-phase concentrations patterns observed in the earlier part of the year do not correspond to any change in activity/biomass or in community structure.

Neptunium behavior displays no correlation with the development of the microbial community, with its porewater concentrations falling before the microbial community blooms. It is not surprising that Np displays different behavior to Pu and Am since it predominantly exists as Np(V), the low charge NpO_2^+ species. The similarity in Am and Pu behavior from April suggests that Pu(IV) dominates at this site. Plutonium(IV) and Am(III), with their high formal charges, would be expected to react with microbial cell wall sites more readily than the NpO_2^+ ion. The question arising from the behavior of ^{237}Np is why it is so soluble in February compared to the rest of the year, but this is difficult to answer with the limited information available. The February sample displays suppressed Am and elevated Np concentrations in the porewater, which suggests that the chemistry of the system is quite dynamic at this time, despite biomass being at a minimum.

Acknowledgments

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