Work Scope Document for 'Actinide Migration Studies at the Rocky Flats Environmental Technology Site'
Fiscal Year 2000

Peter H. Santschi,
Texas A&M University at Galveston

1. Overview, Questions and Hypothesis

The goal of the Actinide Migration Evaluation (AME) is to provide data in support of Site closure, including: 1) soil action levels vis-à-vis surface water quality; 2) long-term disposition of the ponds; 3) 'far-field' actinide behavior during long-term closure.

Four broad areas of investigation emerged from group discussions with AME members and site personnel for consideration for FY 2000 work:

1) Phase speciation studies of actinides in surface waters;
2) Colloid characterization studies;
3) Colloid stability studies;
4) In-situ removal time studies for particles and colloids in ponds.

The following question will be addressed in the proposed research:
What causes exceedances of Pu and Am concentrations in RFETS surface waters, which often are associated with storm runoff?

The following Hypothesis will be tested in the proposed research:
The exceedances are related, besides hydrodynamic conditions (i.e., storms vs base flow), to the nature and types of organic matter present in soils, surface and pond water at the time of sampling. Organic matter can modify the surface charge and characteristics of particle and colloid aggregates. On the one hand, humic and fulvic acids can impart a negative surface charge to particles and colloids, which can promote disaggregation and dispersion of aggregates, and thus, increased mobility and concentrations of colloidal species in surface waters. On the other hand, large, surface-active, organic molecules such as exopolymeric acid polysaccharides from bacteria and algae act to bind colloidal and particulate species together, and thus, cause their removal and lower their concentrations in surface waters.

2. Justification

A wide range of work at Rocky Flats has demonstrated that 'particulate' and 'colloidal' forms of Pu and Am make up a significant fraction of actinides in surface waters and suggests that surface water transport of Pu and Am is dominated by aggregation and disaggregation processes of particles and colloids. A clear understanding of the phase speciation of Pu is a prerequisite for the development of defensible closure strategies. Questions concerning the environmental form of Pu and Am have direct bearing on evaluating the importance of various

migration pathways and in the development and refinement of Data Quality Objectives (DQO: i.e., model parameters and uncertainty levels).

3. Tasks

3.1 Task 1: Colloid and particulate associations of Pu and Am

We propose for FY2000 to continue the phase speciation work of Pu and Am in stream water, using the same sites investigated in 1998 and 1999.

3.1.1 Objectives:

1. To determine the association of Pu and Am with: 1) particulate, 2) colloidal and 3) dissolved phases for field samples from a selected pond, pond release waters and a future compliance point.
2. To determine if natural organic matter plays a role in the formation of colloids that facilitate transport of actinides from contaminated soil source terms.
3. To determine the chemical nature of the colloidal carrier phase (e.g., Fe, Mn, C, Al, etc.).

3.1.2 Justification:

FY 98&99 work has demonstrated that 0.5 µm filter-passing Pu is predominantly in a colloidal form. The issue of the speciation of filter-passing forms of Pu is crucial for understanding of transport and bioavailability, i.e., 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 particles sizes and colloid molecular weights is important for developing management controls on surface water quality.

3.1.3 Analytical Plan:

Phase association studies of Pu and Am investigations involve the following subtasks:

a) Surface water sampling by CFUF,
b) Colloid isolation and characterization,

1) The sampling sites will be from a selected pond, pond release waters and a future compliance point. Exact sites to be sampled will be determined together with Site personnel. Grab samples will be collected by bailing water from the stream using a small container followed by compositing the water into clean 15 to 20 Liter Nalgene carboys for processing and analysis in the laboratory (e.g., at the Colorado Department of Public Health and the Environment (CDPHE) at Lowry). In addition, soil samples will be collected for extraction of natural organic matter fractions to be used in the colloid stability experiments at TAMUG.

2) The protocols of Guo and Santschi (1996,1997) and Wen *et al.* (1996, 1999) will be followed for isolating colloidal and particulate phases of metals such as Pu, Am from surface waters by CFUF. Chemical parameters to be measured in the aqueous sample fractions are:

- total organic carbon (TOC),
- dissolved organic carbon (DOC),
- colloidal organic carbon (COC),
- particulate organic carbon (POC),
- pH,
- alkalinity, and
- Al, Fe and Mn.

Chemical parameters to be measured in the filtered solids (colloid and particulate phases) are:

- % organic carbon,
- Al, Fe and Mn

Analytical methods follow the protocols of Guo and Santschi (1997) and Wen *et al.* (1999). These measurements will be conducted on the isolated aqueous solution phases or on resolubilized freeze dried material, or both.

3) Aliquots of colloid and particle samples will be kept for SEM and/or TEM imaging analyses. These analyses will be used to visually identify the gross composition of the particulate and colloidal phases.

4) In selected cases, electrophoretic focusing experiments (Quigley, 1999) will determine points of zero charge of isolated colloids.

3.1.4 Strategy:

Surface water samples from the field will be taken in two sampling expeditions, preferably April and early June. Laboratory processing of samples will be carried out in the following months.

3.1.5 Expected results:

- Determine the phase speciation (particulate, colloidal and dissolved) of Pu and Am in surface waters under experimental conditions which vary in storm intensity, amounts of suspended inorganic and organic matter, and temperature;
- Determine the chemical (elemental and perhaps structural) composition of colloidal carrier phases.

3.1.6 Site support for sampling:

We anticipate the need for water samples from pond releases, and from present and future compliance points.

3.2 Task 2: Colloid stability experiments

The laboratory experiments will involve treatment of actinide-contaminated soil with extracted, natural organic matter to investigate natural mechanisms of colloid formation during storm water runoff.

3.2.1 Objectives:

1. To determine if natural organic matter plays a role in the formation of colloids that facilitate transport of actinides from contaminated soil source terms.
2. To experimentally determine what natural processes favor particle and colloid stabilization or destabilization using experimental approaches given in Wilkinson et al. (1998).

3.2.2 Justification:

A better understanding of the process(es) which control the speciation of filter-passing forms of Pu is crucial for evaluating their transport and bioavailability. A major focus of this task is to determine the dominant Pu and Am species generated during soil resuspension during storm runoff. Some of the major processes which control colloid formation will be studied in controlled laboratory experiments, with the purpose of relating colloid stability to organic matter composition. The type of natural organic matter can control the tendency of particles and colloids to aggregate. For example, small organic molecules such as fulvic acid and other organic acids can increase dispersion of soil colloids through their effect on particle charge, while large, surface-active, organic molecules such as polysaccharides act to bind colloid particles together (e.g., Gu and Doner, 1993; Kretzschmar et al., 1997; Wilkinson et al., 1998). Colloid stability is an important colloid characteristic because it reflects the extent to which colloidal material interacts with particles and immobile soil media. Therefore, colloid stability is a primary parameter for 1) estimating colloid mobility and for 2) development of engineering and management strategies for removing colloidal-associated actinides from surface water.

3.2.3 Analytical Plan:

Colloid formation and associated actinide partitioning will be investigated in controlled soil resuspension experiments, to be carried out with variable amounts of soil extracts (e.g., humic and fulvic acids) and exopolymers of microorganisms (e.g., commercially available alginates, xanthan, and other algal acid polysaccharides). Pu and Am-contaminated soils from the Site will be washed with these natural organic materials, and the wash solutions will be processed as described above to determine if colloid formation occurs. The colloids in the wash solutions will

be analyzed for Pu and Am to determine whether colloid formation also liberated Pu and Am from the soils. A schematic of some preliminary experiments, which will help us to design a more rigorous set of experiments, is displayed in Figure 1. Pu-contaminated soil in U.V. irradiated DOC-free water will serve as a control.

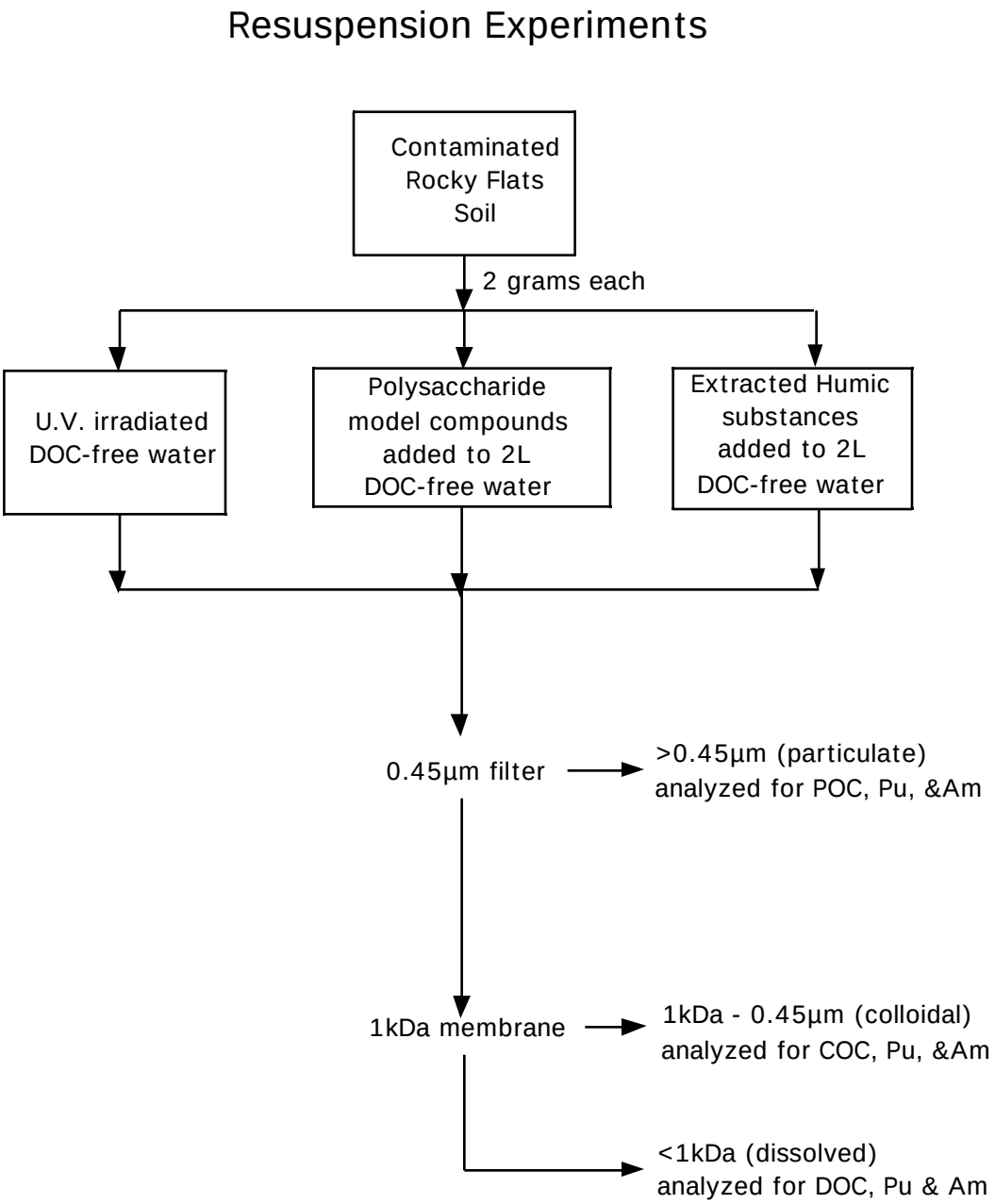


Figure 1. Schematic of preliminary soil resuspension experiments.

3.2.4 Strategy:

The strategy will be to start colloid stability experiments using existing samples. Laboratory processing of these samples will be carried out throughout the year.

3.2.5 Expected results:

- Determine the phase speciation (particulate, colloidal and dissolved) of Pu and Am in surface waters under experimental conditions which vary in storm intensity, amounts of suspended inorganic and organic matter, and temperature;
- Determine the stability of colloids under different organic matter regimes (i.e., dominated by pedogenic organic matter, e.g., humics and fulvics, or aquagenic organic matter, e.g., predominantly algae exudates such as acid polysaccharides) to act as stabilizers or coagulants for particulate and colloidal actinides;
- Determine the chemical (elemental and perhaps structural) composition of colloidal carrier phase.

3.2.6 Site support for sampling:

We anticipate the need for soil samples from both contaminated and relatively un-contaminated areas within the same soil series (i.e. soil type).

3.3 Task 3: In-situ particle and colloid residence time determination

We will attempt to determine in-situ particle and colloid residence times in pond waters using the $^{234}Th/^{238}U$ disequilibrium technique (e.g., Baskaran et al., 1996; Guo et al., 1997; Santschi et al., 1999).

3.3.1 Objective

To determine in-situ particle and colloid residence times in pond waters using the $^{234}Th/^{238}U$ disequilibrium technique, provided this method proves to be feasible in the ponds.

3.3.2 Justification:

FY 98&99 work has demonstrated that 0.5 µm filter-passing Pu is predominantly in a colloidal form. Colloid stability is a primary parameter for 1) estimating colloid mobility and for 2) development of engineering and management strategies for removing colloidal-associated actinides from surface water. Particle and colloids residence times in ponds are likely short, as actinides are removed to better than 90% in the pond water in about 45 days, according to Site sources. Better knowledge of residence times of particles and colloids would facilitate a future decision about pond operations.

3.3.3 Analytical Plan:

If ^{238}U concentrations are high enough (i.e., 1 dpm/l, or higher), and relatively constant over time, the $^{234}Th/^{238}U$ disequilibrium technique (e.g., Baskaran et al., 1996; Guo et al., 1997; Santschi et al., 1999) can provide estimates of particle and colloid residence times at steady state from the deficiency of ^{234}Th with respect to its mother nuclide, ^{238}U, in particle, colloid and solution phases. Large volumes of water will be pumped from the ponds through one prefilter and two MnO_2 impregnated fiber filters, which efficiently extract ^{234}Th. The efficiency of extraction is determined from the activity ratio in the two cartridges, and is usually over 90% (Baskaran et al., 1993).

3.3.4 Strategy:

Surface water samples from the field will be taken in two sampling expeditions, preferably April and early June, by pumping water through extractor cartridges in the field. Laboratory processing of samples will be carried out in the month following sampling.

3.3.5 Expected results:

- Estimate the in-situ residence times of colloids and particles in selected ponds.

3.3.6 Site support for sampling:

We anticipate the need for water samples from ponds, which will be pumped in-situ through several filter cartridges.

3.4 Task 4: Meetings.

Three two-day meetings at RFETS with two days prior to the meetings set aside for the review of meeting-related documents.

4. Quality Assurance/Quality Control.

Rocky Flats Environmental Technology Site Analytical Services Division Modules RC01-B.2 (Isotopic determinations by alpha spectroscopy) and GR01-B.1 (General laboratory requirements) will provide guidance, where appropriate, for QA/QC protocols. Documentation of FY 97 work will follow procedures to be established through discussions between CSM, TAM and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Study Data Quality Objectives final document will serve as the framework of recording and reporting the results of these investigations (i.e., PARCC requirements).

Limits on data uncertainty will correspond to the required margin of uncertainty specified for final computed parameters, as outlined in the data quality objectives (DQO). With respect to the outlined task, there are three major sources of error contributing to overall parameter uncertainty: 1) accuracy with respect to instrument calibration; 2) random analytical error; 3) sample representativeness. Errors 1 and 2 will be minimized through standard laboratory protocols for

instrument calibration and replicate sample analysis. Fundamental to the successful completion of this task is development of a strategy to determine the sample size (error 3) that will permit the baseline reproducibility required to meet the specified margins of uncertainty (e.g., ± 10% uncertainty in phase distribution). The margin of uncertainty on computed parameters will correspond to those specified on the final AMS DQO document.

The use of plutonium and americium at the CDPHE laboratory and Texas A&M University is regulated by the states of Colorado and Texas, respectively. Training of personnel is governed by each of the university's radioactive materials licenses. Worker Health and Safety at CDPHE and TAM are governed by the respective laboratory/university health and safety department.

Schedule and deliverables.

Task	**Time requirement***	**Target for completion**
1. Colloid and particulate associations of Pu and Am, and colloid characterization.	Twice (April, June). Each req. 1 month for preparation, 1 week for each sampling expedition, 2 months for sample processing.	31 July 2000
2. Colloid stability experiments	3 months	31 July 2000
3. In-situ particle and colloid residence time determination	1 month/each after sampling expedition.	31 July 2000
4. Meetings	3 times per year, w ith 2 days before, 2 days at meeting.	winter/spring/ summer
5. QA/QC	2 months throughout the project	31 July 2000
6. Draft Final Report	1 month	Aug. 15, 2000
7. Final Report	1 month after comments received	Sept. 30, 2000

*) Total time requirement for proposed experimental work is about 8 months. Some of the tasks indicated will be carried out in parallel.

Reports:
Monthly updates on projects tasks in 'bullet form'.
Interim Project Report due at Kaiser-Hill for internal review: 15 August 2000
Receipt of comments on Draft Final Report: 1 September 2000
Final Project Report due at Kaiser-Hill: 30 September 2000

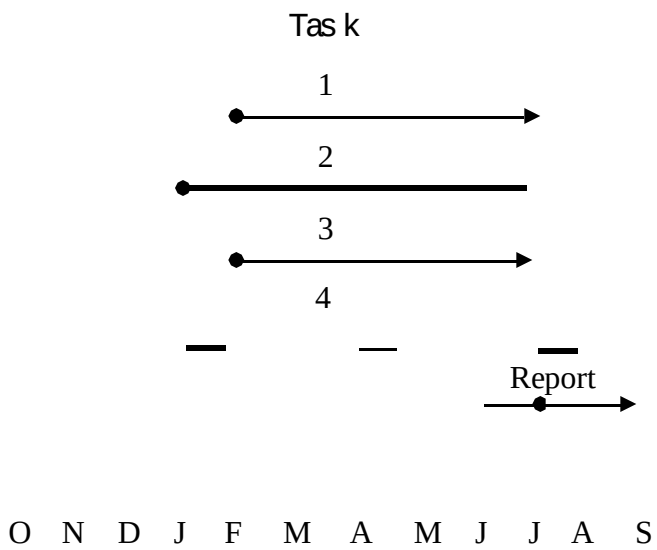
The Final Project Report will contain the following sections:

- **Methods and Procedures**.
  Complete descriptions of methods used such that the work could be reproduced by personnel of similar qualifications and resources.

- **Results and Discussion**.
  This section will present and describe the results of the FY 2000 work. The results will be related to findings of previous investigations. The results will also be discussed in terms of their applicability to the data needs of the conceptual model.

- **QA/QC**.
  Analytical data for both target environmental samples and QA/QC samples with uncertainties, DMA's, and a clear description of the methods for calculating the Midas and uncertainties; an analysis of data quality as pertains to Data Quality Objectives.

Schedule of tasks.



Task 1 Colloid and particulate associations of Pu and Am
Task 2 Colloid stability experiments
Task 3 In-situ particle and colloid residence time determination
Task 4 Meetings

6. References.

Baskaran, M., Murphy, D.J., Santschi, P.H., Orr, J.C., and Schink, D.R. 1993. A method for rapid in situ extraction of Th, Pb and Ra isotopes from large volumes of seawater, Deep Sea Research, 40, 849-865.

Baskaran, M., Santschi, P.H., Guo, L., Bianchi, T.S., and Lambert, C. 1996. ^{234}Th:^{238}U disequilibria in the Gulf of Mexico: importance of organic matter and particle concentration, Continental Shelf Res.,16, 353-380..

Gu, B., and Doner, H.E. 1993. Dispersion and aggregation of soils as influenced by organic and inorganic polymers. Soil. Sci. Soc. Am. J., 57, 709-716.

Guo, L., and P.H. Santschi. 1996. A critical evaluation of the cross-flow ultrafiltration technique for the sampling of colloidal organic in seawater. *Marine Chemistry*, **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. *Marine Chemistry*, **59**, 1-15.

Guo, L., Santschi, P.H., and Baskaran, M. 1997. Interactions of thorium isotopes with colloidal organic matter in oceanic environments. *Colloids and Surfaces A*, **120**, 255-271.

Kretzschmar, R., Hesterberg, D., and Sticher, H. 1997. Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. Soil Sci. Soc. Am. J., 61, 101-108.

Quigley, M. 1999. Tracing Colloid-Colloid and Colloid-Particle Interactions using Thorium. Ph.D. Dissertation, Texas A&M University, College Station, TX (in progress).

Santschi, P.H., Guo, L., Walsh, I.D., Quigley, M.S., and Baskaran, M. 1999. Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight. Implications for organic carbon fluxes. Cont. Shelf Res., 19, 609-636.

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.

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.