

**FINAL REPORT ON PHASE SPECIATION OF Pu AND Am FOR  
'ACTINIDE MIGRATION STUDIES AT THE  
ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE'**

Peter H Santschi, Kim Roberts and Laodong Guo  
Texas A&M University, 5007 Ave U, Galveston, TX 77551  
28 September, 1999

Significant Findings in FY99

- 1) Total  $^{239, 240}\text{Pu}$  and  $^{241}\text{Am}$  concentrations were high in the storm runoff sample, with Pu close to the discharge limit of 0.15 pCi/L. Both Pu and Am activity concentrations in storm runoff (GS10 on April 30, 1999, instantaneous flow = 8 cfs, TSS =  $120 \pm 6$  mg/L) and pond discharge (GS03 on April 27, 1999, instantaneous flow = 2.3 cfs, TSS =  $39 \pm 5$  mg/L) samples were also higher than those determined in the August 26-27, 1998 samples from Walnut Creek at GS03. Contrary to the August 1998 samples, however, both storm runoff and pond discharge sampled this year showed a higher percentage (~60%) in the 0.5  $\mu\text{m}$  filter-passing fraction. Higher total and 0.5  $\mu\text{m}$  filter-passing Pu and Am activity concentrations measured in 1999 are due to physico-chemical or biological processes which operate under oxic rather than anoxic conditions.
- 2) Phase partitioning coefficients,  $R_p$ , defined here as the activity concentration ratio in particles  $\geq 0.5 \mu\text{m}$  to that in 0.5  $\mu\text{m}$  filter-passing phases, were 1-2 orders of magnitude lower for Pu and Am than previously observed, i.e., 0.4 to  $2 \times 10^4 \text{m}^3/\text{g}$  in April 1999, vs  $1.7 \times 10^6 \text{m}^3/\text{g}$  in August 1998, reflecting the higher relative concentration of actinides in the 0.5  $\mu\text{m}$  filter-passing phase during 1999, and thus higher mobility.
- 3) Approximately 75% of the Pu and 50% of the Am in the 0.5  $\mu\text{m}$  filter-passing fraction was colloidal, i.e., it was filtered out by 100 kDa or 3 kDa ultrafilters using cross-flow ultrafiltration (CFUF), with, on average, only about 30% of 0.5  $\mu\text{m}$  filter-passing Pu (and 50% of Am) passing a 100 or 3 kDa ultrafilter. Thus, during the spring 1999, we observed higher fractions of Pu and Am as colloidal forms than in August 1998. This higher colloidal actinide fraction in 1999 could be related to some physical or chemical process which operated during that time, a time when significant fractions of fresh organic matter (i.e., leaves, grasses) had accumulated during the fall/winter which more easily disintegrate after frozen soils are thawing. More hydrophilic or surface active forms of colloidal organic matter (e.g., with fulvic acid-like behaviour) could have been produced during that time which would have been responsible for the changing phase speciation of Pu and Am through more efficient dispersion of Pu and Am polymers associated with clay-organic matter complexes (e.g., Wilkinson et al., 1997).

1/42

## Final Report-Santschi

Higher colloidal Pu and Am fractions are also the cause of lower phase partition coefficient ( $R_p$ ) values. However, the exact mechanism of colloidal actinide generation remains to be investigated.

- 4)  $^{239}Pu/^{241}Am$  activity ratios in both particles and in the 0.5  $\mu m$  filter-passing phase, containing both colloidal and dissolved phases, were low (i.e., ~1-3), reflecting the fact that significant additional amounts of Am had previously been discharged into this watershed.
- 5) Pu activity concentrations in the particulate fractions (>20  $\mu m$  & 0.5-20  $\mu m$ ) were higher than observed in August 1998 (i.e., 0.3-0.6 pCi/g in spring, vs 0.1-0.3 pCi/g in summer), but still lower than what was found in other creeks at RFETS (i.e., ~1 pCi/g). This might suggest more vigorous soil erosion transport processes operating over longer distances during the time of higher flow rates.
- 6) Attempts to determine Pu oxidation states in 0.5  $\mu m$  filter-passing water samples failed because of the predominant colloidal nature of the Pu, which caused it to concentrate at the interface between water and organic phase rather than distribute between aqueous and organic phases.
- 7) Isoelectric focusing of  $^{14}C$  radiolabelled colloids showed that they contain strong acid functional groups which impart the organic fraction a negative charge at natural pH's. Bulk colloidal matter contains also strong basic functional groups, as was evident from  $^{59}Fe$  labeling experiments. Colloids isolated from the pond discharge and storm runoff samples contained about 4-5 % organic carbon, 2-5% Fe, and 4-9% Al, reflecting the predominant inorganic nature of bulk colloidal matter.

### Objectives

- 1 To determine the association of Pu and Am with 1) particulate, 2) colloidal, and 3) dissolved phases, and attempt to determine oxidation states of the dissolved phase, for field samples from a selected pond, pond release waters and compliance point baseflow waters, as well as for samples from controlled laboratory resuspension experiments from wetland samples.
- 2 To gain information on the charge distribution of colloids isolated from wetlands and surface waters, using isoelectric focusing gel electrophoresis.
- 3 To examine the chemical nature of the colloidal carrier phase (e.g., Fe, Mn, C, Al, etc.)

### Justification

FY 98 work has demonstrated the likelihood that Pu and Am in the 0.5  $\mu m$  filter-passing fraction is predominantly in a colloidal form. The issue of the phase speciation of Pu and Am is crucial for understanding the relationship between surface water quality and soil action levels, as well as to support the scientific defensibility of RESRAD model simulations. The distribution of

Pu and Am among different particle and colloid sizes or molecular weights is also important for developing management controls on surface water quality. Another important focus of this task is to determine the dominant oxidation state of the filter-passing Pu species in stream water as well as those generated while resuspending sediments in controlled laboratory experiments, and to relate that information to composition and charge of colloids. Surface charge is an important colloid characteristic because it regulates the extent to which colloidal material interacts with dissolved actinides and particles and immobile soil media and, therefore, is a primary parameter for estimating the extent to which colloids are mobile and for the development of strategies for removing colloidal material and associated actinides from the water through engineered systems.

#### Analytical Methods

The first task of phase association of Pu and Am investigations consists of three sub-tasks: a) Cross-flow ultrafiltration (CFUF) evaluation (e.g., model compound filtration efficiency), b) surface water sampling, and c) colloid generation for sediment samples in controlled lab experiments. The sampling sites consist of pond discharge from GS03 and storm run-off samples from GS10 (Figure 1). Grab samples were collected by bailing water from the stream using a beaker followed by compositing the water into clean 15 to 20 L Nalgene carboys for processing and analysis at CSM. A schematic of how the samples were processed by filtration and ultrafiltration is given in Figure 2. Pond sediment samples were collected for sediment resuspension experiments with subsequent filtration and cross-flow ultrafiltration in the laboratory (Guo and Santschi, 1999). Field sampling protocols are described in the Site Sampling and Analysis Plan for this experiment (RMRS, 1999). For references: RMRS, LLC, March 9, 1999, Sampling and Analysis Plan: Collection of Wetland Sediments and Surface Water for the Fiscal Year 1999 Actinide Migration Evaluation at the Rocky Flats Environmental Technology Site, Rev 0, RF/RMRS-99-330, Golden, CO.

Since CFUF is not a standard analytical tool, system calibrations were conducted according to protocols of Guo and Santschi (1996,1997), Guo et al. (1999), and Wenzel (1996, 1998). Chemical parameters to be measured include total organic carbon (TOC), dissolved organic carbon (DOC,  $\leq 0.5 \mu\text{m}$ ), colloidal organic carbon (COC,  $3\text{kDa}-0.5\mu\text{m}$ ), particulate organic carbon and nitrogen (POC and PON,  $\geq 0.7\mu\text{m}$ ), pH, alkalinity, Al, Fe and Mn of the  $0.5\mu\text{m}$  filter-passing water, and % organic carbon, Al, Fe and Mn in the colloidal and particulate phases, according to Guo and Santschi (1997) and Wenzel et al (1999). These measurements were conducted on the isolated aqueous phases and on resolubilized freeze dried material.

## Final Report-Santschi

Oxidation state determinations of Pu in the 0.5 µm filter-passing fraction were carried out using methods described by Bertrand and Choppin, 1982, Saito and Choppin (1983), Kobashi et al (1988). Other pertinent papers on this subject are those of Choppin (1991), Lovett and Nelson (1981), Nitsche et al (1988), and Saito et al (1985).

The charge of the colloids were determined by isoelectric focusing, after radiolabelling of colloidal macromolecular organic matter using  $^{14}\text{C}$  (e.g., Wolfenbarger and Crosby, 1983, Quigley et al., 1999), and of colloidal inorganic and organic matter with  $^{59}\text{Fe}$ . The electrophoresis gels were sectioned at the end of each experiment, leached in 3ml of 1% SDS detergent for 24 hours, added to a scintillation cocktail and the final sample measured on a Liquid Scintillation Counter.

Aliquots of all samples were kept for chemical characterization of the colloidal phases.

*A note on terminology* We denote all fractions with either the upper or lower size or nominal molecular weight cutoff limit, or both. The terms "dissolved", "filtrate" are ambiguous, and the terms "retentate" and "permeate" are reserved for fractions which were retained by or had permeated an ultrafilter.

We sampled and processed a discharge sample on 4/27/99 (RIN 99Q6890) at GS03 and a storm runoff sample on 4/30/99 (RIN 99D7102) at GS10 (Figure 1). For the pond discharge sample, approximately 160 liters of water was taken from GS03 and brought in various containers to CSM where it was combined in a 55 gallon drum. The 150 liters of storm runoff were collected from GS10 and brought to CSM in two 55 gallon drums. Both samples were size fractionated in duplicate for a total of 4 samples of approximately 60-80 liters each (i.e., about 320 L total). Ten liters of whole water (unfiltered) was set aside for total activity measurement for each sample. The remaining water was passed through 20 µm and 0.5 µm filters and collected in 5 gallon carboys. One carboy (~20L) of 0.5 µm filtered water was set aside for later analysis of the total 0.5 µm filter-passing fraction. The remaining 0.5 µm filter-passing water was used for the cross flow ultrafiltration (CFUF). Thirty to forty liters were run through a 3 kDa filter membrane and another thirty to forty liters were run through a 100 kDa filter membrane. A schematic of how the samples were filtered and ultrafiltered is given in Figure 2. All size fractions of aqueous phases were further processed by  $\text{Fe}(\text{OH})_3$  precipitation. The resultant precipitate was sent to TAMUG for radiochemical analysis of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$ .

The methods for isotope separation were adapted from EPA Method 908.0 (1980), USDOE (1979), USEPA (1979), and Yamato (1982) as described also in last year's report (Appendix 2).

Each sample was acidified with concentrated nitric acid to pH <2 and allowed to sit for at least 16 hours. For each sample concentrated hydrochloric acid was added at 5ml/L and  $^{241}\text{Am}$  and  $^{242}\text{Pu}$  yield tracers were added. The samples were placed on a stir plate and 5 ml of 40 mg/ml Fe(III) carrier was added. The pH was measured and concentrated hydrochloric acid added until pH is <1. The sample was covered and stirred for 30 minutes and the pH measured again.

Once the pH was <1, concentrated ammonium hydroxide was added until turbidity remained constant then an additional 50 mls was added. The sample was again covered and stirred. After 30 minutes, the sample was removed from the stir plate, the stir bar removed and the precipitate was allowed to settle. The supernate was decanted until the precipitate slurry could be transferred to 250 ml centrifuge tubes. The samples were centrifuged for 30 minutes at 3000 rpm. The supernate was decanted and the precipitate was shipped to Texas A&M University. Once at Texas A&M University, the samples were dissolved in concentrated HCl to which 75 mls of 9 N HCl and 2 ml saturated sodium nitrite were added. The samples were then run through a series of three anion exchange columns (Appendix 2). The first column separated the Am from the Pu fractions. The Pu was then microprecipitated on a filter, mounted on a stainless steel planchet and alpha counted. The Am fraction was carried through a methanolic anion exchange column followed by a TEVA resin column. The Am fraction was microprecipitated, mounted on a stainless steel planchette and alpha counted.

## Results and Discussion

### *a) Phase Speciation of surface water samples*

Cross-flow ultrafiltration (CFUF) cartridges were checked for proper functioning before taking them out to the field (Guo and Santschi, 1996, Guo et al, 1999). The Pu and Am, including propagated errors (1 SD = 1 standard deviation), as well as ancillary data are summarized in Tables 1-11. The data in Tables 1-2 include the average activities of the duplicate samples run except where indicated by \*. Pu and Am partitioning data are also shown in Figures 3-6. The partitioning data (%) for the 0.5µm filter-passing fraction, the 20µm filter-passing fraction (filtered in series), and the particle fraction contained between 0.5µm – 20µm sizes are presented as the ratio of each fraction divided by the sum of the measured fractions. For the ultrafiltration data, collected in parallel (using ultrafilters with a nominal molecular weight cut-off of 3kDa and 100kDa), the 3kDa ultrafilter-passing fraction and 100kDa – 0.5µm fractions are measured, while the 3-100kDa fraction was calculated by subtracting the measured 100kDa-0.5µm fraction (retentate) from the measured 3kDa-0.5µm fraction (retentate). The partitioning data for the ultrafiltration are

determined by each fraction divided by the total measured 0.5  $\mu$ m filter-passing fraction. The key findings are as follows

1) Total Pu and Am activity concentrations are significantly higher in the storm sample, and Pu concentration in the storm runoff sample is close to the discharge limit of 0.15 pCi/L. Pu and Am activities in both spring 1999 samples are also higher than the August 1998 values which were close to the detection limit of 0.0003 pCi/L.

2) Both pond discharge and storm runoff samples showed very similar actinide distribution among different particle sizes, with a large (~60%) fraction of total activity in the 0.5  $\mu$ m filter-passing fraction.

3) This 0.5  $\mu$ m filter-passing fraction of Pu and Am is largely composed of colloids (between 3 kDa and 0.5  $\mu$ m) with values ranging from ~40% to ~80%.

4) The Pu and Am partitioning data are characterized by a low phase partitioning coefficients,  $R_p$ , defined here as the activity concentration ratio in particles  $\geq 0.5 \mu$ m to that in 0.5  $\mu$ m filter-passing phases (Table 12) and low Pu/Am ratios (Table 13), which could be indication of different source materials and/or differential (biogeo-) chemical reactions controlling the distribution and partitioning of Pu and Am in this system. Higher colloidal fractions of Pu and Am may also be responsible for their lower  $R_p$  values observed here.

#### *b) Redox Speciation of surface water samples*

Emphasis for redox speciation focused on two different extraction reagents, Thenoyltrifluoroacetone, TTA (Figure 7) and Dibenzoylmethane, DBM (Figure 8). TTA at pH < 1 extracts Pu(IV) and TTA at pH > 4 extracts everything but Pu(V). The DBM extraction is a two step procedure. The first step extracts Pu (III & VI) and leaves Pu (IV & V). The second step separates the III from VI and IV from V. An attempt was made to change the oxidation state of Pu tracer in our test experiments but this was not successful. A visit was made to Dr. Choppins lab to clarify these procedures. The results of the test experiments, both from TAMUG and in Dr. Choppins lab, are discussed in Appendix 3. They essentially show that the procedure works well at elevated actinide concentrations, but is less reliable at the low concentration levels encountered in the environment, likely due to the colloidal and non-exchangeable nature of the Pu in the water.

Three samples (Pond Discharge, Storm Set A, and Storm Set B) were run for oxidation state determination. A TTA extraction at pH < 1 was carried out to extract Pu(IV) from a sample aliquot

The activity of all samples required preconcentration prior to analysis, which was accomplished via rotary evaporation with a concentration factor of 10 times (see Appendix 3) The data from this TTA extraction is summarized in Table 14 The results show that the Pu was neither found in the organic nor the aqueous phase but in the interfacial fraction which contained ~~part~~ either phase (50ml of 300ml), including the interface The Pu was thus recovered in exactly the fraction which one would predict if the Pu is indeed associated with colloids and non-exchangeable, i.e., in the interfacial fraction These results would therefore suggest that most Pu is not in a low molecular weight, ionic or labile form, in these waters

*c) Colloid Characterization*

The surface charge distribution of the colloids by gelelectrophoretic focusing (Figure 9) was determined in 4 samples 3kDa - 0.5µm Discharge, 3kDa - 0.5µm Storm, and two analyses of 1kDa - 0.5µm from the resuspension experiment In one experiment the organic fraction was labeled with C-14 on the carboxylic acid sites (Table 15, Figure 10) In the second experiment, more of the inorganic fraction was labeled with Fe-59 (Table 16, Figure 10) The organic fraction shows the majority of the C-14 is found at ~~pH~~, indicating that organic colloids contain strong acid functional groups which gives them a negative charge at natural pH of 7-8 The sum of the fractions was less than the total activity counted from an equivalent volume (100µl) Likely, small losses occurred due to less than 100% efficiency in introducing the sample into the gel Fe-59 labelled colloids, on the other hand, showed a distribution with maxima at both ~~pH~~  $\geq 11$ , indicating that bulk colloids contain strong acid and basic functional groups, which makes them amphiprotic

Colloids from stream and pond release water contained, on the average, 4-6 % of organic carbon, 0.25-0.5 % nitrogen, 4-9% Al, and 2-5% Fe Such a composition resembles that of average soils (e.g., Salomons and Forstner, 1984, and references therein) Our results therefore suggest that colloids sampled in spring were mostly composed of inorganic mineral phases, with organic matter occluded within the other phases, and/or covering the surfaces of the inorganic material as an organic coating More detailed experiments are needed to distinguish between these two possibilities

**References:**

Bertrand, P A and Choppin, G R 1982 Separation of actinides in different oxidation states by solvent extraction *Radiochim Acta* **31**, 136-137

Final Report-Santschi

- Choppin, G R 1991 Redox speciation of plutonium in natural waters *J Radioanal Nucl Chem* , **147**, 109-116
- EPA Method 908 0 1980 Prescribed Procedures for Measurement of Radioactivity in Drinking water EPA-600/4-80-032
- Guo, L , and P H Santschi 1996 A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic matter in seawater *Mar Chem*, **55**, 113-128
- Guo, L , and Santschi, P H 1997 Isotopic and elemental characterization of colloidal organic matter from the Chesapeake Bay and Galveston Bay *Mar Chem* , **59**, 1-15
- Guo, L , Wen, L -S , Tang, D , and Santschi, P H 1999 Re-examination of cross-flow ultrafiltration for sampling marine colloids evidence from molecular probe *Mar Chem*, in press
- Guo, L , and Santschi, 1999 Sedimentary sources of old high molecular weight dissolved organic matter from the ocean margin benthic nepheloid layer *Geochim. Cosmochim Acta*, in press.
- Kobashi, A , Choppin, G R , and Morse, J W 1988 A study of techniques for separation of plutonium in different oxidation states *Radiochim. Acta* **43**, 211-215
- Lovett, M B , and Nelson, D M 1981 Determination of some oxidation states of plutonium in sea water and associated particulate matter IN *Techniques for Identifying Transuranic Speciation in Aquatic Environments*, IAEA, Vienna, pp 27-35
- Nitsche, H , Lee, S C , and Gatti, R C 1988 Determination of plutonium oxidation states at trace levels pertinent to nuclear waste disposal *Radioanal Nucl. Chem* , **124**, 171-185
- Quigley, M S , Santschi, P H , and Honeyman, B D 1999 Laboratory studies of Th complexation by marine organic matter using ultrafiltration, electrophoresis, and titration techniques in preparation
- Saito, A , and Choppin, G R 1983 Separation of actinides in different oxidation states from neutral solutions by solvent extraction *Anal Chem.*, **55**, 2454-2457
- Saito, A , Roberts, R A , and Choppin, G R 1985 Preparation of solutions of tracer level plutonium(V) *Anal Chem.*, **57**, 390
- Salomons, W , and Forstner, U 1984 *Metals in the Hydrocycle* Springer-Verlag, New York, pp 349
- USDOE 1979 Procedure AS-5 RESL/ID
- USEPA 1979 Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air and Biological Tissue EMSL/LV
- Wen, L S , M C Stordal, G A Gill, and P H Santschi 1996 An ultra-clean cross-flow ultrafiltration technique for the study of trace metal phase speciation in sea water *Mar Chem* , **55**, 129-152

Final Report-Santschi

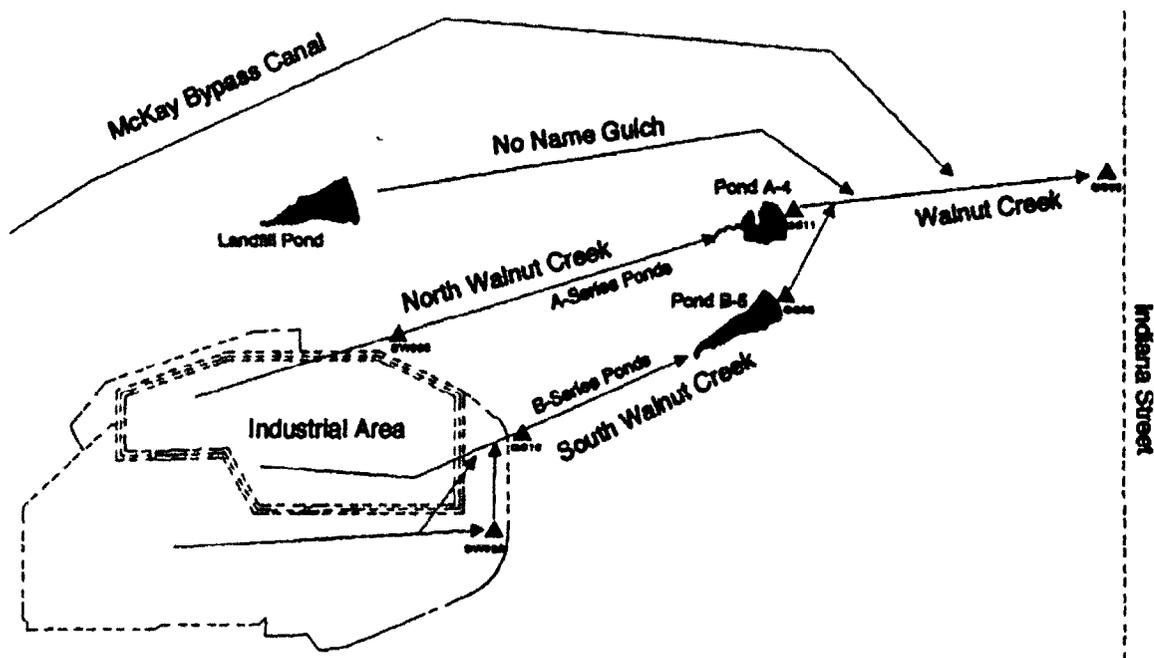
Wen, L S , P H Santschi, C Paternostro, and G Gill 1999 Estuarine trace metal distributions in Galveston Bay I Importance of colloidal forms in the speciation of the dissolved phase, *Mar Chem*, **63 (3-4)**, 185-212

Wilkinson, K J , Joz-Roland, A , and Buffle, J. 1997 Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters *Limnol Oceanogr* , **42(8)**, 1714-1724

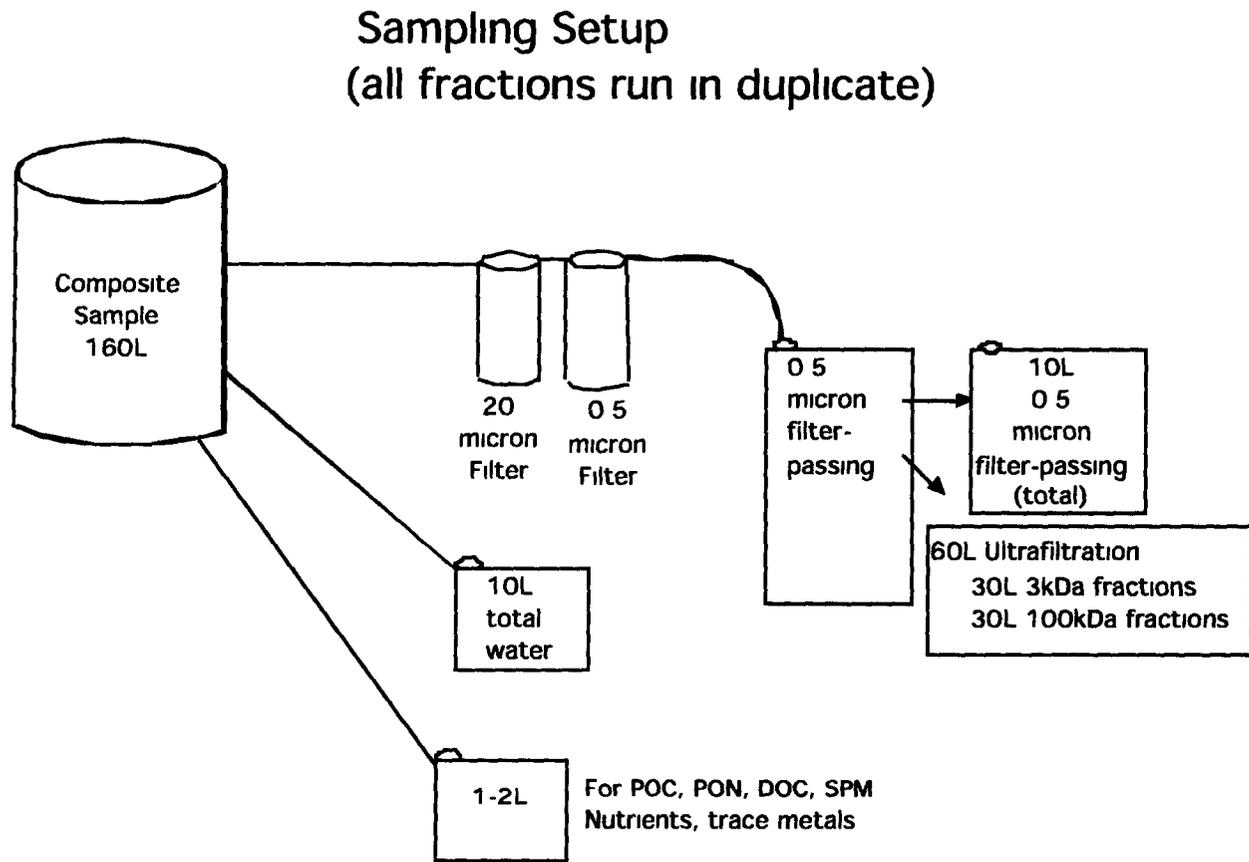
Wolfenbarger Jr , L , and Crosby, M P 1983 A convenient procedure for radiolabeling detritus with [<sup>14</sup>C]dimethylsulfate *J Exp Mar Bio Ecol* **67**, 185-198

Yamato, A 1982 An Anion Exchange Method for the Determination of <sup>241</sup>Am and Plutonium in Environmental and biological Samples *J Radioanal Nucl Chem* , **75(1-2)**, 265-273.

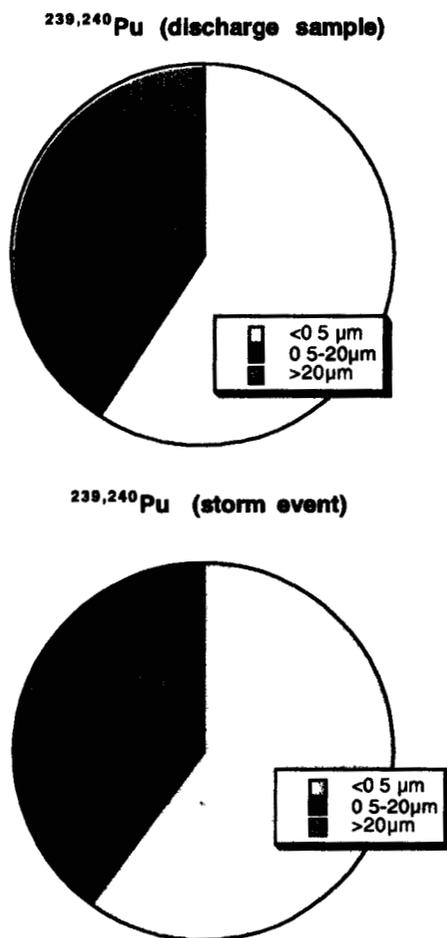
Figure 1. Map of sampling locations, with GS10 at the upstream end of the B Series ponds, and GS03 on Walnut Creek near Indiana Street.



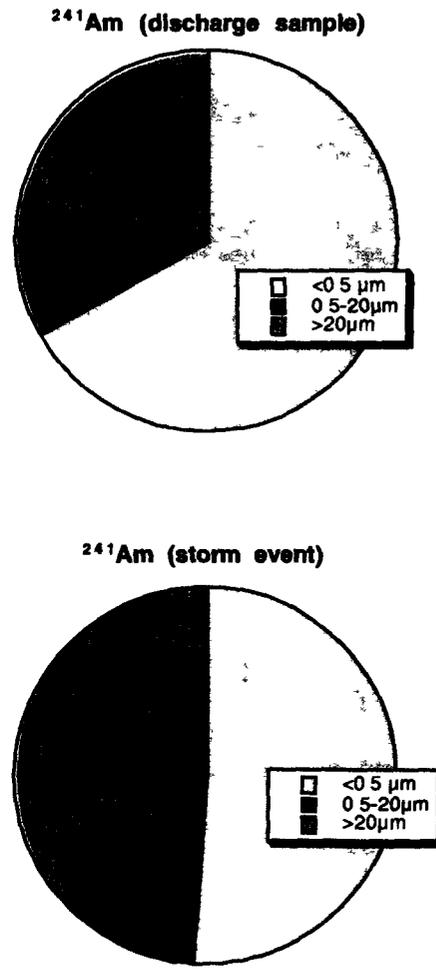
**Figure 2. Schematic of field sampling.**



**Figure 3. Partitioning of  $^{239,240}\text{Pu}$  between particulate ( $0.5\mu\text{m} - 20\mu\text{m}$  and  $>20\mu\text{m}$ ) and  $0.5\mu\text{m}$  filter-passing phases in discharge and storm event samples.**

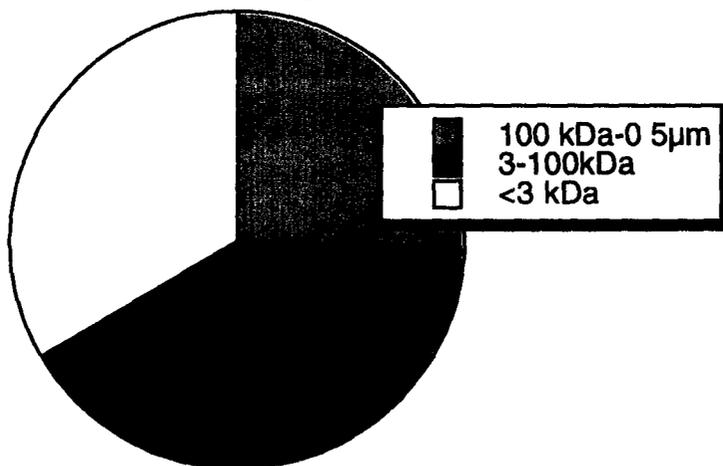


**Figure 4. Partitioning of  $^{241}\text{Am}$  between particulate ( $0.5\mu\text{m} - 20\mu\text{m}$  and  $>20\mu\text{m}$ ) and  $0.5\mu\text{m}$  filter-passing phases in discharge and storm event samples.**

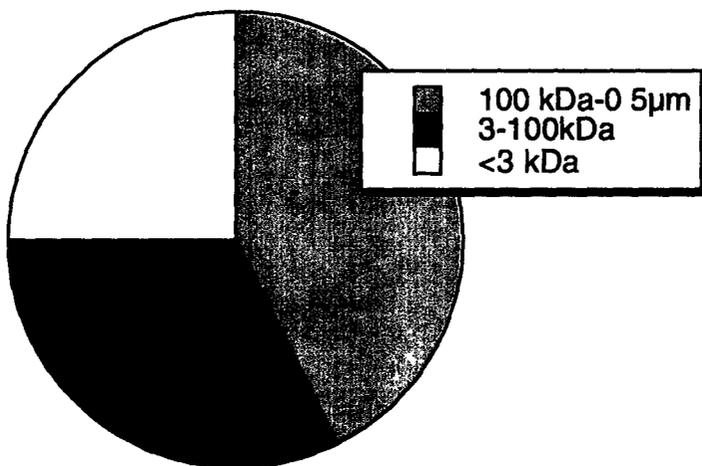


**Figure 5. Partitioning  $^{239,240}\text{Pu}$  between colloidal and dissolved phases in the  $0.5\ \mu\text{m}$  filter-passing fraction in discharge and storm event samples. The retentate equals the material retained on the filter plus filter washings.  $3\text{kDa}$ - $100\text{kDa}$  is calculated by subtracting the  $100\text{kDa}$  retentate from the  $3\text{kDa}$  retentate. The  $<3\text{kDa}$  fraction is the difference between TD and total colloidal.**

**$^{239,240}\text{Pu}$  (discharge sample)**

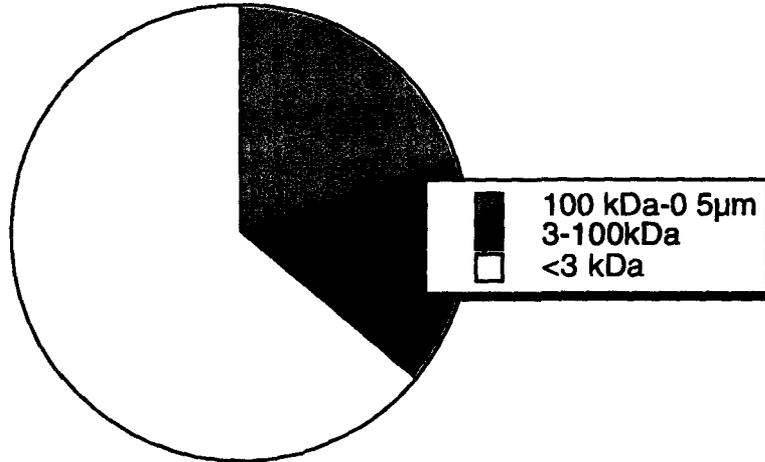


**$^{239,240}\text{Pu}$  (storm event sample)**

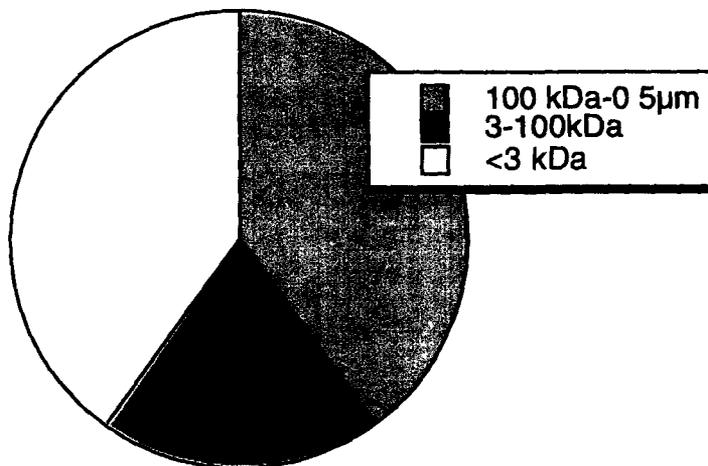


**Figure 6. Partitioning  $^{241}\text{Am}$  between colloidal and dissolved phases in the 0.5  $\mu\text{m}$  filter-passing fraction in discharge and storm event samples. The retentate equals the material retained on the filter plus filter washings. 3kDa-100kDa is calculated by subtracting the 100kDa retentate from the 3kDa retentate. The <3kDa fraction is the diggerence between TD and total colloidal.**

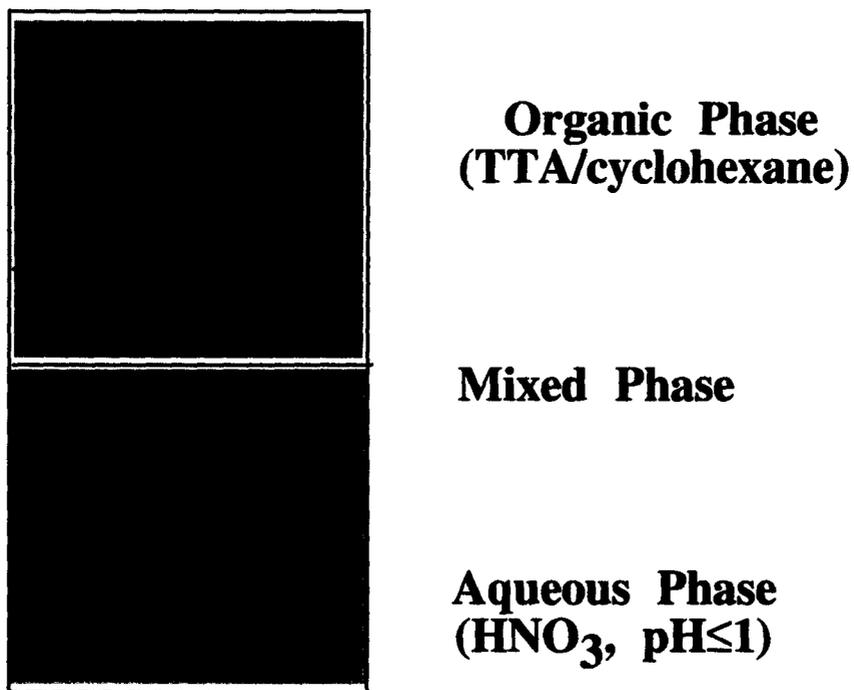
**$^{241}\text{Am}$  (discharge sample)**



**$^{241}\text{Am}$  (storm event sample)**

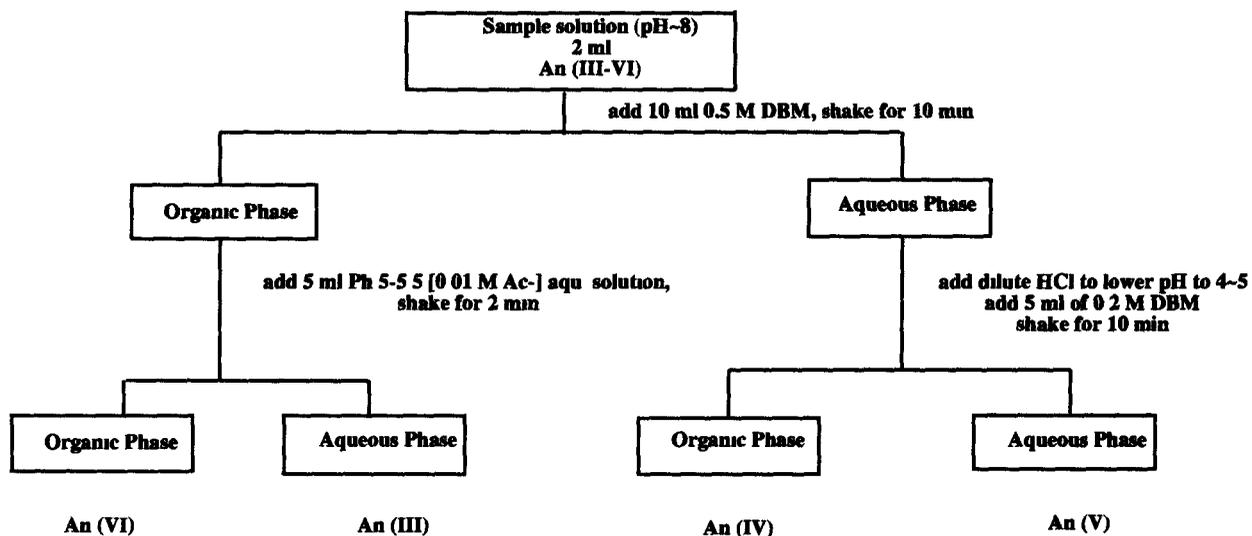


**Figure 7. Schematic of TTA solvent extraction fractions.**



**Solvent Extraction Schematic for  
Chemical Speciation Determination**

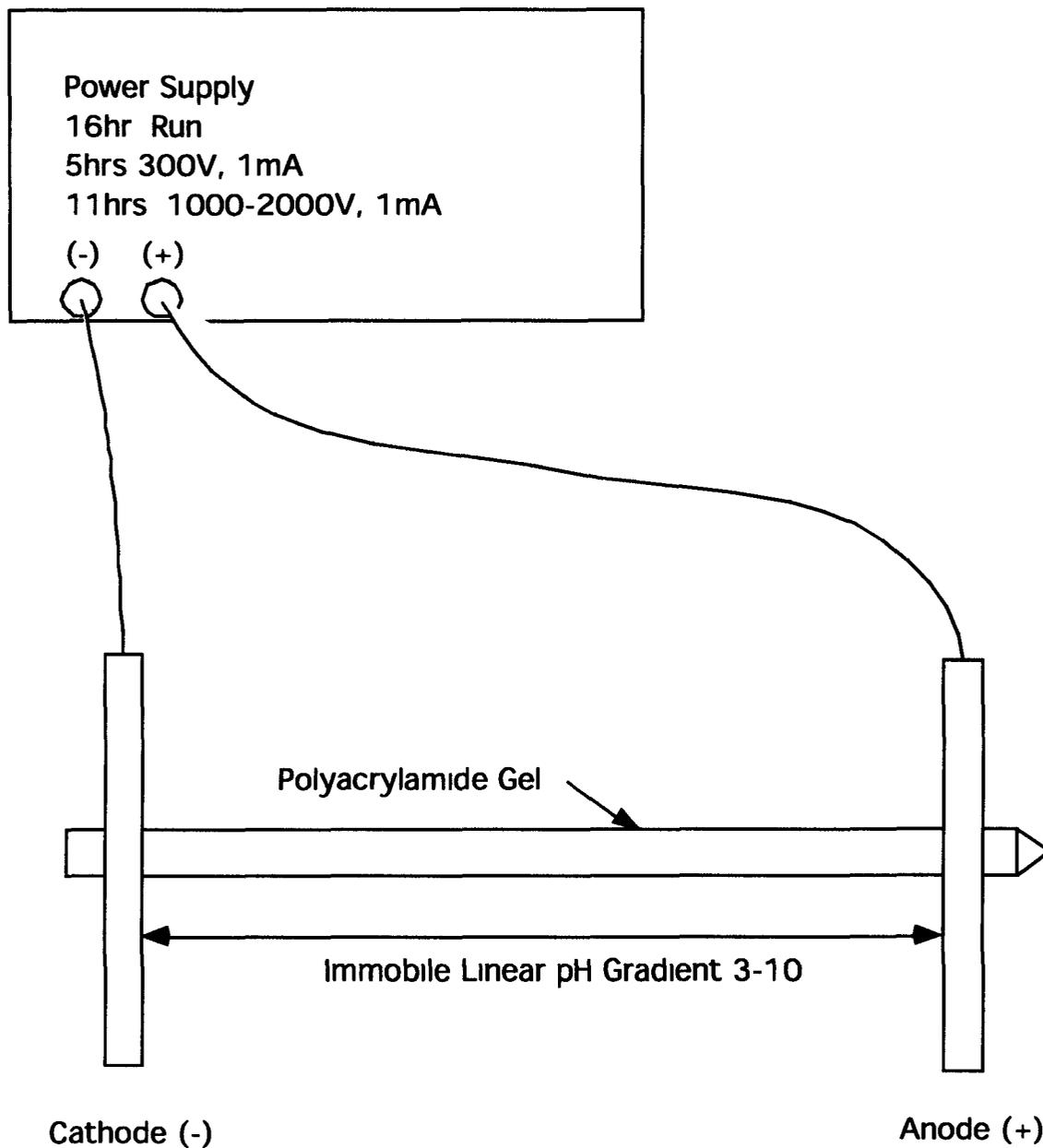
Figure 8. Schematic of DBM solvent extraction fractions for actinides (An).



**DBM Extraction Scheme using Chloroform as the organic phase**

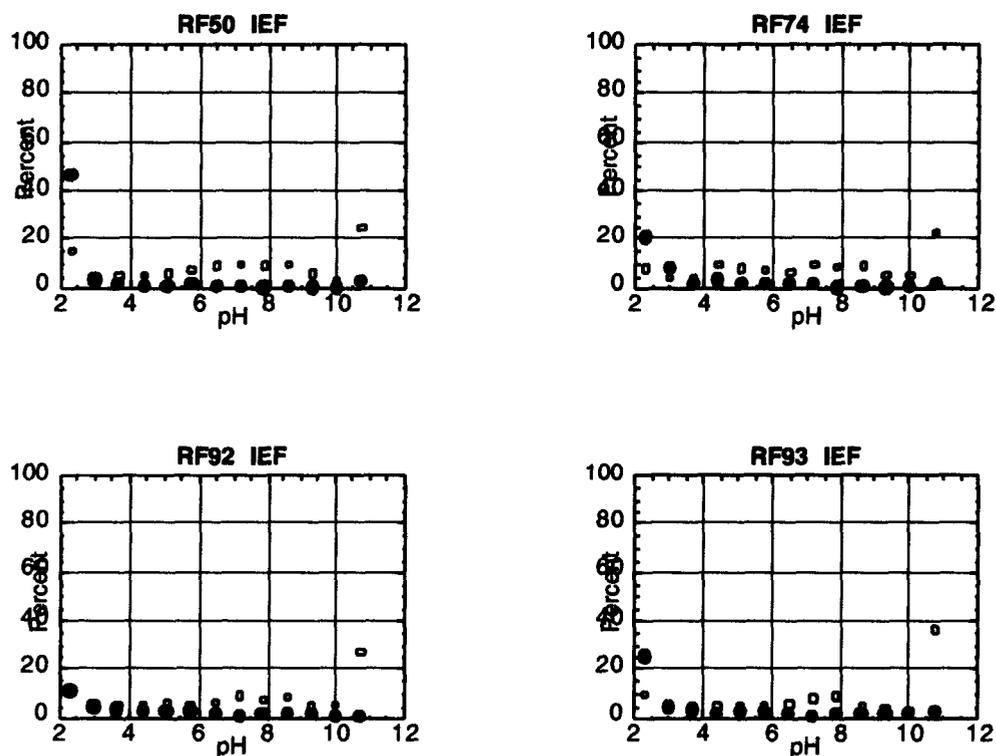
Figure 9. Schematic of electrophoresis set-up.

### Schematic of Isoelectric Focusing Apparatus



Sample introduced homogenously throughout gel prior to isoelectric focusing

**Figure 10. Percent recovery versus pH for** determined by isoelectric focusing of colloidal material within an electrical field which sets up a pH gradient within the gel. Organics are labeled with C-14 (solid symbol). Fe-59 used to label predominantly inorganics (hollow symbol). The pH range of the strip used was 3-10. The data at 2.3 represents  $\text{pH} < 3$  and the data at 10.7 represents  $\text{pH} > 10$ . The radiolabeled colloids are introduced along the strip, and are allowed to travel until they are immobilized at their isoelectric point. The results show that the organic matter contains strong acid functional groups, which impart them a point of zero charge, PZC of  $\text{pH} \leq 3$ . The inorganic matter contain strong basic functional groups which give them a PZC of  $\text{pH}$ .



**Table 1. Summary of  $^{240}\text{Pu}$  data using average activities from duplicate analysis except where noted**

Sample ID	Fraction	pCi/l	SD	Partitioning (%)
4/27/99 (Discharge)	Total	0.0263	0.0033	100
	0.5 $\mu\text{m}$ filter-passing	0.0175	0.0021	60
	20 $\mu\text{m}$ filter-retained	0.0073	0.0006	25
	0.5 $\mu\text{m}$ -20 $\mu\text{m}$ (by Difference)	0.0044	0.0006	15
	0.5 $\mu\text{m}$ filter passing	0.0175	0.0021	100
	100kDa-0.5 $\mu\text{m}$ (R)	0.0045	0.0011	26
	100kDa ultrafilter-passing (U)	0.0130	0.0024	74
	0.5 $\mu\text{m}$ filter-passing	0.0175	0.0021	100
	3kDa-0.5 $\mu\text{m}$ (R)	0.0116	0.0017	65
	3kDa ultrafilter-passing (U)	0.0059	0.0027	35
Sample ID	Fraction	pCi/l	SD	Partitioning (%)
4/30/99 (Storm)	Total	0.1373	0.0111	100
	0.5 $\mu\text{m}$ filter-passing*	0.1073	0.0080	60
	20 $\mu\text{m}$ filter-retained	0.0468	0.0025	26
	0.5-20 $\mu\text{m}$ (by Difference)	0.0250	0.0018	14
	0.5 $\mu\text{m}$ filter-passing*	0.1073	0.0080	100
	100kDa-0.5 $\mu\text{m}$ (R)	0.0457	0.0029	39
	100kDa ultrafilter-passing (U)	0.0616	0.0085	61
	0.5 $\mu\text{m}$ filter-passing*	0.1073	0.0080	100
	3kDa-0.5 $\mu\text{m}$ (R)	0.0806	0.0048	74
	3kDa ultrafilter-passing (U)	0.0267	0.0093	26

\* indicates average not used, TD = Total dissolved or <0.5 $\mu\text{m}$ , R = Retentate or the fraction retained + filter wash, U = ultrafiltrate (permeate) calculated by subtracting R from the TD (TD=Retentate + U)

**Table 2. Summary  $^{241}\text{Am}$  data using average activities from duplicate analysis.**

Sample ID	Fraction	pCi/l	SD	Partitioning (%)
4/27/99 (Discharge)	Total	0 0112	0 0015	100
	0 5 $\mu\text{m}$ filter-passing*	0 0106	0 0011	67
	20 $\mu\text{m}$ filter-retained	0 0035	0 0050	22
	0 5-20 $\mu\text{m}$ (by Difference)	0 0018	0 0003	11
	0 5 $\mu\text{m}$ filter-passing*	0 0106	0 0011	100
	100kDa-0 5 $\mu\text{m}$ (R)	0 0021	0 0005	20
	100kDa ultrafilter-passing (U)	0 0085	0 0012	80
	0 5 $\mu\text{m}$ filter-passing*	0 0106	0 0011	100
	3kDa-0 5 $\mu\text{m}$ (R)	0 0039	0 0006	37
	3kDa ultrafilter-passing (U)	0 0067	0 0013	63
	Sample ID	Fraction	pCi/l	SD
4/30/99 (Storm)	Total	0 0738	0 0041	100
	0 5 $\mu\text{m}$ filter-passing	0 0430	0 0031	51
	20 $\mu\text{m}$ filter-retained	0 0303	0 0023	36
	0 5-20 $\mu\text{m}$ (by Difference)	0 0109	0 0009	13
	0 5 $\mu\text{m}$ filter-passing	0 0430	0 0031	100
	100kDa-0 5 $\mu\text{m}$ (R)	0 0172	0 0013	37
	100kDa ultrafilter-passing (U)	0 0258	0 0034	63
	0 5 $\mu\text{m}$ filter-passing	0 0430	0 0031	100
	3kDa-0 5 $\mu\text{m}$ (R)	0 0257	0 0016	60
	3kDa ultrafilter-passing (U)	0 0173	0 00	40

\* indicates average not used, R = retentate or the fraction retained + filterwash, U = ultrafiltrate (permeate) calculated by subtracting R from 0 5 $\mu\text{m}$  filter-passing fraction

**Table 3. Suspended Particulate Matter (SPM,  $\leq 4.5\mu\text{m}$ ) Concentration.**

Sample ID	Filter #	SPM (mg/l)	Average (mg/l)	SD	SD (%)
4/27/99	1	42.7	38.8	4.8	12.4
"	2	36.7			
"	3	31.3			
"	4	41.3			
"	5	42.0			
4/30/99	1	114.9	120.2	6.3	5.3
"	2	123.1			
"	3	117.0			
"	4	130.0			
"	5	116.0			

**Table 4. Particulate Organic Carbon (POC,  $\leq 7\mu\text{m}$ ) Concentration.**

Sample ID	Filter #	POC (mg-C/l)	Avg(mg/l)	SD	SD(%)
4/27/99	CSM01	0.99	1.27	0.20	15.6
"	CSM02	1.29			
"	CSM03	1.36			
"	CSM04	1.45			
4/30/99	CSM05	3.65	3.88	0.19	4.8
"	CSM06	3.82			
"	CSM09	4.09			
"	CSM10	3.95			

**Table 5: Particulate Organic Nitrogen (PON,  $\leq 7\mu\text{m}$ ) Concentration.**

Sample ID	Filter #	PON (mg-N/l)	Avg (mg-N/l)	SD	SD(%)
4/27/99	CSM01	0.17	0.19	0.02	12.3
"	CSM02	0.22			
"	CSM03	0.17			
"	CSM04	0.20			
4/30/99	CSM05	0.30	0.41	0.11	26.8
"	CSM06	0.33			
"	CSM09	0.52			
"	CSM10	0.48			

**Table 6. C/N atomic Ratio of suspended particulate matter (<math>0.45\mu\text{m}</math>).**

Sample ID	Filter #	POC (mg-C/l)	PON (mg-N/l)	C/N Ratio	Avg	SD
4/27/99	CSM01	0.99	0.17	6.7	7.8	1.3
"	CSM02	1.29	0.22	6.8		
"	CSM03	1.36	0.17	9.2		
"	CSM04	1.45	0.20	8.6		
4/30/99	CSM05	3.65	0.30	14.4	11.6	2.6
"	CSM06	3.82	0.33	13.4		
"	CSM09	4.09	0.52	9.2		
"	CSM10	3.95	0.48	9.6		

**Table 7. Dissolved organic carbon (DOC, <math>0.7\mu\text{m}</math>) concentration.**

Sample ID	Container #	DOC(ppm)	Avg (ppm)	SD (ppm)	Avg ( $\mu\text{M}$ )	SD ( $\mu\text{M}$ )
4/27/99	1	9.23	8.02	0.98	668	82
"	2	9.52				
"	3	8.26				
"	4	8.15				
"	5	7.48				
"	6	7.70				
"	7	6.93				
"	8	6.86				
4/30/99	1	3.90	3.71	0.56	309	47
"	2	3.68				
"	3	3.14				
"	4	4.56				
"	5	3.28				

**Table 8. Carbon and Nitrogen (%) in colloids, as average of duplicate measurements.**

Sample ID	Description	Size	%C	%N	C/N
RF50	Discharge	3kDa-0.5 $\mu\text{m}$	5.68	0.54	12.2
RF74	Storm	3kDa-0.5 $\mu\text{m}$	4.18	0.25	19.4
RF92	Resuspension	1kDa-0.5 $\mu\text{m}$	2.57	0.15	19.5
RF92	Resuspension	1kDa-0.5 $\mu\text{m}$	2.02	0.14	17.1

**Table 9. Inorganic anion (F, Cl, NO<sub>3</sub>, HPO<sub>4</sub>, and SO<sub>4</sub>) concentrations.**

Sample ID	Subsample	F (ppm)	Cl (ppm)	NO <sub>3</sub> (ppm)	HPO <sub>4</sub> (ppm)	SO <sub>4</sub> (ppm)
4/27/99	1	0.406	12.52	4.32	0.69	10.6
"	2	0.408	12.50	4.34	0.78	10.7
"	3	0.412	15.60	7.05	0.78	17.6
"	4	0.406	15.57	7.07	0.82	17.5
"	5	0.419	14.68	6.05	0.67	15.3
"	6	0.413	14.68	6.11	0.69	15.4
4/27/99	Average=	0.411	14.26	5.82	0.74	14.53
	SD	0.005	1.42	1.24	0.06	3.16
4/30/99	1	0.592	9.75	2.41	BD	5.3
"	2	0.593	9.81	2.40		5.3
"	3	0.366	9.30	2.12		4.2
"	4	0.512	9.30	2.11		4.2
"	5	0.570	9.90	2.44	BD	5.5
"	6	0.539	9.92	2.43		5.5
"	7	0.577	10.15	2.60		5.8
"	8	0.568	10.26	2.60		5.8
4/30/99	Average=	0.539	9.80	2.39	BD	5.18
	SD	0.075	0.35	0.19		0.63

# NO<sub>3</sub> Concentrations are below detection limit (BD)

**Table 10. Ancillary data taken at time of sampling by site personnel.**

Parameter	GS03 4/27/99 @ 09 00	GS10 4/30/99 @ 08 55
pH	7.52	8.12
Temperature (°C)	8.1	11.2
SC (µS/cm)	496	249
DO(mg/L)	8.8	-
ORP	61	-
Alkalinity	92 @ 4.5pH @ 11°C	-
EH	-	49.7

**Table 11. Trace Metal Concentrations in aqueous (4/27/99 and 4/30/99) and colloidal (RF50, RF74, RF92) samples.**

Sample ID	Subsample	Fe (ppb)	Al (ppb)	Mn (ppb)
4/27/99	1	258 ± 3	224 ± 15	42 ± 2.2
	2	233 ± 15	208 ± 5	41 ± 1.9
4/30/99	A	150 ± 13	105 ± 9	39 ± 2.7
	B	127 ± 9	96 ± 5	36 ± 0.8

Sample ID	Colloid size	Fe (mg/g)	Al (mg/g)	Mn (µg/g)
RF50	3kDa-0.5µm	15.0	35.8	156.4
RF74	3kDa-0.5µm	47.2	92.7	445.8
RF92	1kDa-0.5µm	15.5	40.7	185.7

**Table 12. Phase distribution coefficients, ( $\mu\text{g/kg}$  or  $\text{ml/g}$ ) of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$ .**

Isotope	Sampling Date	Sample Name	$C_p$ (mg/l)	$R_p$ (ml/g)
$^{239,240}\text{Pu}$	4/27/99	Discharge	38.8	$1.7 \times 10^4$
$^{239,240}\text{Pu}$	4/30/99	Storm event	120	$4.1 \times 10^3$
$^{241}\text{Am}$	4/27/99	Discharge	38.8	$1.3 \times 10^4$
$^{241}\text{Am}$	4/30/99	Storm event	120	$7.9 \times 10^3$

$C_p$  (mg/l) is the concentration of suspended particulate matter

**Table 13.  $^{239,240}\text{Pu}/^{241}\text{Am}$  ratios in dissolved, colloidal and particulate samples.**

Date	Sample Name	Fraction	Pu/Am-1	Pu/Am-2	Pu/Am-Avg	SD
4/27/99	Discharge	WH	2 770	2 023	2 396	0 334
		TD	1 716	-	1 716	0 164
		>20 $\mu\text{m}$	2 005	2 103	2 054	0 204
		0 5-20 $\mu\text{m}$	2 156	2 725	2 440	0 406
		<100kDa	0 398	0 285	0 341	0 998
		>100kDa	2 146	2 669	2 408	0 692
		<3kDa	1 113	-	1 113	2 223
		>3kDa	2 749	3 335	3 042	0 437
		100kDa wash	0 835	1 139	0 987	0 711
		3kDa wash	0 688	1 846	1 267	0 628
4/30/99	Storm event	WH	2 037	1 660	1 848	0 151
		TD	2 734	3 967	3 350	0 299
		>20 $\mu\text{m}$	1 518	1 571	1 544	0 089
		0 5-20 $\mu\text{m}$	2 456	2 149	2 303	0 176
		<100kDa	2 605	2 058	2 331	0 875
		>100kDa	2 787	2 608	2 697	0 184
		<3kDa	2 654	1 201	1 927	2 411
		>3kDa	3 291	3 055	3 173	0 201
		100kDa wash	0 597	0 849	0 723	0 235
		3kDa wash	1 826	2 378	2 102	0 199

WH=whole water, TD=total dissolved (i e., <0.5 $\mu\text{m}$ )

**Table 14. Redox speciation results. Comparison of <0.5µm fraction activity and activities for different oxidation states based on TTA extraction at pH<1.**

Sample	<0.5µm pCi/l	Pu (interfacial)*		Pu (III,V,VI) aqueous phase		Pu (IV) organic phase	
		pCi/l	±	pCi/l	±	pCi/l	±
Discharge	0.02	-0.056	0.078	-0.011	0.016	-0.011	0.016
Storm Set A	0.11	0.105	0.085	-0.001	0.016	0.005	0.016
Storm Set B	0.19	0.103	0.069	0.004	0.016	0.0003	0.0134

\* interfacial fraction of aqueous and organic phase including material in between. In order to obtain lower relative errors, we are currently recounting these samples for 10 days or longer. Colloidal Pu would likely not be easily extractable due to the detergent properties of natural organic matter which likely is responsible for keeping Pu and Am in the 0.5µm-filter-passing fraction. Detergents and molecules with detergent properties would be expected to accumulate in the interfacial region between hydrophobic (organic phase) and hydrophilic (aqueous phase) solvents. Only ionic forms or labile complexes would be expected to be extractable for oxidation state determination. For this reason no other extractions were completed. These results would therefore suggest that most Pu is not in a low molecular weight ionic or labile form in these waters. However, the activities in this interfacial fraction were lower than the total dissolved activities of the corresponding sample, which can be attributed to some adsorption losses to container walls or rotary evaporation equipment. Pu concentrations in acid extracts of the recondensed water from the rotary evaporation and post rotovapped sample bottle were negligible, indicating that wall losses most likely occurred in the rotary evaporation glassware, despite silanization, and even more likely in the original sample container which, however, was not acid leached and analyzed.

**Table 15. Percent of total C-14 recovered during isoelectric focusing.**

<b>pH</b>	<b>RF50</b>	<b>RF74</b>	<b>RF92</b>	<b>RF93</b>
<3	46.8	21.2	11.4	25.6
3.0	3.7	9.0	4.8	5.0
3.7	1.7	2.5	3.4	3.3
4.4	1.2	3.5	2.7	1.9
5.1	1.2	2.4	2.7	3.0
5.8	1.4	1.9	2.7	2.9
6.5	1.2	1.7	1.8	1.7
7.2	1.2	1.4	1.2	1.1
7.9	0	0.6	1.3	1.8
8.6	0.7	0.7	2.4	1.9
9.3	0.2	0.4	1.3	2.4
10	0.6	0.8	1.1	1.8
>10	2.9	2.1	1.2	2.7

**Table 16. Percent of Total Fe-59 Recovered during isoelectric focusing.**

<b>pH</b>	<b>RF50</b>	<b>RF74</b>	<b>RF92</b>	<b>RF93</b>
<3	12.2	5.4	7.9	7.2
3.0	0.8	1.1	1.8	0.4
3.7	1.6	1.2	2.5	1.3
4.4	2.4	7.1	2.2	1.4
5.1	2.9	5.3	3.4	2.2
5.8	4.7	4.3	3.2	2.3
6.5	6.1	3.7	4.0	3.0
7.2	6.7	7.1	6.6	4.9
7.9	6.6	5.6	4.5	6.2
8.6	7.0	6.8	6.3	1.5
9.3	2.7	2.6	2.3	0.8
10	0.4	2.3	2.6	1.1
>10	22.2	20.7	25.6	34.3

**Appendices****Appendix 1: Summary of Sample Identification Numbers.**

RF#	LOCATION	RIN	DESCRIPTION	TYPE	ANALYSIS
RF33	GS03	99Q6890	total	ppt	A, B
RF34	GS03	99Q6890	<0 5 $\mu$ m	ppt	A, B
RF35	GS03	99Q6890	>20 $\mu$ m	cartridge	A, B
RF36	GS03	99Q6890	0 5-20 $\mu$ m	cartridge	A, B
RF37	GS03	99Q6890	<100kDa	ppt	A, B
RF38	GS03	99Q6890	100kDa - 0 5 $\mu$ m	ppt	A, B
RF39	GS03	99Q6890	<3kDa	ppt	A, B
RF40	GS03	99Q6890	3kDa - 0 5 $\mu$ m	ppt	A, B
RF41	GS03	99Q6890	Blank spike	ppt	A, B
RF42	GS03	99Q6890	Blank	ppt	A, B
RF43	GS03	99Q6890	total	ppt	A, B
RF44	GS03	99Q6890	<0 5 $\mu$ m	ppt	A, B
RF45	GS03	99Q6890	>20 $\mu$ m	cartridge	A, B
RF46	GS03	99Q6890	0 5 - 20 $\mu$ m	cartridge	A, B
RF47	GS03	99Q6890	<100kDa	ppt	A, B
RF48	GS03	99Q6890	100kDa - 0 5 $\mu$ m	ppt	A, B
RF49	GS03	99Q6890	<3kDa	ppt	A, B
RF50	GS03	99Q6890	3kDa - 0 5 $\mu$ m	ppt	A, B, C
RF51	GS03	99Q6890	Blank spike	ppt	A, B
RF52	GS03	99Q6890	Blank	ppt	A, B
RF53	GS03	99Q6890	set#1 100kDa wash	ppt	A, B
RF54	GS03	99Q6890	set#1 3kDa wash	ppt	A, B
RF55	GS03	99Q6890	set#2 100kDa wash	ppt	A, B
RF56	GS03	99Q6890	set#2 3kDa wash	ppt	A, B
RF57	GS10	99D7102	total	ppt	A, B
RF58	GS10	99D7102	<0 5 $\mu$ m	ppt	A, B
RF59	GS10	99D7102	>20 $\mu$ m	cartridge	A, B
RF60	GS10	99D7102	0 5-20 $\mu$ m	cartridge	A, B
RF61	GS10	99D7102	<100kDa	ppt	A, B
RF62	GS10	99D7102	100kDa - 0 5 $\mu$ m	ppt	A, B
RF63	GS10	99D7102	<3kDa	ppt	A, B
RF64	GS10	99D7102	3kDa - 0 5 $\mu$ m	ppt	A, B
RF65	GS10	99D7102	Blank spike	ppt	A, B
RF66	GS10	99D7102	Blank	ppt	A, B
RF67	GS10	99D7102	total	ppt	A, B
RF68	GS10	99D7102	<0 5 $\mu$ m	ppt	A, B
RF69	GS10	99D7102	>20 $\mu$ m	cartridge	A, B
RF70	GS10	99D7102	0 5-20 $\mu$ m	cartridge	A, B
RF71	GS10	99D7102	<100kDa	ppt	A, B
RF72	GS10	99D7102	100kDa - 0 5 $\mu$ m	ppt	A, B
RF73	GS10	99D7102	<3kDa	ppt	A, B
RF74	GS10	99D7102	3kDa - 0 5 $\mu$ m	ppt	A, B, C
RF75	GS10	99D7102	Blank spike	ppt	A, B
RF76	GS10	99D7102	Blank	ppt	A, B

## Appendix 1: Cont.

RF#	LOCATION	RIN		DESCRIPTION	TYPE	ANALYSIS
RF77	GS10	99D7102	setA	100kDa wash	ppt	A, B
RF78	GS10	99D7102	setA	3kDa wash	ppt	A, B
RF79	GS10	99D7102	setB	100kDa wash	ppt	A, B
RF80	GS10	99D7102	setB	3kDa wash	ppt	A, B
RF86	GS10	99D7102		cartridge blank		A, B
RF87	SED029	99D5920			sediment	A, B
RF88	B4 POND	99D5920			sediment	A, B
RF89	GS10	99D7102	set A	TTA ext pH<1-org (IV)		D
RF90	GS10	99D7102	set A	TTA ext pH< -aq (III,V,VI)		D
RF91	GS10	99D7102	set A	TTA ext pH<1- aq/org		D
RF92	B4 POND	99D5920		>1kDa resuspension	inorganic	C
RF93	B4 POND	99D5920		>1kDa resuspension	organic	C
RF94	GS10	99D7102	set A	TTA ext pH<1 - org (IV)		D
RF95	GS10	99D7102	set A	TTA ext pH<1- aq (III,V,VI)		D
RF96	GS10	99D7102	set A	TTA ext pH<1- aq/org		D
RF97	GS10	99D7102	set A	TTA ext pH<1-org (IV)	bottle leach	D
RF98	GS10	99D7102	set A	TTA ext pH<1-aq (III,V,VI)	bottle leach	D
RF99	GS10	99D7102	set A	TTA ext pH<1- aq/org	bottle leach	D
RF100	GS10	99D7102	set A		bottle leach	B
RF109	GS10	99D7102	set B	TTA ext pH<1 org (IV)		D
RF110	GS10	99D7102	set B	TTA ext pH<1 aq(III,V,VI)		D
RF111	GS10	99D7102	set B	TTA ext pH<1 aq/org		D
RF112	GS10	99D7102	set B	bottle leach		D
RF113	GS03	99Q6890		TTA ext pH<1 org (IV)		D
RF114	GS03	99Q6890		TTA ext pH<1 aq(III,V,VI)		D
RF115	GS03	99Q6890		TTA ext pH<1 aq/org		D
RF116	GS03	99Q6890			bottle leach	D

A= <sup>241</sup>Am activity, B=<sup>239</sup> <sup>240</sup>Pu activity, C = Electrophoresis, D= Pu oxidation state

**Appendix 2: Procedure used for  $^{241}\text{Am}$  and  $^{239,240}\text{Pu}$ -activity determinations.**

**Coprecipitation**

- 1 To 10L of sample add of conc.  $\text{HNO}_3$  until pH <2 Let sample sit for 16 hours after acidification before processing
- 2 Add 50 ml conc HCl
- 3 Add tracers ( $^{243}\text{Am}$  and  $^{242}\text{Pu}$ )
- 4 Add 5 ml ferric chloride carrier (40 mg  $\text{Fe}^{3+}$ /ml)
- 5 Mix sample and measure pH with pH paper; if pH >1 add 12N HCl until pH <1 Cover and stir for 30 min
- 6 Check pH again If <1, gently add conc  $\text{NH}_4\text{OH}$ , add until turbidity persists than add additional 50 ml
- 7 Stir for 30 minutes then let settle overnight
- 8 Siphon ~9L of solution, discard
- 9 Transfer remaining ~1L into 250ml centrifuge tubes, rinsing bucket and transfer beaker (if used) with minimum DI
- 10 Centrifuge for 15 min at 3500 rpm
- 11 Decant and discard supernate
- 12 To dissolve precipitate add 3 times ppt volume of conc HCl and mix by vortexing.\*
- 13 Add 75 ml of 9 N HCl
- 14 Add 2 ml of saturated  $\text{NaNO}_2$  to samples, mix well and set aside for 15 minutes

\*Note For samples containing material that did not dissolve in HCL and complete digestion was done as follows

concentrated nitric, hydrochloric and hydrofluoric acids → dryness  
concentrated, hydrochloric and nitric (hydrogen peroxide if necessary) → dryness  
hydrochloric → dryness

**Pu column**

- 1 Fill disposable plastic column with 7 cm AG1x8 resin (by resin/DI slurry)
- 2 Place funnel on top of column with Whatman filter paper
- 3 Wet filter paper with 9N HCl
- 4 Condition resin with 50 ml 9 N HCl
- 5 Load sample through filter, rinse 2x with 20 ml 9N HCl (= Am fraction)
- 6 Rinse 2x with 20 ml 9N HCl, discard
- 7 Elute Pu with 20ml 9N HCl + 15 ml HI
- 8 Add 1 ml conc HNO<sub>3</sub> evaporate to dryness

**Pu Microprecipitation**

- 1 Add 1 ml conc HCl, mix well to resolubilize
- 2 Add 14 ml DI, mix well
- 3 Add 10 ml lanthanum carrier + 0.5 ml CH<sub>3</sub>COOH, mix well
- 4 Add 5 ml 3N HF
- 5 Let sample sit for min 15-20 minutes
- 6 Set up filtration apparatus place 25 mm filter membrane on support screen and lock
- 7 Apply vacuum, rinse filter with 1-2 ml methanol, rinse filter with DI
- 8 Transfer sample, rinsing beaker once with 5 ml DI
- 9 Rinse filter with 10-15 ml DI
- 10 Turn off vacuum, use "sharpie" and place dot on outside edge of filter marking which side is up  
Place filter in pyrex beaker and put in drying oven (90-100°C) for ~ 1min
- 11 Mount filter on stainless steel planchet with double sided adhesive tape

**Am Methanolic Anion Exchange Column**

- 1 Mix anion exchange resin with twice the volume of 1N  $\text{HNO}_3$  90% methanol solution (for 160 ml 10ml conc  $\text{HNO}_3$ , 150 ml methanol) overnight
- 2 Add 5-10 ml conc  $\text{HNO}_3$ ,
- 3 Add 100-125 ml DI,
- 4 Add 10 ml Fe carrier
- 5 Transfer to cent tube and ppt with conc  $\text{NH}_4\text{OH}$  Cent. @3500 rpm for 15 min/
- 6 Add conc  $\text{HNO}_3$  and evaporate, Repeat
- 7 Add conc  $\text{HNO}_3$  until dissolved Add methanol (15 ml of methanol for each 1 ml conc  $\text{HNO}_3$ )
- 8 Pour resin slurry into disposable column and let resin settle to 7cm, place a layer of silica or glass beads on top of resin
- 9 Place funnel on top of column with Whatman filter paper, wet filter with 1N  $\text{HNO}_3$  90% methanol solution
- 10 Condition column with 40 ml of 1N  $\text{HNO}_3$  90% methanol solution
- 8 Load the sample onto column through filter, rinse with 25 ml 1N  $\text{HNO}_3$  90% methanol solution
- 9 Remove and discard filter and rinse twice with 25 ml 1N  $\text{HNO}_3$  90% methanol solution Discard into methanolic waste receptacle.
- 10 Strip Am by passing three 20 ml volumes of 8 N  $\text{HNO}_3$  through the column allowing each rinse to pass completely before adding next rinse Collect eluate in beaker for Teva column
- 11 Evaporate to dryness

**Am Teva Resin**

- 1 Redissolve sample from above in 10 ml 2M  $\text{NH}_4\text{SCN}$ / 0.1M formic acid (for 100ml 15.2 g  $\text{NH}_4\text{SCN}$  & 0.35 ml 98% formic acid in 100ml DI) Allow sample to sit for 1 hour to ensure dissolution
- 2 Condition a TEVA resin 2 ml column with 5 ml of 2M  $\text{NH}_4\text{SCN}$ / 0.1M formic acid solution
- 3 Transfer sample into TEVA column in two portions using disposable polyethylene transfer pipet Rinse the sample container with 1 ml of 2M  $\text{NH}_4\text{SCN}$ / 0.1M formic acid and transfer to column Repeat rinse and add to column
- 4 Rinse the TEVA column with two 5 ml volumes of 1M  $\text{NH}_4\text{SCN}$ / 0.1M formic acid (for 100 ml dissolve 7.6 g  $\text{NH}_4\text{SCN}$  and 0.35 ml 98% formic acid in 100 ml of DI) Allow first wash to pass completely before adding the second wash (This washes lanthanides from column)
- 5 Strip Am from column with 15 ml of 2N HCl in three 5ml portions allowing each 5 ml to pass completely
- 6 To decompose thiocyanate, add 2.5 ml conc  $\text{HNO}_3$  and 7.5 ml conc HCL to the Am solution Swirl gently Evaporate until ~1 drop solution is remaining
- 7 Add 5 ml conc  $\text{HNO}_3$  Evaporate until volume is ~1 drop

**Am Micro-precipitation (SOP 780)**

- 1 Add 1 ml conc HCl to sample Heat for 5 minutes Add 15 ml DI
- 2 Add 0.5 ml lanthanum carrier mix well Add 5 ml HF Mix well
- 3 Allow sample to stand for 15-20 minutes minimum.
- 4 Place 25 mm filter membrane in a filter funnel assembly and turn on vacuum Rinse with 1-2 ml alcohol
- 5 Load sample into filter Rinse sample beaker once with 5 ml DI and add to funnel
- 6 After sample has passed through filter Rinse filter with 10-15 ml DI
- 7 Turn off vacuum, use "sharpie" and place dot on outside edge of filter marking which side is up Place filter in pyrex beaker and put in drying oven (90-100°C) for ~ 1min
- 8 Mount filter on stainless steel planchet with double sided adhesive tape

### Appendix 3: Pu oxidation state determinations

#### Extraction Experiments

The initial focus of the Pu oxidation state determinations was on the DBM extraction as described by Saito and Choppin (1983). This two step extraction procedure determines all four oxidation states in a solution with sample pH ~8. Activity levels on the order of 10's of dpms were used in the initial extractions to determine if such activities could be measured using this extraction. Attempts were made to alter the oxidation state of our Pu standards ( $^{240}\text{Pu}$  and  $^{242}\text{Pu}$ ) by both electrolysis (Lovett and Nelson, 1981) and chemical alteration (Gehmecker et al, 1986 and Kobashi et al, 1988). Recoveries of these initial experiments were low (~10%).

Then, we began using teflon vials for DBM extractions to determine the oxidation state of Pu instead of untreated glass to assess the importance of adsorption to the walls. These experiments showed 90-100% recovery of the Pu tracer added. Extractions were then run on solutions altered to different oxidation states of Pu. The solutions were made by electrolysis of the Pu tracer or by adding either potassium permanganate to hold Pu(VI) or hydroxylamine HCL to reduce Pu to Pu(III). These extractions showed that most of the Pu was Pu(V) (78-98%) which is not what would be expected in an acidic solution of tracer. Extractions were also run on a buffer solution, used to simulate pH of surface water, but these experiments were not successful in recovering the tracer added. It was unclear whether the extractions or if the changing of oxidation states failed.

#### FSU visit

Kim Roberts visited Dr Choppin's lab to work with Dr Morgenstern, a postdoc in Dr Choppin's lab, who has been working with the extraction procedures for oxidation state determination of Pu. Both TTA and DBM extractions were run on a Pu-238 standard solution. The TTA extraction was run twice at two different pHs. In the first TTA extraction, (pH<1)  $^{238}\text{Pu}$  was added to dilute nitric acid and Pu (IV) is extracted out in the organic portion and the rest remain in the aqueous portion. The second TTA extraction using pH =4-5,  $^{238}\text{Pu}$  was added to sodium acetate solution, Pu(III, IV, VI) is extracted in the organic fraction and Pu(V) remains in the aqueous portion. The amount of Pu(VI) is calculated by difference of the two aqueous phases assuming there is no Pu (III) in these solutions. For the DBM extraction the starting solution was sodium chloride and Borax solution. The last two experiments were run with first ultrafiltering the sample (10kDa) to prevent losses due to sorption of Pu(IV). The following table summarizes the percent recovery for  $^{238}\text{Pu}$  standard with the two different extraction methods.

Table A3a Percent of total Pu in each oxidation state from lab extractions conducted at FSU

Exp	Species	TTA	DBM
Experiment 1	Pu(IV)	82	12
	Pu(V)	4	46
	Pu(VI)	16	0
Experiment 2	Pu(IV)	84	21
	Pu(V)	2	60
	Pu(VI)	11	1
Experiment 3 Initial pH ~7.3	Pu(IV)	82	8
	Pu(V)	22	66
	Pu(VI)	0	<1
10kDa ultrafiltration	Pu(IV)	82	
	Pu(V)	30	
	Pu(VI)	0	
10kDa ultrafiltration repeated	Pu(IV)	76	
	Pu(V)	25	
	Pu(VI)	0	

These results indicate the TTA extraction at pH<1, used to extract Pu(IV) is consistent regardless of what the starting pH was. Therefore, the determination of the percent of Pu(IV) out of the total Pu activity was the primary goal regarding the three surface water samples for oxidation state analysis. Due to the low activities, as compared to the laboratory experiments, it was necessary to preconcentrate the samples prior to analysis. Three samples were preconcentrated by rotary evaporation from 7500 ml to 750ml (Table A3b). The preconcentrated samples were stored until time of analysis. For the analysis 150ml of sample was added to 150ml of 0.5M HNO<sub>3</sub> in a teflon separatory funnel. After adding 300 ml of 0.5M TTA the separatory funnel was covered in Al foil and shaken for 20-30minutes. The 600ml was dispensed from the separatory funnel as follows: 250ml (of 300ml) of the aqueous fraction (Pu(III,V,VI)), 50ml of the aqueous and 50ml of the organic fractions which contains the interface between the two phases, and 250ml of the organic fraction (Pu(IV)). <sup>242</sup>Pu tracer was added and each sample aliquot was evaporated to dryness. Any remaining residue was digested using concentrated HCl, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. Once the samples were dissolved, the same procedure used for determining Pu activity in the size fraction samples was applied (Appendix 2). In all three samples the organic Pu(IV) and the aqueous (Pu(III,V,VI)) had no measurable Pu activity. Both storm samples (A & B) showed activity in the interfacial fraction that was 55 – 95% of the total dissolved activity measured previously for the corresponding samples albeit with large errors. We are currently recounting these samples for 10 days or longer. The losses that occurred are probably attributed to sorption onto the original sample container walls as these samples were not run immediately after collection. Because the

## Final Report-Santschi

activity of the discharge sample was an order of magnitude smaller than the storm samples, the activity may have been too low to be detected with the extraction. The existence of Pu in the interfacial fraction and not in either the aqueous or organic phases suggest that the Pu in these samples is colloidal and therefore not extractable in these experiments,

Table A3b Ancillary data for samples analyzed for oxidation state of Pu measured after rotary evaporation

Sample	Initial Volume (L)	Final Volume (L)	Sal	pH	TDS (mg/L)	Cond ( $\mu$ S/cm)
Discharge	7230	775	1.2	7.99	2500	2500
Storm Set A	7500	800	0.6	8.1	1559	1559
Storm Set B	7700	700	0.6	7.3	1544	1544

**Appendix 4. Quality assurance summary****Precision**

All samples were run in duplicate for the size fraction activity determination of Pu and Am and trace metals were run in duplicate and duplicate error ratio (DER) was calculated (Table A4a). The samples analyzed for POC, PON, DOC, SPM, and inorganic anions were run a minimum of four replicates (Tables 3-8).

**Table A4a: Duplicate error ratio (DER) for  $^{239,240}\text{Pu}$** 

ID	Sample	$^{239,240}\text{Pu}$		ID	Sample	$^{239,240}\text{Pu}$		Duplicate Error Ratio
		pCi/l	+/-			pCi/l	+/-	
RF33	Total	0.0200	0.0271	RF43	Total	0.0193	0.0251	0.0187
RF34	<0.5 $\mu\text{m}$	0.0260	0.0182	RF44	<0.5 $\mu\text{m}$	0.0245	0.0166	0.0608
RF35	>20 $\mu\text{m}$	0.0289	0.0070	RF45	>20 $\mu\text{m}$	0.0286	0.0076	0.0312
RF36	0.5-20 $\mu\text{m}$	0.0249	0.0041	RF46	0.5-20 $\mu\text{m}$	0.0333	0.0048	1.3401
RF37	100kDa U	0.0161	0.0003	RF47	100kDa U	0.0159	0.0002	0.6362
RF38	100kDa R	0.0171	0.0030	RF48	100kDa R	0.0200	0.0036	0.6089
RF39	3kDa U	0.0161	0.0003	RF49	3kDa U	0.0168	-0.0001	2.2717
RF40	3kDa R	0.0200	0.0066	RF50	3kDa R	0.0544	0.0160	1.9904
RF41	Blank spike	0.0495	1.9375	RF51	Blank spike	0.0156	0.0618	0.0175
RF42	Blank	0.0154	-0.0137	RF52	Blank	0.0497	1.6584	0.0207
RF53	100kDa wash	0.0204	-0.0301	RF55	100kDa wash	0.0163	0.0006	0.1374
RF54	3kDa wash	0.0169	0.0008	RF56	3kDa wash	0.0167	0.0016	0.1010
RF57	Total	0.0000	0.0000	RF67	Total	0.0169	0.0573	0.2953
RF58	<0.5 $\mu\text{m}$	0.0951	0.1600	RF68	<0.5 $\mu\text{m}$	0.0564	0.1144	0.1969
RF59	>20 $\mu\text{m}$	0.0797	0.1072	RF69	>20 $\mu\text{m}$	0.0939	0.1855	0.0662
RF60	0.5-20 $\mu\text{m}$	0.0967	0.0487	RF70	0.5-20 $\mu\text{m}$	0.1232	0.0448	0.4009
RF61	100kDa U	0.0539	0.0269	RF71	100kDa U	0.1004	0.0232	1.3097
RF62	100kDa R	0.0185	0.0034	RF72	100kDa R	0.0231	0.0036	0.9213
RF63	3kDa U	0.0522	0.0394	RF73	3kDa U	0.0549	0.0449	0.0443
RF64	3kDa R	0.0167	0.0015	RF74	3kDa R	0.0194	0.0006	1.7305
RF65	Blank spike	0.0968	0.0731	RF75	Blank spike	0.0962	0.0859	0.0058
RF66	Blank	0.0480	1.4710	RF76	Blank	0.0162	0.7535	0.0192
RF77	100kDa wash	0.0541	2.1443	RF79	100kDa wash	0.0169	0.0040	0.0174
RF78	3kDa wash	0.0155	-0.0135	RF80	3kDa wash	0.0267	0.0140	0.5755

**Table A4b. Duplicate error ratio (DER) <sup>241</sup>Am.**

ID	Sample	<sup>241</sup> Am pCi/l	+/-	ID	Sample	<sup>241</sup> Am pCi/l	+/-	Duplicate Error Ratio
RF33	Total	0 0103	0 0098	RF43	Total	0 0099	0 0125	0 0214
RF34	<0 5µm	0 0204	0 0106	RF44	<0 5µm	1 9285	-0 0113	122 7581
RF35	>20µm	0 0248	0 0035	RF45	>20µm	0 0247	0 0036	0 0329
RF36	0 5-20µm	0 0191	0 0019	RF46	0 5-20µm	0 0122	0 0018	2 6453
RF37	100kDa U	0 0074	0 0007	RF47	100kDa U	0 0070	0 0007	0 4257
RF38	100kDa R	0 0086	0 0014	RF48	100kDa R	0 0101	0 0014	0 7959
RF39	3kDa U	0 0065	0 0003	RF49	3kDa U	0 0066	0 0004	0 2789
RF40	3kDa R	0 0084	0 0024	RF50	3kDa R	0 0204	0 0048	2 2386
RF41	Blank spike	0 0487	1 9295	RF51	Blank spike	0 0058	-0 0003	0 0222
RF42	Blank	0 0064	-0 0018	RF52	Blank	0 0474	2 1263	0 0193
RF53	100kDa wash	0 0060	0 0008	RF55	100kDa wash	0 0078	0 0008	1 6313
RF54	3kDa wash	0 0089	0 0010	RF56	3kDa wash	0 0097	0 0015	0 4661
RF57	Total	0 0000	0 0000	RF67	Total	0 0061	0 0052	1 1785
RF58	<0 5µm	0 0307	0 0786	RF68	<0 5µm	0 0271	0 0690	0 0343
RF59	>20µm	0 0235	0 0393	RF69	>20µm	0 0203	0 0468	0 0526
RF60	0 5-20µm	0 1174	0 0321	RF70	0 5-20µm	0 0799	0 0285	0 8721
RF61	100kDa U	0 0433	0 0110	RF71	100kDa U	0 0308	0 0108	0 8169
RF62	100kDa R	0 0075	0 0013	RF72	100kDa R	0 0107	0 0018	1 4424
RF63	3kDa U	0 0251	0 0142	RF73	3kDa U	0 0225	0 0172	0 1171
RF64	3kDa R	0 0065	0 0006	RF74	3kDa R	0 0072	0 0005	0 9258
RF65	Blank spike	0 0277	0 0222	RF75	Blank spike	0 0376	0 0281	0 2752
RF66	Blank	0 1502	1 8552	RF76	Blank	0 0114	0 2364	0 0742
RF77	100kDa wash	0 0667	2 9121	RF79	100kDa wash	0 0249	0 0068	0 0144
RF78	3kDa wash	0 0063	-0 0042	RF80	3kDa wash	0 0173	0 0077	1 2609

**Table A4c: Duplicate error ratio (DER) for aqueous trace metal samples.**

Metal	ID	ppb	+/-	ppb	+/-	Duplicate Error Ratio
Fe	4/27/99	258	3	233	15	1.63
	4/30/99	150	13	127	9	1.45
Al	4/27/99	224	15	208	5	1.01
	4/30/99	105	9	96	5	0.87
Mn	4/27/99	42	2.2	41	1.9	0.34
	4/30/99	39	2.9	36	0.8	1.00

**Accuracy**

To ensure accuracy of activities determined by alpha spectrometry, the alpha spectrometer was calibrated from 3-7MeV using a NIST traceable 1" stainless steel planchete. Calibration checks were performed weekly during the time of instrument use. No recalibration was needed as the four standard peaks used to monitor calibration did not exceed a shift greater than 40keV. The efficiency for the detector is calculated with the 1"stainless steel standard but all samples have an internal tracer added which provides the necessary efficiency information for data reduction.

**Representativeness**

Chain of custody forms for samples 99D5920, 99Q6890, and 99D7102 were received and retained for this years work.

**Comparability**

Analytical methods used have followed established methods where necessary. All protocols have been referenced and any deviations from the accepted methods have been documented.

**Completeness**

The number of samples analyzed matches the work plan.

Room	Idle Equipment Number	SET#	Description	Material	Quantity
131	777-0033	6	Five-Axis Mill (GB-636)	Oil, Carbon Tetrachloride & Pu	Empty
131, 430, 134A	777-0035	78	Carbon Tetrachloride Supply System	Carbon Tetrachloride	Empty
131, 415, 430, 437, 452	777-0037	78	TCA Supply System (Ultrasonic Cleaning Process)	TCA	Empty
134A	777-0038	11	Excello Lathe (GB-746)	Oil, Carbon Tetrachloride & Pu	Empty
134A	777-0039	11	Pneumo Lathe (GB-747)	Oil, Carbon Tetrachloride & Pu	Empty
134A	777-0040	11	Excello Lathe (GB-748)	Oil, Carbon Tetrachloride & Pu	Empty
134A	777-0041	11	Pneumo Lathe	Oil, Carbon Tetrachloride & Pu	Empty
134A	777-0042	10	Drill Press (GB-752)	Oil, Carbon Tetrachloride & Pu	Empty
430	777-0045	18	Equipment (GB-368)	TCA	Empty
430	777-0046	18	Freon Tank, Old Density Balance	TCA, Freon	Empty
430	777-0051	21	Ultrasonic Vapor Cleaner (including ancillary piping to first valve) (GB-426)	TCA	Empty
430	777-0054	22	Ultrasonic Vapor Cleaner (including ancillary piping to first valve) (GB-446)	TCA	Empty
430	777-0056	18	Ultrasonic Vapor Cleaner (including ancillary piping to first valve) (GB-465)	TCA	Empty
430	777-0057	24	Zeiss (GB-756)	Nyes Watch Oil, Carbon Tetrachloride	Empty
430	777-0058	24	Sheffield Sweep Gage (GB-758)	Freon TF, Lube Oil, Duct Sealers, Noucure 28 Catalyst or Polygel	Empty
437	777-0065	29	Grit Blasting Unit and Ultrasonic Cleaner (including ancillary piping to first valve) (GB-A2)	TCA, Metals from Blasting	Empty
437	777-0066	29	Ultrasonic Vapor Cleaner (including ancillary piping to first valve) (GB-A3)	TCA	Empty
440	777-0067	27	Ultrasonic Cleaner, TRIC Lines	TCA	Empty
447	777-0083	32	X-OMAT Processor Tank (NDT#2470)	Process Developer Replenisher	Empty
447	777-0084	32	X-OMAT Processor Tank (NDT#2471)	Fixer Replenisher	Empty
452	777-0090	35	Ultrasonic Vapor Cleaner (including ancillary piping to first valve) (GB-524)	TCA	Empty

### 6.3 Wastes Requiring Further Processing Prior to Off-Site Disposal

Most of the remediation waste generated during decommissioning will be the same or similar to routine waste for which there is a clear disposal path. However, as described below, certain

42/42