Work Scope Document for 'Actinide Migration Evaluation at the Rocky Flats Environmental Technology Site' Fiscal Year 2001

Peter H. Santschi
Texas A&M University at Galveston

1. Overview, Questions and Hypothesis

The goals of the Actinide Migration Evaluation (AME) Group is to provide data in support of Site closure, specifically to answer the following questions:

1) What are the important actinide migration sources and migration processes that account for recent surface water quality standard exceedances?
2) What will be the impacts of actinide migration on planned remedial actions? To what level do sources need to be cleaned up to protect surface water from exceeding action levels for actinides? What affect do the planned remedial actions have on actinide migration? For example, what is the long-term disposition of the ponds?
3) How will actinide migration affect surface water quality after Site closure (or what soil action levels will be sufficiently protective of surface water over the long-term)?
4) What is the long-term actinide migration, and will it impact downstream areas (e.g. accumulation)?

Four broad areas of investigation emerged from group discussions with AME group members and site personnel for consideration for FY 2001 work:

5) Colloid stability experiments;
6) In-situ particle and colloid time determination in selected ponds;
7) Exploration of intrinsic vs. pseudo-colloids of Pu;
8) Actinide concentration determination in selected groundwater samples.

The following general question will be addressed in the proposed research (point 1):
What is the relationship between particle erosion, resuspension, colloid production, and colloid stability in soils and streambed sediments during storm runoff to exceedances of Pu and Am concentrations in RFETS surface waters?
During FY2001, we will continue to test the following Hypothesis:
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, could 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 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.

3.1.1 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. (1997) and Santschi et al. (2000).

3.1.2 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 soluble 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., 1997). 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.
Of particular importance is colloidal Pu release potential from GS27 soil. The soil activity at GS27 is only about 3 pCi/gram, yet the runoff at station GS27 has Pu concentrations which are high, i.e., 40 – 90 pCi/L, which could be largely in a colloidal size range. There is no obvious "hot" source term in the small area (ca. 3/4 acre) that drains to GS27. There is a process waste valve vault in the drainage area, and these vaults have a history of overflowing in the past. Pu may be dilute enough in the soil matrix to produce a soil with only 3 pCi/g activity, but colloids containing Pu may be more susceptible to erosion or remain in suspension when larger particle sizes settle out; producing runoff with higher activity and low TSS his will be tested in laboratory settings with surface (upper 3 mm, max. 1 cm) soil samples collected from the drainage, using methodologies developed in FY2001. First, soil samples will be compared with well sorted soil. Results from three samples from the industrial area soil from GS27 (Figure 1) and one grassland soil sample from GS42 buffer zone (with about 30 pCi/g) will be compared. The results of these experiments will help to address how to mitigate Pu movement by erosion. Soil stabilizer was sprayed on the GS27 drainage, runoff activity was reduced by an order of magnitude for 2 years, the soil stabilizer has a 2-year effective life. Is this a good management practice or does the broken down soil stabilizer make soil particles more mobile when it breaks down?

3.1.3 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 alginic acid). 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 the extent of colloid formation. 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 the proposed experiments is displayed in Figure 2. Pu-contaminated soil in filtered tap water will serve as a control. The experiment will be performed with duplicate samples to help account for environmental sample heterogeneity.

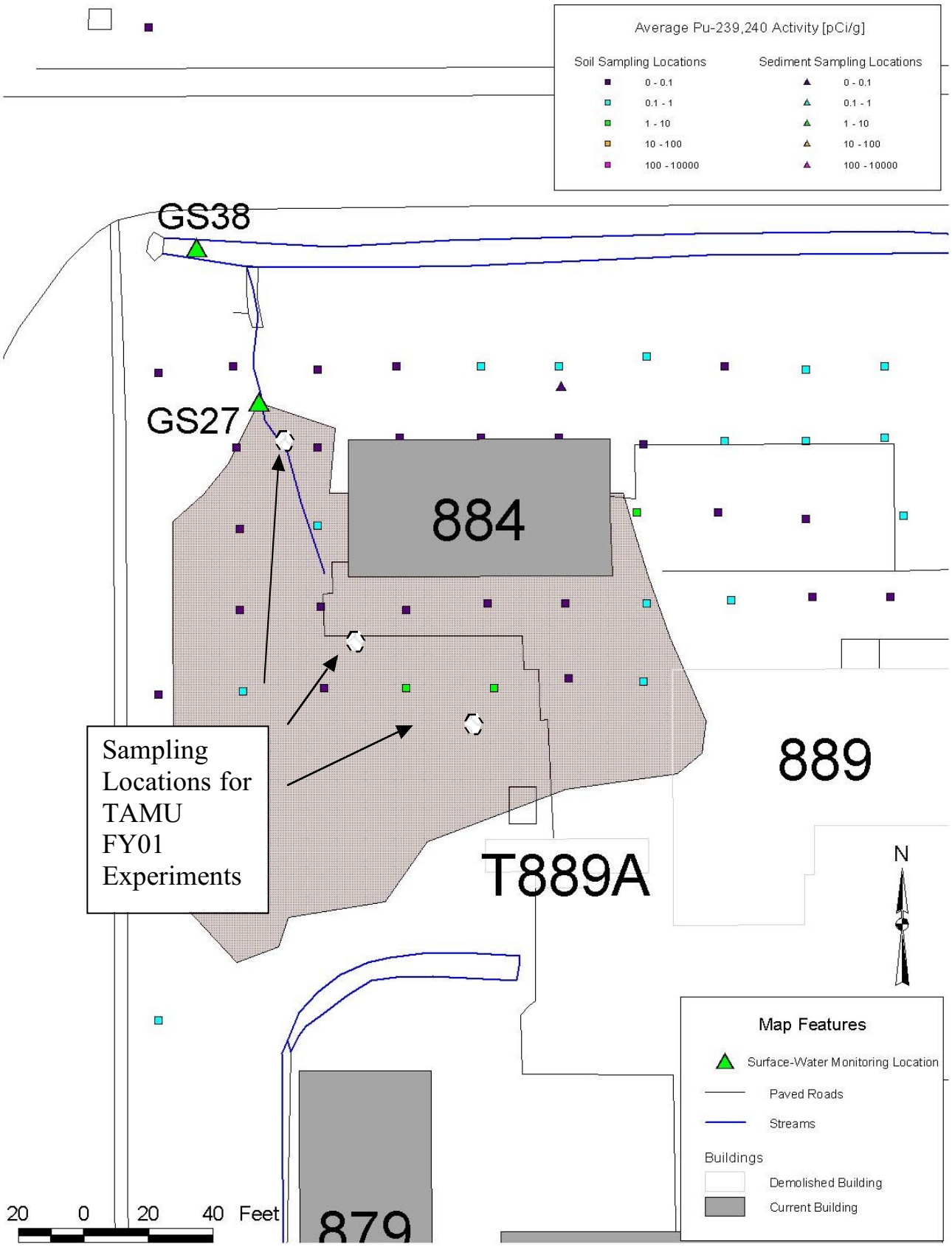

Figure 1. Location of sampling sites at GS27.

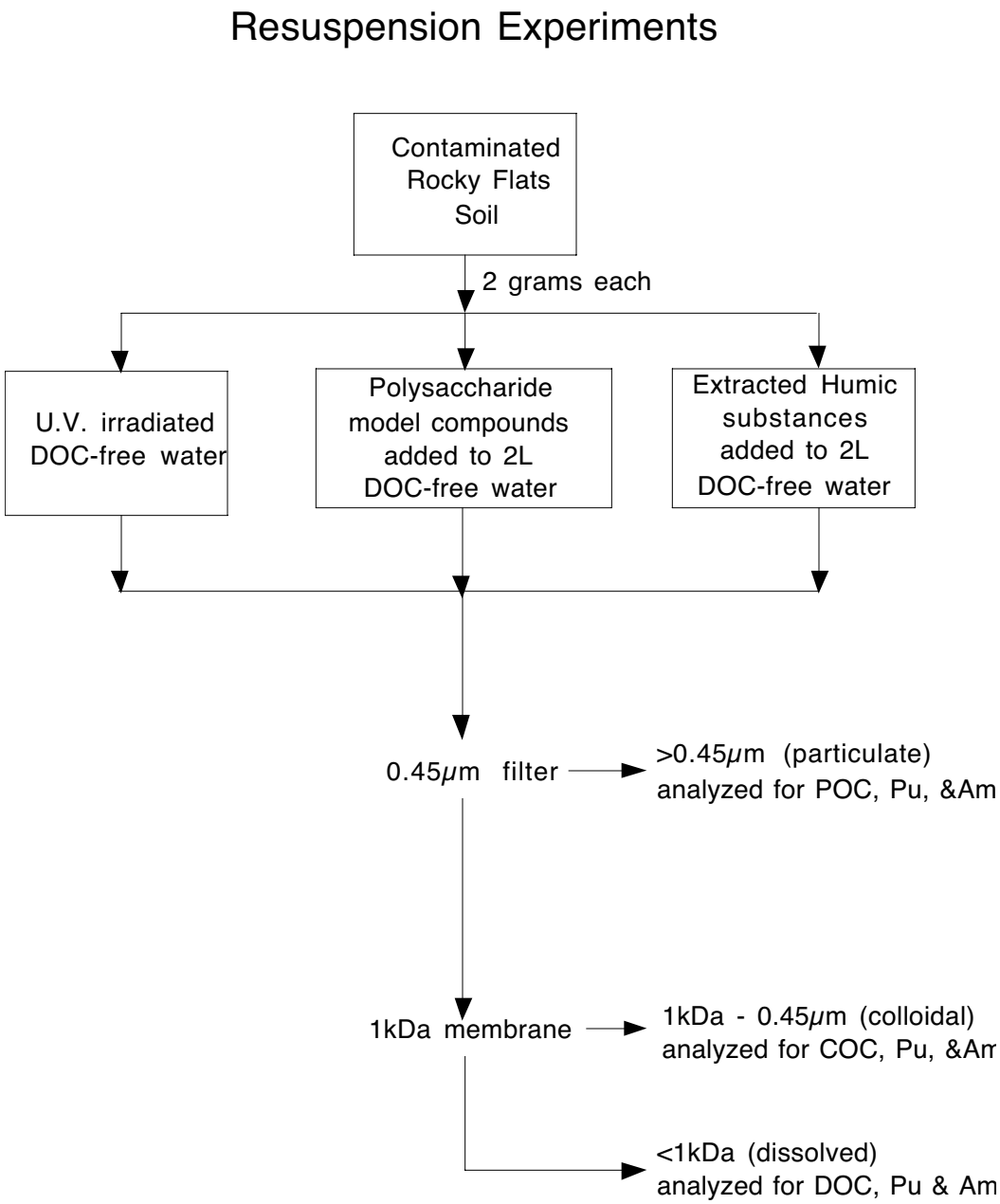

Figure 2. Schematic of preliminary soil resuspension experiments.

3.1.4 Strategy:

The strategy will be to carry out colloid stability experiments using soil samples from selected sites. Laboratory processing of these samples will be carried out throughout the year.

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 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.

3.1.6 Site support for sampling:

We anticipate the need for three soil samples from each contaminated (e.g., GS27 and GS42 buffer zone) and relatively un-contaminated area within the same soil series (i.e. soil type).

3.2 Task 2: 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, 2000).

3.2.1 Objective

Continue 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.

3.2.2 Justification:

FY 98&99&00 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 pond B5 is one day or less (Santschi et al., 2000). Better knowledge of residence times of particles and colloids in other ponds will facilitate a future decision about pond operations.

3.2.3 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 in the water produced by ^{238}U decay. The efficiency of extraction is determined from the activity ratio in the two cartridges, and is usually over 90% (Baskaran et al., 1993).
In FY2000, we determined, using $^{234}Th/^{238}U$ disequilibrium measurements, that particle residence times in Pond B5, which receives wastewater effluents, is fast, i.e., 1 day or less. In FY2001, we will determine particle and ^{234}Th residence times in ponds A3 and C2, which do not receive wastewater effluents. Having nutrient inputs into ponds can have beneficial and detrimental effects on the removal efficiency of Pu. The beneficial effects include algae blooms, which would help to remove Pu from the water. Detrimental effects would include anoxic conditions in the bottom waters and sediments, which might help to remobilize Pu. Even though Pu is settling out in the Pond A-3 / Pond A-4 system without mixing with wastewater, it important to know if there is any benefit to the Building 995 effluent entering Ponds B-4 and B-5. At closure, this source of dilution water, organic carbon, algae, and nutrients won't exist. Will this affect removal efficiency in Pond B-5?

3.2.4 Strategy:

Surface water samples from the field will be taken by site personnel in two sampling expeditions, preferably April and early June, by pumping water through extractor cartridges in the field (supplied by TAMUG.) Cartridges and other material will be shipped by special courier. Laboratory processing of samples will be carried out at TAMUG in the month following sampling.

3.2.5 Expected results:

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

3.2.6 Site support for sampling:

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

3.3 Task 3: Exploration of intrinsic vs pseudo-colloids of Pu.

The relative proportions of true Pu colloids (a.k.a. intrinsic colloids) and Pu sorbed to mineral/organic colloids is not known. The proportions could vary spatially and by the types of environments in which the Pu resides. For example, more PuO_2 might form its own colloidal phase near the 903 Pad, but in aquatic / wetland environments where the PuO_2xH_2O colloids might be associated with organic and mineral phase colloids, it could exist as pseudo- or intrinsic colloids. This type of a study may employ nuclear track techniques (e.g., mixed radiography)

that Higley (Povetko and Higley, 1999, 2000) used to distinguish between true colloidal PuO_2 and more complex colloids in more contaminated areas at RFETS (near 903 Pad area). During FY2001, in order to obtain exploratory results, we will pursue a collaborative effort with Kathryn A. Higley (Oregon State University). We will generate colloidal samples from soil resuspension experiments, evaporate them onto one or several of their CR-39 track detectors, and have them analyzed for Pu fission tracks by mixed radiography at Oregon State University. In addition, we will seek alternative funding sources to pursue this work further. The results will help determine the differential mobility of the two types of colloids, pseudo-colloids and intrinsic colloids. This knowledge may give insight on how to manage the contaminated soils and sediments.

3.3 Task 3: Actinide concentrations in groundwater

3.3.1 Objective

Determination of actinide concentrations in selected groundwater samples, which have already been collected by RFETS personnel.

3.3.2 Justification:

Measurable concentrations of Pu and Am nuclides in near-surface groundwater could have been caused by the drilling of the groundwater well(s), or could indicate migration of these nuclides in the near-surface ground water.

3.3.3 Analytical Plan:

Pu and Am nuclide analysis will be carried out according to Santschi et al. (2000).

3.3.4 Strategy:

Measurement of water samples according to established procedures.

3.3.5 Expected results:

Confirmation of Pu and Am nuclide concentrations previously determined by RFETS.

3.3.6 Site support for sampling:

Samples were previously sent to TAMUG.

3.4 Task 3: Meetings.

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

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 01 work will follow procedures to be established through discussions between CSM, TAMUG and Site QA/QC personnel. The Data Quality Objectives outlined in the Actinide Migration Evaluation Data Quality Objectives (Kaiser Hill, April 2000) 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., $\pm$10% uncertainty in phase distribution). The margin of uncertainty on computed parameters will correspond to those specified on the final AME DQO document.

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

5. Schedule and deliverables.

Task	Time requirement*	Target for completion
1. Colloid stability experiments	5 months	31 July 2001
2. In-situ particle and colloid residence time determination	1 month/each after sampling expedition.	31 July 2001
3. Meetings	1 times per year, with 2 days before, 2 days at meeting.	fall 2001
4. QA/QC	2 months throughout the project	31 July 2001
5. Draft Final Report	1 month	Aug. 15, 2001
6. Final Report	1 month after comments received	Sept. 30, 2001

*) 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 2001
Receipt of comments on Draft Final Report:	1 September 2001
Final Project Report due at Kaiser-Hill:	30 September 2001

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 2001 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.

6. References.

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