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Subsurface Mobile Plutonium Speciation: Sampling Artifacts for Groundwater Colloids

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INTRODUCTION

A recent review [1] found several conflicting conclusions regarding colloid-facilitated transport of radionuclides in groundwater and noted that colloids can both facilitate and retard transport. Given these contrasting conclusions and the profound implications even trace concentrations of plutonium (Pu) have on the calculated risk posed to human health, it is important that the methodology used to sample groundwater colloids be free of artifacts [2,3]. The objective of this study was: (1) to conduct a field study and measure Pu speciation, (^{239}Pu and ^{240}Pu for reduced-Pu$_{aq}$, oxidized-Pu$_{aq}$, reduced-Pu$_{colloid}$, and oxidized-Pu$_{colloid}$), in a Savannah River Site (SRS) aquifer along a pH gradient in F-Area, (2) to determine the impact of pumping rate on Pu concentration, Pu speciation, and Pu isotopic ratios, (3) determine the impact of delayed sample processing (as opposed to processing directly from the well).

METHODS

Four wells were sampled in F-Area of the SRS along a pH gradient and characterized using the methods described in Buesseler et al. [4]. F-Area is a uranium separations facility used to produce Pu. During production between 1955 and 1988, acidic waste containing radioactive and metal bearing waste was disposed in seepage basins. The seepage basins have since been closed, and the resulting contaminants of concern are ^{99}Sr, $^{235/238}$U, ^{3}H, and ^{129}I. Pu exists at SRS in trace, non-regulatory levels (detailed below) but provides an excellent tracer for doing environmental studies.

For this study, well purging prior to sampling typically required a half a day to a day to come to steady state with respect to a number of chemical in-line measurements, including light scatter Eh, O_2, temperature, and pH. Groundwater samples were then recovered at a rate slower than groundwater flow, ~150 mL/min, using a Teflon bladder pump and Teflon tubing. The groundwater was passed directly through a 0.2-µm filter, into a nitrogen tent containing a cross-flow filtration system (100,000 molecular weight cut-off (MWCO membrane). Strict protocols with respect to trace metal and trace-organic clean sampling techniques were adopted during collection and field processing of samples. Thermal ionization mass spectrometry (TIMS) analyses were conducted at the Pacific Northwest National Laboratory. The detection limit was about 10^4 atoms; all samples contained $>10^8$ atoms Pu. The drinking water limit for ^{239}Pu is 15 pCi L^{-1} or 50,000 x 10^6 atoms kg^{-1}; the greatest Pu concentration measured in this study was 200 x 10^6 atoms kg^{-1}.

RESULTS & DISCUSSION

We operationally defined dissolved Pu and colloidal Pu as that which could be separated by the 100,000 MWCO cross-flow filtration unit, which has a nominal size of about 5 nm. This membrane was selected because it can receive groundwater from the well at a rate of 150 mL min^{-1}. We recognize that the true definition between dissolved and colloidal Pu is in fact a continuum.

Groundwater Plutonium Speciation

Groundwater Pu speciation varied greatly within the plume in its tendency to associate with nanoparticles: further along the 0.6 km transect from the point source, there was a much greater tendency for Pu to associate with colloids. There was a strong inverse correlation between the redox potential and the fraction of reduced Pu (Pu(III/IV)$_{aq}$) as well as with the colloidal Pu: at 210 mV (SHE) the colloidal fraction was 0.95; at 225 mV the colloidal fraction was 0.61; at 325 mV the fraction colloidal was 0.30.

Pump and Field Speciation Testing

Well pumping rates should ideally be below the groundwater recharge rate so as not to mechanically detach colloidal material that would otherwise be immobile. We used variable pumping rates to study this artifact for Pu in groundwater. Concentrations increased with increasing pumping rate by 300% for dissolved Pu (that passing through a 0.2-µm filter) and over 6000% for an unfiltered sample. Perhaps more interestingly, Pu isotopes also varied systematically with flow rate, with lower ^{240}Pu/^{239}Pu ratios with increasing pumping rates. In this case we can explain this isotopic shift due to somewhat unique sources of these Pu isotopes in this plume. At SRS the bulk of ^{240}Pu originates in a more oxidized form from ^{244}Cm decay (t ½ = 18.1 years), whereas ^{239}Pu, originates in a more reduced form directly from the F-Area seepage basins [4]. Hence, lower ^{240}Pu/^{239}Pu ratios are associated with the more reduced

forms of Pu that sorb more strongly to colloid surfaces ($^{240}Pu/^{239}Pu$ colloids = 0.055 vs. 0.15 for oxidized fraction). At standard well sampling rates of >10 L min^{-1}, Pu concentrations were biased high, as well as the percent Pu thought to be associated with groundwater colloids.

Finally, delaying processing samples by three-days and permitting air exposure resulted in the percent of reduced ^{239}Pu to decrease from 40±5% to 18±1%.

Given the large amount of uncertainty that colloid-facilitated transport introduces to risk models, and the difficulty that scientists have faced in studying unambiguously this mode of contaminant transport in the subsurface, there is a greater need to become aware of the various pitfalls associated with sample artifacts. Much of the difficulty of this problem lies in that there are few Pu plumes, and those that exist are at very low concentrations, pushing analytical limits and limiting the types of analytical tools that can be utilized Pu of course is a very reactive and chemical complicated species, and as such is very difficult to sample *in situ*; any changes in local environments long the sampling path often result in changes in its speciation. Accurately describing how Pu and other long-lived radionuclides move in the subsurface is important for reducing the uncertainty associated with radiological waste disposal. Describing colloid facilitated transport incorrectly may have grave consequences on the costs of waste disposal and more broadly of nuclear energy.

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