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COMPANY

April 20, 1998 98-RF-02025

Mr. LeRoy Moore
Rocky Mountain Peace and Justice Center
P.O. Box 1156
Boulder, CO 80306

RE: RESPONSE TO LETTER DATED MARCH 27, 1998 CONCERNING QUESTIONS ABOUT DR. LITAOR, CSD-004-98

Dear LeRoy:

This letter is in response to your letter dated March 27, 1998 in which you raised some questions regarding Dr. Iggy Litaor. I have researched the answers to your questions, and have found more detail on some issues than others. The responses to your specific questions are as follows:

Comment #1: When was the review of Litaor's work commissioned? By whom was it commissioned? Who selected the reviewers? What was the basis for their selection? Were some of the reviewers already under contract with Kaiser-Hill for Rocky Flats work at the time of their selection? What specifically were the reviewers asked to do? What timeline were they given? What was their budget for this review? What was the precise source of funds?

Response #1: An independent and unbiased review of Dr. Litaor's work was commissioned by the Kaiser-Hill team in the late Summer of 1995 (August-September 1995). The reviewers were selected by the Kaiser-Hill team based upon their credentials, availability, and their area of specialty. As far as I have been able to ascertain, none of the reviewers were under contract with Kaiser-Hill at the time of their selection. The reviewers were asked to do a narrowly-focused review of Dr. Litaor's work related to plutonium transport in the environment. The reviewers were given a short time-frame (three or four weeks) to conduct the review. The budget for the FY95 review was in the neighborhood of $30,000 which came from environmental restoration funds.

Comment #2: In his reply to the critique produced by Honeyman et al, Litaor says four key documents governing the scope of his work and thirteen other documents reporting the findings of his team were not made available to those asked to review his work. Honeyman et al specify the documents made available to them for the review. Who made the decision regarding what documents to provide to the reviewers?

ADMIN RECORD

Kaiser-Hill Company, L.L.C.
Courier Address: Rocky Flats Environmental Technology Site, State Hwy. 93 and Cactus, Rocky Flats, CO 80007 • [redacted]
Mailing Address: P.O. Box 464, Golden, Colorado 80402-0464

1/49

Response #3: The Kaiser-Hill team decided which documents to provide to the reviewers based upon doing a focused evaluation of Dr. Litaor's work on plutonium transport in the environment.

Comment #3: Was Litaor informed that this review was being done? If so, by whom and when? Why was Litaor not asked to provide all documents pertinent for the evaluation of his work? Who made the decision to deny him this opportunity and to exclude him from the process?

Response #3: The Kaiser-Hill team did not inform Dr. Litaor of the review or of the documents to provide because they wanted an unbiased review of Dr. Litaor's work. Dr. Bruce Honeyman of the Colorado School of Mines (CSM) informally told Dr. Litaor of the review. Dr. Honeyman was the technical lead for the Environmental Institute through which Dr. Litaor's contract was funded.

Comment #4: Litaor's rebuttal points to Kaiser-Hills failure to provide the reviewers with all pertinent existing documents and call for a new review. He offers to help Kaiser-Hill prepare a detailed dossier so the full scope and merit of the investigations by his team can be ascertained. Who made the decision not to do a new review? Was any communication made to Litaor in reply to his call for a new review?

Response #4: A new review of all information related to actinide migration was conducted in fiscal year 1996 (FY96). The Actinide Migration Group-consisting of Dr. Bruce Honeyman of CSM, Dr. Dave Janecky of Los Alamos National Labs (LANL), Dr. Dave Clark of LANL, and Dr. Peter Santschi of Texas A&M Galveston-was tasked to review Site documentation about actinide migration and to provide recommendations to the Site on a path forward. As part of this review, the Actinide Migration Group met with Dr. Iggy Litaor during the first week of June 1996 to discuss his work at the Site.

Comment #5: My last two sets of questions focus on the reviewers. At the time the review was done, did any of the reviewers know of the existence of documents pertinent to the review task that had not been provided? Did any of the reviewers ask if there were other documents or data that should be examined as part of the review?

Response #5: Please see the attached response from Dr. Honeyman and Dr. Clark.

Comment #6: What is the responsibility of reviewers who learn after the fact that they have produced a review for which they were given incomplete information? Do reviewers in a situation of this sort have a professional obligation to call for a new review -- not simply for the one reviewed but so that their own reputations will not be tarnished by having participated in a professionally questionable process?

Response #6: Please see the attached response from Dr. Honeyman and Dr. Clark. As indicated above in response to Comment #4, a new review of Site information on actinide migration, including a meeting with Dr. Litaor, was commissioned in FY96.

Per your request, attached to this letter is the following documents:

- "Technical and Peer Review" of M. Iggy Litaor's work produced by Bruce D. Honeyman of the Colorado School of Mines (technical lead) with David L. Clark, Edward H. Essington, Wayne R. Hansen, and Brian P. Wilcox of the Los Alamos Lab (subcontract No. KH353044ED3), dated September 22, 1995, 33 pages; and

- Litaor's reply in a letter sent to Mr. Honeyman, dated November 1, 1995, 6 pages.

I hope that these responses clarify some questions that you had concerning Dr. Litaor. Please call John Corsi at 966-6526 if you have any questions or require additional information.

Sincerely,

Christine S. Dayton
Environmental Compliance and Management
Kaiser-Hill, LLC.

CSD:csd

Attachments:
As Stated

cc:
Steve Gunderson, CDPHE
Russell McCallister, DOE-RFFO
Tim Rehder, USEPA
Rocky Flats Citizens Advisory Board

Los Alamos

INSTITUTE FOR TRANSACTINIUM SCIENCE

April 15, 1998

Christine S. Dayton
Environmental Compliance and Management
Kaiser-Hill, LLC
P.O. Box 464
Golden, CO 80402-0464

April 15, 1998

Re: Letter from Mr. Leroy Moore, March 27, 1998

Dear Chris,

I would like to preface my comments with the fact that peer review of scientific data and interpretation of said data is an essential step in the scientific method. Every scientist has a professional obligation to perform their fair share of peer-reviewing, and their own scientific work must also withstand critical review by the scientific community. For my own part, I have published over 80 peer-reviewed publications, and in every case, I have had to subject my work to the criticism of my scientific peers. This is not always a pleasant exercise, but it is a necessary fact of life in scientific endeavors, and an important mechanism for getting at scientific truth.

During the past 10 years I have served in the capacity as a peer-reviewer for the *Journal of the American Chemical Society, Angewandte Chemie, Inorganic Chemistry, Polyhedron, Macromolecules, The Journal of Inclusion Phenomena and Molecular Recognition, Journal of the Chemical Society - Chemical Communications, Journal of the Chemical Society - Dalton Transactions, The New Journal of Chemistry, Chemistry - A European Journal, The Journal of Alloys and Compounds, Radiochimica Acta, Organometallics, Geochimica et Cosmochimica Acta,* and many others. I routinely perform peer-review of proposals for the National Science Foundation (US), the Office of Basic Energy Sciences (US), The Engineering Programs Science Research Council (EPSRC, Great Britain), the National Science and Engineering Research Council (NSERC, Canada), The Research Corporation (US), and others.

I was asked by Dr. Honeyman to examine a set of six documents provided by the Los Alamos Technical Office, and comment specifically on plutonium speciation, and whether, in my expert opinion, the fate and transport of plutonium at the RFETS had been adequately characterized and studied. I received NO funding for my participation in this review, and I treated the review like any other professional peer review activity. In addition to studying the six documents provided by LATO, I performed my own literature search on Dr. Litaor's work, and I looked into the history of the site to see what additional information I could glean. I submitted a seven page summary of my findings to the review team, and prefaced my remarks by stating "I do not have any experience in field work, groundwater monitoring, etc. Therefore, I will restrict my comments to those areas in

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which I can make a knowledgeable assessment." In short, I found that an extensive monitoring program had been underway at the site for some time, that the data were undoubtedly valuable, but that the chemical form of plutonium and the mechanism of transport had not been adequately determined.

For my role in this peer review exercise, I acted totally independent of the other reviewers. I searched the literature for additional information, and I submitted my findings to the review team to be merged into a final document. As a reviewer I judged objectively the quality of the documents, the experimental and theoretical work, and the interpretations and expositions, with due regard to the maintenance of high scientific and literary standards. When the results of the review were questioned, the Site organized an opportunity for me to come hear Dr. Litaor present the full details of his work. Based on the above discussion, I applied the same scholarly and ethical standards employed in every peer review activity, and reiterate that I received no funding for my efforts. Based on the above, I find it hard to understand how Mr. Moore can possibly conclude that my reputation is somehow "tarnished" or that I acted in a "professionally questionable" manner.

Regards,

David L. Clark

David L. Clark

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COLORADO SCHOOL OF MINES
GOLDEN, COLORADO 80401-1887

Ms. Christine Dayton
Kaiser-Hill Rocky Flats
P.O. Box 464
Golden, CO 80402-0464

6 April 1998

Dear Chris:

The following are replies to questions posed by Dr. Moore in his letter to dated March 27, 1998.

Question 5:

The review panel composed of Clark, Essington, Hansen, Wilcox and Honeyman was asked to review a set of documents supplied to the committee by RMRS, who contracted for the review. In his response to the review, Dr. Litaor (letter of November 11, 1995) indicated that a number of documents were not made available to the *ad hoc* review panel. When the Actinide Migration Group was formed the following summer (June 1996), Dr. Litaor was asked to supply the documents that he deemed critical for the actinide group to review. The set of documents supplied by Dr. Litaor in June 1996 was essentially the set supplied by RMRS the previous fall with the exception that some of the 1996 documents were publications rather than manuscripts. Consequently, the updated review list provided by Dr. Litaor was not substantially different from the set of documents reviewed in the Fall of 1995, with the exception of a galley proof on phase speciation (published in *J. Environ. Qual.*, 25, 1144) which was apparently developed during the time period between the two reviews. The Actinide Migration Group also requested that Dr. Litaor provide them with documentation of Pu migration during the summer of 1995. A draft document, 'The hydrogeochemistry of plutonium in soils of Rocky Flats, CO', was provided to the Actinide Migration Group in which it was indicated that ca. 1 μCi of Pu was transported in near-surface flow at the 903 Pad hillside.

Question 6:

The Actinide Migration Group, responding to Dr. Litaor's concerns that not all of the relevant documents were reviewed during the Fall 1995 review, asked Dr. Litaor to supply a complete list of materials for review. Dr. Clark and I, as members of the original review, felt an obligation to extend the group's work to include any new or overlooked material. As stated in my response to #5, material supplied by Dr. Litaor was not substantially different from the review set of materials for Fall 1995. Dr. Litaor also was also provided with the opportunity to summarize his work through a series of presentations that he made to the Actinide Migration Group over a two day meeting in June 1996. It should be noted

that the conclusions the Actinide Migration Group reached in September 1996 regarding Dr. Litaor's work at the Site were essentially the same as those reached by the *ad hoc* review panel convened in Fall 1995: movement of water through unsaturated Rocky Flats soils was well characterized by Litaor *et al.*; Pu environmental chemistry and transport at Rocky Flats remains poorly known.

Sincerely,

BDHoney

Bruce D. Honeyman, Ph.D.
Associate Professor

November 1, 1995

Dr. Bruce Honeyman
Environmental Science & Engineering
Colorado School of Mines
Golden CO 80401-1887

Dear Dr. Honeyman

Last week I have received from Kaiser-Hill (KH) a copy of a technical review conducted by you and four scientists from LANL. I was shocked by the lack of integrity throughout the review process. This review was initiated due to a public outcry resulted from the termination of the soil study team by KH. on June 16, 1995. Unfortunately, I was not asked to provide the necessary information for this review. KH has provided you with a terribly incomplete list of publications and reports. Worse yet. KH did not provide you with the work plans for OU 2 & 3, the governing documents that dictated the scope of my work in Rocky Flats.

The following documents should have been the foundation of this review:

1. Department of Energy. 1991. Final RFI/RI Work Plan for Operable Unit 2, Alluvial: 903 Pad, Mound, and East Trenches Area. EG&G Rocky Flats Inc. Golden Colorado.

2. Department of Energy .1992 Final RFI/RI Workplan for OU 3, Rocky Flats Plant. February 28, 1992, EG&G Rocky Flats Inc. Golden Colorado.

All the site characterization work proposed in the above work plans was summarized in the following documents:

3. EG&G, 1995. Draft Final. Phase II RFI/RI Report: 903 Pad, Mound, and East Trenches Area. Operable Unit 2. RF/ER-95-0079.UN. US Department of Energy, Rocky Flats Environmental Technology Site. Golden Colorado, May, 1995. This report contains 17 volumes, in which the soil study team work was summarized in Volume 8, Appendix D: Investigations of Actinides Distribution and Fate and Transport in Soils, 855 p.

4. The final draft for OU-3 is currently under review. The soil study team has provided a detailed volume for this draft discussing Pu, Am, U, and metals distribution in the soil of OU 3, approximately 600 p.

Document # 3 provides detailed account of the work performed between summer of 1991 to the end of 1993. It also includes a detailed account of the QA/QC practices, the results of field and laboratory duplicates, counting errors, data qualifiers, below detection levels, and other pertain QA information. Document # 4 contains detailed account of the work performed in OU 3 under the strict objectives outlined in Document # 2.

Document # 3 was reviewed by DOE and the regulatory agencies and received few comments. In fact, some comments from DOE-HQ asserted that too much site characterization is being done and further work is unwarranted... Clearly the soil study team did not agree with that statement and the work continued till KH terminated the team.

It is clear that you and your team has little or no understanding of the working environment under which I was operating in Rocky Flats. The implication as if I had 12 Million dollars for research is preposterous. Over 80 percent of the funding supported self sustain bureaucracy, health and safety requirements, endless training stipulations, unreasonable schedule and milestones that made working in Rocky Flats extremely expensive. I had no control over these expenditures and cannot be held responsible for the system that created that monster

called Rocky Flats. I have always said that it is hard to believe that the same nation who put a man on the moon also created Rocky Flats. To compare this environment to a university setting or even a National Laboratory is ludicrous!

In spite of this environment, the soil study team has made a serious attempt to publish the work in referred journals. This effort was not considered part of my job at Rocky Flats. In fact, most of EG&G managers made it very clear that the soil study team should not engaged in research and development. Numerous times the statement was made that Rocky Flats is not a university or a national laboratory and I should not expect management to support the team self declared mission. In spite of these detractors. I have convinced EG&G upper management that publications in refereed journals will add credibility to our work. Hence, an uneasy truce was declared between the scientists and management. Once again, your criticism that the soil study team did not publish *enough* simply ignore the working conditions and reality at Rocky Flats.

The soil study team grew from one soil scientist during 1990 and 1991 to a vigorous team of a PI and five graduate students starting in 1993. One of the more inflammatory and misleading statement made in your executive summary is that I elected not to ask guidance and support from the scientific community. In fact, the team closely collaborated with several scientists across the country. For example, Professor T. Illangasekare of the University of Colorado, Department of Civil and Environmental Engineering was given a grant to support our effort to model the fate and transport of water and contaminants in the vadose zone of Rocky Flats. Modeling of the vadose zone in Rocky Flats was proven difficult especially on the scale attempted. A string of papers, reports, and two MS theses were produced (see below). None of this work was provided by KH to you and your team for review. Furthermore, this work was eliminated last summer by KH in mid course.

Professor M. Thompson, of Iowa State University, Department of agronomy was awarded a grant to support the site soil characterization study. Last January I initiated an autoradiography study that used an innovative approach perfected by Professor Thompson to locate the 'elusive' Pu on an extremely large thin sections prepared from soil column that retained the original structure and texture of the soil. Using an advanced autoradiography technique the exact location of the discrete particle of Pu oxide would have been located and further studied by advanced microscopy techniques. This work was eliminated by KH before significant advancements were made. Currently, Professor Thompson and Professor K. Heigley from Oregon State University are seeking additional funding from DOD to finish this work.

Professor S. Ibrahim of Colorado State University, Department of Radioecology was given a grant to support my effort to fractionate Pu in the soil matter using a sequential extraction experiment. This work had experience some delay because we failed to acquire Pu-237 isotope tracer (consequences of the end of the cold war). The implementation of this tracer in the experimental design was critical, so the magnitude of the postextraction readsorption phenomenon could be assessed. We finally, decided to use Th isotopes but were swayed to use Np-237 tracer following <u>your</u> suggestion. This tracer was acquired and used although funding for this project already dried out. A manuscript detailed the sequential extraction experiment was recently submitted to Journal of Environmental Quality (see below). Obviously KH did not provide this report to you for review.

Your assessment that soluble complexes of natural organic matter will enhance Pu mobility is misleading in the context of the soil geochemical conditions encountered in Rocky Flats. The findings of our sequential extraction experiment, supported by an extensive literature review of Pu sequential extraction experiments demonstrated that Pu associated with soil organic matter will not be released easily to the soil solution. You also have cited several old reports from the processing lab in Rocky Flats that demonstrated that metallic Pu will quickly transformed in the environment. It is true that the exact chemical form of the 'elusive Pu' is unknown. However, a detailed analysis of Pu and U distribution in the soil environment around the 903 Pad (Document # 3; and Litaor, 1995a; not provided by KH) showed that the differences in spatial distribution between the two contaminants originated from different solubility and leachability characteristics of these actinides. Over 31 kg of U-235+238 leaked from the barrels stored at the 903 area and all infiltrated and were arrested on a Bk horizon. Hardly any of the estimated 86 to 120 grams of Pu that were leaked from the barrels was leached into the soil. Since Pu remained in some form of solid phase on the surface of the soil it became available to wind transport once the protective layer of the

barrels was removed. The first sighting of Pu contamination in the 903 area was detected back in 1958. The barrels were removed in 1968 and the study by McDowell and Whicker was published in 1978. Hence, almost 20 years after the initial release most of the Pu was still found as a discrete particle of some form of Pu oxides. More recently, autoradiography study conducted by Langer (1986) clearly demonstrated that discrete particles of Pu oxides were attached to grass blades and were occasionally resuspended.

Following the work by Harnish et al. (1994) and the suggestion given by Dr.John McCarthy of Oak Ridge National Laboratory I have made a serious attempt in the summer of 1994 to provide you with a grant to study the 'speciation' (more appropriately called fractionation) of Pu in soil solution. Unfortunately, budget constrains dictated that your study was not funded. Thus, I diverted limited funds from other projects to purchase an ultrafiltration and tangential flow filtration apparatus. I extensively consulted with Mr. R. Harnish of the USGS before and after acquiring the filtration system and adjusted it to the unique field conditions at Rocky Flats (i.e., extremely small volumes of soil solution). It took over a year to eliminate all the analytical problems associated with the fractionation of Pu in soil solution. Over the course of that year we have fractionated over 100 samples following rain simulations, snowmelt, and natural rain events. However, I do not considered this work useful because of serious coagulation artifact observed during the filtration of the smaller colloidal size. We continuously consulted with and finally exhausted the knowledge of Mr. R. Harnish of the USGS. We even called upon your lab and solicited advise, just to learn that Dr. Ranville is fully aware of the problem but was not sure how to solve it. Finally, one of my graduate student came with a reasonable 'working' solution to the problem and collected and partially fractionated six water samples from various depths (see below) before KH terminated the project.

During the summer of 1993, a grant was awarded to Professor J. Ryan of the University of Colorado, Department of Civil and Environmental Engineering to study the movement of Pu particles through the soil system following certain rain simulation conditions. This work was done with some support from your laboratory. A paper summarizing the results of that experiment is currently being written. This work should also be considered when you review the performance of the soil study team.

The major criticism of your review is my failure to study Pu 'speciation' in the soil of Rocky Flats. Obviously, I strongly disagree with your assessment. The most important information for risk assessment in Rocky Flats is the total activity of Pu in a given media and what is the potential for Pu transport in the environment. The form of Pu in the transport process is important, "nice to have" but not necessary. This is the philosophical difference between National Laboratory and academia setting and an industrial facility such as Rocky Flats. This difference translates immediately to the nature and emphasize of the environmental work performed in Rocky Flats. My main objectives in the study of fate and transport of Pu has been the characterization and quantification of the physical processes that control Pu mobilization (see Document # 1). Since, Webb et al. (1993) hypothesized that up to 80 percent of the initial Pu loading on the surface of Macroplot 1 has been remobilized downhill, the soil study team conducted numerous rain simulations to quantify the proposed runoff mechanism. Most of the rain simulations suggested that the runoff in the undisturbed soil of Rocky Flats is insignificant. Most of the Pu observed in the deepest soil horizons resulted from the large quantities of water applied. During 'normal' natural rain event little or no water were collected by the ZTS in the deepest sampling interval (60 - 80 cm). Hence, the recharge rates under those conditions were negligible and the translocation of Pu was nil. So what is the point of Pu fractionation under those conditions?

The spring and early summer of 1995 was unseasonably wet. On March 17, 1995 a significant overland flow occurred across the soilscape all over this short grass prairie ecosystem. Between **10 million to 200 million pCi** of Pu were remobilized. The monitoring system that I installed on the hill was instrumental in quantifying this event. It immediately became clear, that near-surface and surface processes are by far more important than subsurface processes in assessing the fate and transport of Pu in the environment. Elevated Pu activity observed in the water of C2 holding pond and the distribution of "hot spots" across the hill side can be explained by this phenomenon. So how important would have been Pu speciation performed prior to this event?
On the basis of soil color determination, macropore distribution, saturated hydraulic conductivity, and DO measurements it was clear that the soil is highly oxic. However, as a consequence of the unseasonable wet

spring and early summer of 1995, the soil became anoxic starting Julian day 150 and remained completely anoxic for the next 65 days (Attached Figure 1). Strong odor of H2S has been experienced by the field crew. We observed strong and steady lateral flow that originated from the 903 Pad. Because of my research priority and experimental design of real-time in-situ remotely controlled monitoring system an unexpected phenomenon has been observed! Lateral flow in the upper reaches of the catena resurfaced in the foot and toeslope positions, potentially translocating Pu from the subsurface to the surface. The sequential extraction experiment showed that up to 40 percent of the Pu is associated with sesquioxides. It is conceivable, that some of the occluded Pu was released to the soil solution by the dissolution of sesquioxides as a consequence of the anoxic conditions. Moreover, some Pu oxides may dissolve under these conditions. We finally observed a geochemical induced transport mechanism that probably affect the fate and transport of the actinide. Pu speciation under these conditions are paramount to evaluate how much Pu was transported from the hill to Woman Creek. The six samples mentioned above were taken in the Julian Day 152 (Figure 1). The project was eliminated immediately thereafter. Pu speciation of soil solution taken prior to May 17, 1995 provides little important information and does not account for the spatial and temporal aspects of Pu transport in the environment.

Most of the studies mentioned in your review described the experimental conditions observed in a... beaker. How much of that information can be used in a real soil contamination study is not clear. While I was analyzing the results of the sequential extraction experiment I consulted with Dr. I. Triay of LANL regarding some adsorption mechanisms studied by her. During the conversation it became obvious that none of her excellent studies can be easily extrapolated and used in the messy conditions encountered in the field. When you inject a beaker loaded with clean and highly purified Fe-oxides with *soluble* Pu of known oxidation state you merely study the beaker environment. How much of this can be used to explain Pu in the environment is questionable!

During my tenure in Rocky Flats, I strongly believed in the development of environmental technology. After all, this is the pretend name - Rocky Flats Plant has changed its name to Rocky Flats Environmental Technology Site. All the environmental technology developed by the team was focused on technology that can be used in monitoring contaminated site as well as the integrity of engineered barrier such as the 'tomb' recently suggested by KH. The team has developed a new tensiometer that can operate via remote control resistant to daily temperature fluctuations. This project was eliminated mere 2-3 months before completion. However, a report summarizing the results to date should have been provided to the review team. As you already familiar with the main theme of this response, this was not done!

The second environmental technology device was the modification of the TDR probe to accommodate the conditions encountered in clayey soils. This problem is well known and there are many teams of soil scientists and engineers within the DOE complex and academia that are struggling to find a reasonable solution to the problem. During 1993 I initiated a meeting between my team, LANL (headed by Dr. J. Nyhan) and Sandia National Laboratory to discuss and provide a potential solution to the problem. Once again, your assertion that I failed to ask guidance and advice from the scientific community is false. Moreover, in 1991 I came to LANL and presented Document # 1 in great details to several LANL scientists including several from your review panal. The most significant comment provided at this meeting was the lack of Kd determination. It was generally agreed, that Pu sepciation study was not critical to meet the objectives of EG&G Environmental Restoration (see Document # 1).

For the record, here is the complete list of published papers, reports, and proceedings that should have been provided to the review team in addition to Documents 1 through 4. Several papers that are currently in review are also provided.

1. Litaor, M.I., M. L. Thompson, G. R. Barth, and P.C. Molzer. 1994. Plutonium-239+240 and Americium-241 in Soils East of Rocky Flats, Colorado. Jour. Environ. Quality, 23:1231-1239.

2. Litaor, M.I. 1995. Uranium isotopes Distribution in soils at the Rocky Flats Plant, Colorado. J. Environ. Quality, 24:314-323.

3. Litaor, M.I. 1995. Spatial analysis of Pu-239+240 and Am-241 in soil around Rocky Flats. Colorado Plant. J. Environ. Quality, 24:506-516

4. Litaor, M.I., D. Ellerbroek, L. Allen, Erika Dovala. 1995. A Comprehensive Appraisal of Plutonium-239+240 in Soils of Colorado. Health Physics, 69:923-935.

This paper was extremely well received by the reviewers who termed it the **most definitive work** to come from Rocky Flats, regarding Pu in the environment.

5. Litaor, M.I., and L. Allen. A. 1996. Comprehensive Appraisal of Am-241 in Soils of Colorado. Health Physics. (In Press).

6. Nachabe, MH. and T.H. Illangasekare. 1994. Use of tension infiltrometer data with unsaturated hydraulic conductivity models. Ground Water, 36:1017-1021.

7. Nachabe, M.H., T.H. Illangasekare, M.I. Litaor, and G.R. Barth. 1995. Assessment of free-flowing soil solution using zero-tension samplers. In Wagner et al., (eds). Models for assessing and monitoring groundwater quality. IAHS Publication N0. 227, p. 67-74. Proceedings of an international symposium held in Boulder Colorado, July 2-14, 1995.

8. Nachbe, M.H., A. Islas, and T.H. Illangasekare. 1995. Analytical solution for water flow and solute transport in the unsaturated zone. Ground Water, 37:304-310.

9. Nachabe, M.H., T. Illangasekare, H. Ruan, and R.B. Mapa. 1995. Infiltration over heterogeneous surface: Theory and model development. ASCE J. of Hydraulic Division (In Press).

10. Allen, L.E. and M. I. Litaor. (in press). GSLIB Graphical user interface state of the art software for contamination modeling in soil. Environmental Restoration 95, Proceedings published by US Department of Energy, Denver Colorado, August 13-17, 1995.

11. Nachabe, M.H. and T.H. Illangasekare. 1995. Modeling the vadose zone in Rocky Flats. Draft Report submitted to EG&G Rocky Flats, Golden CO, June 23, 1995.

The following are manuscripts in review:

12. Litaor, M.I. and S. Ibrahim. Plutonium association with selected chemical and mineralogical phases of the soils in Rocky Flats, Colorado. Jour. Environ. Quality.

13. Litaor, M.I., G.R. Barth, E.M. Zika. Fate and transport of Pu-239+240 and Am-241 in soils of Rocky Flats, Colorado. Jour of Environ. Quality.

Three follow up papers are currently in preparation and will be submitted to KH for review by June 30, 1996. The first summarizing the results of the 1994 rain simulations where a large rain simulator provided by LANL was used to eliminate some of the boundary effects and small energy kinetics of the 1993 simulated rain. The second manuscript will compare the differences in Pu fate and transport following snowmelt, 'normal' natural rain events and rain simulations. The third manuscript will assess the impact of the May 17 flooding in Rocky Flats, Colorado on Pu remobilization throughout the environment.

14. Nachabe, M.H., M.I. Litaor, T.H. Illangasekare, and G.R. Barth. Assessment of macropore flow using zero tension samplers. Jour. of Hydrology.

The influx of papers that were published during the last two years clearly demonstrated that the elimination of the soil study team could have not come in a worse time. The program has matured and was about to provide significant contributions to environmental sciences.

Most of my work has been published or submitted to Journal of Environmental Quality. Your statement that this is an applied research journal and its review process is less stringent than Environmental Science & Technology diminishes the credibility of your review. This comment is an insult to over 6000 members of the Soil Science Society of America who see JEQ as their premier journal for environmental issues. I was extremely surprise that Dr. Brian Wilcox and Mr. Essington have subscribed to such a demeaning statement.

I could easily answer all the other comments of your review **point- by- point**. However, before such a time consuming response is made, I believe a new review is required based on the information provided above. A detailed dossier should be prepared by KH with my guidance, so the full scope and merit of the investigations conducted by the soil study team in Rocky Flats can be ascertained.

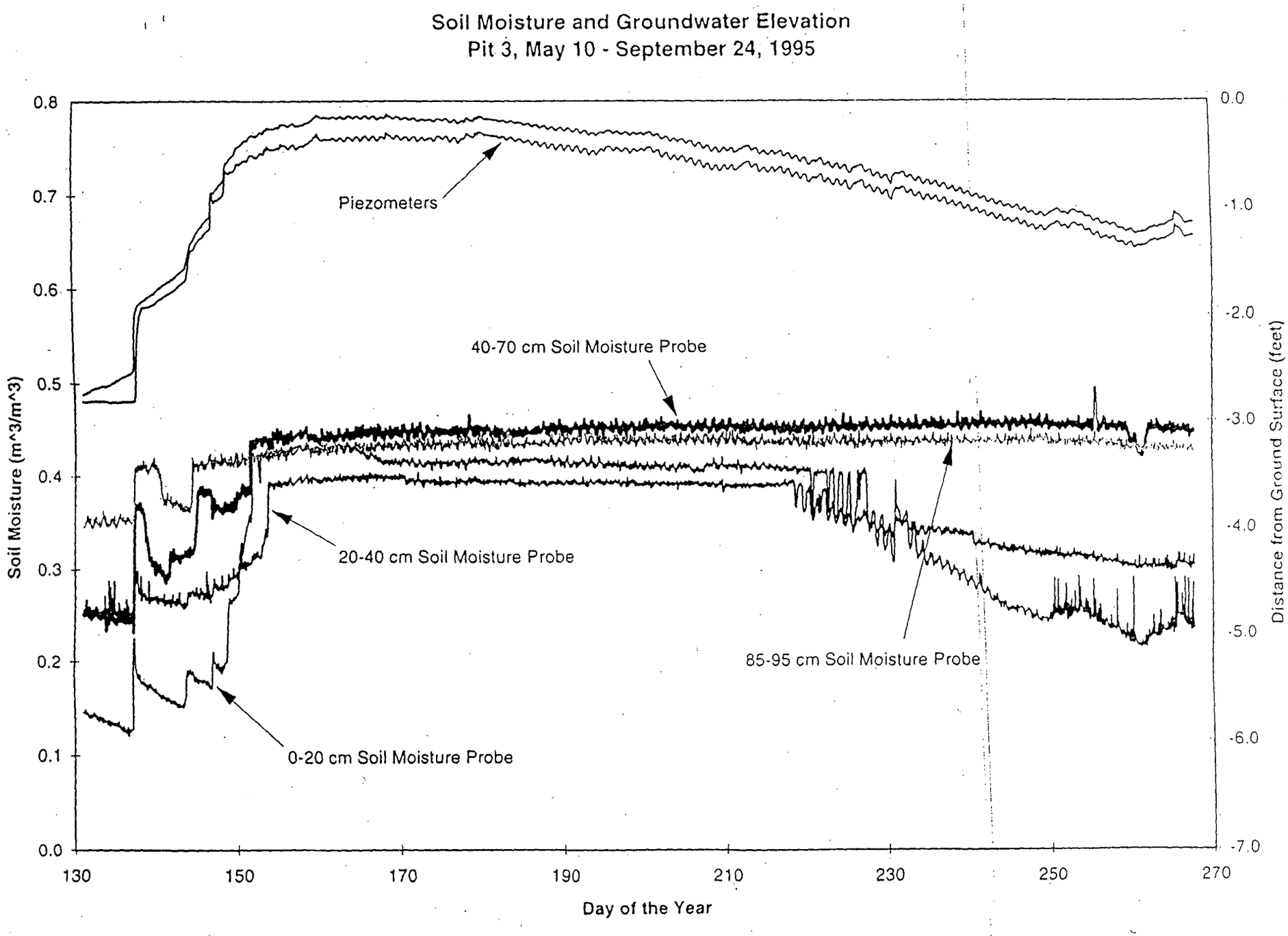
If you care for further informal discussion regarding this response please call me at (303)492-8433 or e-mail to litaori@bechtel.colorado.edu

sincerely,

M. Iggy Litaor
Associate Professor Adjunct
University of Colorado
Department of Civil, Environmental, and Architectural Engineering
Boulder CO 80309-0428.

Iggy

cc: Dave Moody, LATO at RFETS
Dave Clark, LANL
Edward Essington, LANL
Wayne Hansen, LANL
John Law, RMRS at RFETS
Allen Parker, RMRS at RFETS
Brian Wilcox, LANL


Soil Moisture and Groundwater Elevation
Pit 3, May 10 - September 24, 1995
Piezometers
40-70 cm Soil Moisture Probe
20-40 cm Soil Moisture Probe
0-20 cm Soil Moisture Probe
85-95 cm Soil Moisture Probe
Soil Moisture (m^3/m^3)
Distance from Ground Surface (feet)
Day of the Year
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
130
150
170
190
210
230
250
270

CSM

Colorado School of Mines
Golden, Colorado 80401-1887
303/273-3427
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Environmental Science &
Engineering

Gary Konwinski
Rocky Mountain Remediation Services
Rocky Flats Environmental Technology Site
Building 080
P.O. Box 464
Golden, CO 80402

22 September 1995

Dear Gary:

Enclosed is the final report for Subcontract No. KH353044ED3 entitled, 'Technical and Peer Review'.

I will return to Mines on Monday, October 2nd. Please let me know if you have any further questions regarding the review.

Sincerely,

BDHoy

Bruce D, Honeyman, Ph.D.
Associate Professor

cc: Dave Moody, LAPO at RFETS
Dave Clark, LANL
Edward Essington, LANL
Wayne Hansen, LANL
Brian Wilcox, LANL

Technical and Peer Review Letter Report

Kaiser-Hill Company Subcontract No. KH353044ED3 to the Colorado School of Mines
Bruce D. Honeyman, Technical Lead

Dave L. Clark, Edward H. Essington, Wayne R. Hansen and Brian P. Wilcox
Los Alamos National Laboratory

Executive Summary.

A series of EG&G Rocky Flats, Inc. project documents describing plutonium (Pu) 'fate and transport' work at Rocky Flats Environmental Technology Site (RFETS) was reviewed by technical experts from Los Alamos National Laboratory and the Colorado School of Mines. The review covered numerous technical aspects of the Pu in soils program conducted by EG&G, the Management and Operating (M & O) Contractor at Rocky Flats Environmental Technology site until June 30, 1995. Also rendered as part of the review is the assessment as to whether project goals were reached, or could have been reached, given the time and capital commitment given to the project.

The work reviewed was initiated by EG&G and DOE with the goal of understanding the basic issues involved in actinide transport at, and in the vicinity of, Rocky Flats, as an aid in determining pathways of exposure to humans. This report does not address the determination of risk, itself: it addresses the quality of the program established to evaluate the fate of Pu in RFETS soils, a critical component of risk determination.

However, the goal of the EG&G work, understanding Pu environmental behavior, has not been met as a consequence of critical gaps in the program. Most egregious was the failure to address the question of the chemical form, i.e., speciation, of plutonium in the environment. Complete understanding of the fate of an element in the environment depends on two knowledge bases: 1) the chemical form of the element of interest and 2) the physical processes that act to transport those species. The soils program only qualitatively met the latter component and failed to address the former. In addition to the speciation issue, uncertainty exists surrounding a number of other technical aspects of the program; this uncertainty is fostered by a lack of critical self-evaluation of the program results by project personnel.

After five years and expenditures of ca. $12 M, the issue of the fate of plutonium and americium in soils at RFETS has not reached closure. Fundamentally, the failure to meet overall project objectives, understanding Pu fate and transport, was due to an apparent lack of technical guidance from experts in the scientific community.

The overall conclusion reached by project personnel, as well as the review team, is that a small fraction of soil Pu is mobile and migrates from the upper meter of the soil column during each major rain event. This 'elusive' Pu probably amounts to between 3.0×10^{-5} to 2.5×10^{-3} percent of the soil Pu inventory during each event. While the magnitude of the 'elusive' Pu is unlikely to pose a significant health threat to surrounding communities, it will remain detectable and, consequently, on the public's conscience. Because different chemical forms of plutonium migrate through environmental media by vastly different mechanisms and rates, exposure cannot be assessed without a knowledge of Pu speciation. A credible evaluation of Pu fate and transport, both for the public and the scientific community, must, therefore, include an evaluation of Pu environmental speciation.

This report contains the results of a technical review of the plutonium in soils program at the Rocky Flats Environmental Technology Site (RFETS). Reviewers at two institutions were involved: The Los Alamos National Laboratory (LANL) and the Colorado School of Mines (CSM). Bruce D. Honeyman (CSM) provided the technical lead. The LANL reviewers were:

David L. Clark	Plutonium Chemistry
Edward H. Essington	Soil Chemistry and Sampling
Wayne R. Hansen	Radioecology and Environmental Health Physics
Bradford P. Wilcox	Hydrology

The technical lead provided an overall assessment of the soils work and integrated the technical review comments from the two institutions. In some instances portions of the LANL report are excepted in their entirety. The entire LANL report is included in Appendix B.

Primary source materials provided by Kaiser-Hill and Rocky Mountain Remediation Services[1] for the review were:

1. *Spatial Analysis of Plutonium-239/240 and Americium-241 in Soils Around Rocky Flats, Colorado.* Litaor, M.I.. This document is essentially the same as a journal article by the same title which was published in *J. Environ. Quality* (1995: **24**, 506-516).
2. *A Soil Water Monitoring System for Assessing Fate and Transport of Contaminants: Case Study for Pu-239/240 and Am-241.* Litaor, M.I., G.R. Barth, P.C. Molzer, E.M. Zika, H. Daniels and J. Moffitt.
3. *Fate and Transport of Pu-239+240 and Am-241 in the Soil of Rocky Flats, Colorado.* Litaor, M.I., G.R. Barth and E.M. Zika.
4. *Comprehensive Appraisal of Plutonium 239+240 in Soils of Colorado: A Basis for Risk Assessment.* Litaor, M.I., D. Ellerbroek, L. Allen and E. Dovala.
5. *Soil Monitoring.* Litaor, M.I.
6. *OU3 Remedial Investigation Pu-239+240 Isoplot with Exhaustive Surface Soil Sampling Locations.* Litaor, M.I.

A seventh document, 'Plutonium-239+240 and americium 241 in soils East of Rocky Flats, Colorado,' (Litaor *et al.*, 1994: *J. Environ. Qual.*, **23**, 1231-1239), contains additional site work analysis and was included as one of the primary source materials. The work reported on in these documents was conducted during the years 1990 - 1995.

Additional documents, both in the open literature and government documents, were included in the evaluation process when needed for clarification of technical issues or for support documentation. These materials are cited in the review text and documented in the attached bibliography.

[1] Kaiser-Hill began July 1, 1995 as the Integrating Management Contractor at RFETS. Rocky Mountain Remediation Services is the major sub-contractor to Kaiser-Hill for ER/WM at RFETS.

I. General conclusions regarding the Pu soil mobility studies at RFETS:

The EG&G plutonium in soils work conducted at RFETS falls into two broad categories: 1) analysis of the spatial distribution of Pu, U and Am in RFETS soils; 2) studies of the 'fate and transport' of Pu and Am in the unsaturated zone of RFETS soils.

After five years and expenditures of ca. $12 M, the issue of the fate of plutonium and americium in soils at RFETS has not reached closure. While it can be generally concluded that the major portion of Pu is 'quasi-archived' in surface soils, a small fraction of Pu migrates from surface soils to lower horizons (Appendix C) during rain events. This fraction is probably on the order of 3 x 10^{-3} percent, or less, of the vadose zone Pu. The ultimate fate of this mobile faction of soil Pu is unknown because its environmental speciation has not been evaluated, although Pu is likely in the form of soluble complexes of natural organic matter (e.g., McKnight *et al.,* 1995).

Two broad areas of concern are with respect to the project's goal of understanding Pu fate and transport in RFETS soils are:

A) A failure to adequately address the nature of radionuclide speciation.
B) The extrapolation of quantitative results from pit studies to undisturbed soils.

The technical reports generally cannot serve as primary source materials for the evaluation of many aspects of the research program. The reports are written in a manuscript style and are uninformative regarding issues such as sample analysis methodology, quality control/quality assurance (although not discussed in the reports, this program followed RFETS QA/QC ptotocols), and the calibration of pit sampling devices.

Although significant resources were allotted to the soils program, the project has been markedly unproductive: 1) in achieving closure on the overall issue of fate and transport, 2) in the quality of the scientific documentation of the work (crucial experimental details and assumptions are omitted), 3) in a rigorous assessment of the experimental results, and 4) in terms of the number of scientific publications produced to document the work in the scientific community. If funded competitively, it is unlikely that this project as would have survived in the open scientific community without significant modification in personnel and scientific management.

A. Speciation.

It is axiomatic that assessing contaminant fate and transport requires two components: 1) a knowledge of the contaminant's speciation (chemical form); and 2) understanding the physical processes which act to transport those species. The soils program qualitatively met the latter component and markedly failed to address the former.

An crucial component of the failure to reach closure on the Pu in soils issue is the apparent lack of substantive outside technical review of program goals and tasks. It is astounding that such a large program with a significant public interest component should have proceeded without constant and substantial technical oversight. The appearance of some of the work in *J. Environ. Qual.* is insufficient in for this purpose: it is an applied research journal with typically a less

stringent review process than is the case for journals such as *Environmental Science and Technology.*

Characteristic of the problem with respect to technical oversight is the apparent lack of response to the program review conducted in 1992. Dr. John McCarthy of Oak Ridge National Laboratory, a noted expert on the role of colloids in actinide transport, reviewed the three 'colloid' programs in progress at RFETS at the time: a U.S. Geological Survey study conducted by Dianne McKnight and Richard Harnish, a Los Alamos National Laboratory filtration study, and the EG&G study headed by Dr. Litaor. Dr. McCarthy's review is reproduced in Appendix A. With respect to Dr. Litaor's work, Dr. McCarthy stated (p. 3) that the 'vadose zone transport field research *demands* (italics his) integration of chemical aspects of transport to realize the full importance and impact of the research to environmental assessment and remediation at Rocky Flats'. In the three and a half years since the review (February 1992) no substantial progress has been made to address the fundamental issue of Pu speciation in RFETS soils.

B. Pit studies.

While the general conclusions reached by Dr. Litaor and co-workers on the relative importance of macropore Pu and Am transport are likely valid, a quantitative assessment of radionuclide fluxes as relevant to RFETS soils is problematic. The issue is the use of disturbed pit soils as an *in situ* laboratory representing surrounding, undisturbed soils. Although Dr. Litaor attempted to retain the order of soils horizons while emplacing sampling points, it is likely that the fabric of the soils in the pits was altered during pit excavation with a backhoe and backfilling by hand (*Fate and Transport of Pu-239+240 and Am-241 in the Soil of Rocky Flats, Colorado,* p. 6). Similarly, tensiometers inserted into pit walls were emplaced in a modified soil environment. There is no evidence that Dr. Litaor attempted to calibrate collector efficiency or to ascertain the extent of emplacement artifacts. In addition, Dr. Litaor's substantial investment in a high technology sampling infrastructure may have locked him into a field program that precluded other assessment strategies (e.g., the use of large, intact soil monoliths: e.g., Tindall *et al.,* 1992, and references therein).

Although mass balances have not been made to compare the current soil inventories with the initial Pu and Am activities (and it may not be possible to do so), it is clear that a significant fraction (90%) of the current soil-phase Pu (and Am) is quasi-archived in the upper 15 cm of the soil column. Appendix C contains an estimate of the soil inventory of Pu and the fraction of Pu estimated to be mobilized during each rain event. While the fraction mobilized is small (ca. 3.0×10^{-5} to 2.5×10^{-3} % of the soil inventory), the Pu which exits the soil column is likely in relatively soluble forms (e.g., complexes with low molecular weight natural organic matter) which can possibly enter the saturated zone. Data gathered by Dr. Litaor and co-workers shows that there are wide variations in Pu fluxes and that these fluxes do not clearly correlate with rain events or antecedent soil conditions. [As discussed in Section IIB, there is concern with respect to the observation of an apparent lack of correlation between the volume of water collected during rain events and the intensity of the event.] Another uncertainty with respect to soil plutonium is that Pu speciation in the soils is likely in a transient state, either due to the thermodynamic instability of current species, the open nature of the soil systems (e.g., infinite reservoirs of atmospheric

water and carbon dioxide in contact with the soil system and microorganism growth), or a combination of both factors.

While the magnitude of the 'elusive' Pu is unlikely to pose a significant health threat to surrounding communities, it will remain detectable and, consequently, on the public's conscience. A credible, scientifically justified assessment of the magnitude and extent of exposure pathways must include documentation of environmental Pu speciation.

Summary of the overall assessment by LANL:

Understanding Pu fate and transport in RFETS soils will not be furthered by continued sampling of soils with the object of determining actinide distribution. Rather, the greatest area of uncertainty rests in a lack of knowledge about Pu environmental speciation.

II. Specific comments.

A. Plutonium speciation in soils.

The environmental speciation of Pu was not determined as part of the field experiments. This lack of knowledge makes it difficult, if not impossible, to predict the environmental fate of Pu. The speciation issue is compounded by an ill-defined initial condition (i.e., the chemical environment in the waste drums or the soils immediately after leakage).

Assessment of speciation issues by LANL:

> From the site history, the exact chemical form of plutonium in soil and groundwater remains uncertain. From a consideration of kinetics and thermodynamics, it is unlikely that metallic Pu still exists at the site. The reactions of plutonium metal with soil water should produce one of several oxide phases which should limit migration due to the extremely low solubility of plutonium oxides in aqueous solutions [an 'extremely' low solubility means that Pu oxides will tend to remain as a solid in water-dominated environment; they will not migrate with the water]. The soil and groundwater chemistry will play a role in potential migration at the site. In view of the large quantities of organics that were originally present at the 903 Storage Site, there is potential for Pu complexation. The soil water monitoring program seemed to indicate Pu migration was not affected by the volume of interstitial water, soil moisture conditions or intensity of rain. However, there are many reports on the importance of colloid-facilitated transport (e.g., McCarthy and Wobber, 1993; Honeyman and Santschi, 1989, and references, therein), and leaching of [colloidal] Pu through soil under certain conditions that should not be ignored. I do not believe that the fate and transport of Pu at the site is adequately characterized until the speciation of Pu is known.
>
> When the plutonium leaked into the soil it was in the form of metal in machining oils. However, plutonium is a very reactive metal that oxidizes readily when exposed to oxygen

or water vapor, and a number of studies on the oxidation of plutonium have been conducted. Micobalance studies of the oxidation of plutonium in water vapor show different kinetics of pure plutonium and plutonium alloyed with 1 wt. % gallium. Characterization data (XRD, XPS, EDS, metallography) shows that water vapor reactions with unalloyed plutonium produces a diverse mixture of products depending on temperature. These oxidation products include PuO_2, Pu_2O_3, and a monoxide monohydride, HPuO (Haschke and Stakebake, RFP-4392).

The kinetics of the reaction of plutonium with liquid phases is found to be much different than that observed for gaseous reactions. The primary difference appears to be that, in liquid water and carbon tetrachloride reactions, the corrosive liquid is able to diffuse through the oxide coating with an end result of complete oxidation. There have been several reports on the corrosion of plutonium by liquid water from the domestic supply at RFETS (Hodges *et al.*, 1979) synthetic seawater (Hodges and Haschke, RFP-2919) and salt solutions (Haschke *et al.*, 1983). The reactions of alpha and delta plutonium (2.9% Ga) in water and 1 molar salt solutions were studied by measuring the production of hydrogen gas formed by a sequence of hydrolysis reactions (Hodges *et al.*, 1979). In contrast to reactions between plutonium metal and gaseous oxygen that form a protective oxide layer, liquid water is extremely corrosive to plutonium. In liquid water reactions, plutonium metal was found to convert quantitatively to a fine black powder which was identified as plutonium monoxide monohydridge, HPuO, by means of TGA, XRD, and XPS studies. Other hydrolysis products were also identified in aqueous hydrolysis media such as a second hydride, $H_3Pu_7O_9$, and a series of oxides Pu_2O_3, Pu_7O_{12}, Pu_9O_{16}, $Pu_{10}O_{18}$, $Pu_{12}O_{22}$, and PuO_2. Kinetic studies on the liquid water reaction with plutonium reveal that the reaction is catalyzed by salt (Haschke *et al.*, 1983). If submerged in seawater at 25°C, a 1 mm thick sheet of plutonium metal will be converted to HPuO powder in approximately 16 days. From the kinetics of the oxidation of plutonium (Hodges *et al.*, 1979) it can be shown that the lifetime of a 100 micron plutonium particle is only 8.4 days in liquid water, and 4 minutes in a carbon tetrachloride-methanol mixture (Chrisler, 1974). From these discussions one can ultimately conclude that the plutonium in the soil is no longer metallic, but the chemical form of the product is uncertain. [LANL].

The assumed form of Pu in RFETS soils is as PuO_2 particles in an ill-defined association with host soil grains (Litaor *et al.*: *Fate and Transport...*, p. 17-18). Dr. Litaor *et al.* rely on analyses of gross Pu soil speciation (e.g., micron-scale size fractionation) from work in the mid-1970's and apparently do not make an independent assessment of current speciation. While it is possible that the majority of the soil matrix associated Pu is as a plutonium (hydrous)oxide, the dominant species for transport of 'elusive' Pu may be as soluble organic complexes. A second point, and one that is crucial to the issue of long-term Pu migration from the soil, is that the speciation of the bulk of Pu in the soils is not static: Pu is slowly moving through the soils (some 10% of the soil Pu inventory is greater than 15 cm below the top of the soil column after some thirty years of environmental exposure) and the proportion of inventoried Pu in environmentally mobile forms is likely to be gradually increasing. For example, micron-sized (or larger) plutonium oxide particles (the original Pu form) should be essentially immobile in soil environments. Alterations to these particles as the consequence of attacks by soil fluids, and substances dissolved in those fluids,

yield Pu species which are more mobile than are the 'parent' Pu oxide particles. It is possible that 30 to 50% of the current soil Pu is in a form which is potentially mobile (see below).

Three recent reports on work conducted on the issue of Pu mobility suggest that a significant fraction of the soil Pu inventory is in a environmentally mobile form:

Study #1): Triay and Lodge (1994) used a suite of Lewis bases to 'leach' Pu and Am from RFETS soils in batch tests. Sequential extraction methods (e.g., Tessier *et al.,* 1979) have been shown to be useful for the qualitative assessment of metal ion speciation. Their study is significant in that they demonstrated that large fractions of Am and Pu can be released from RFETS soils through the application of relatively-mild leaching solutions. Although Triay and Loge did not follow classical leaching schemes (e.g., Yong *et al.,* 1993), nor did they follow sequential applications of the leaching agents, it is possible to deduce some general associations. As an example:

Extractant	%Am	%Pu	Associated Phase
0.1 M citrate	13	24	amorphous phases
0.1 M $NaHCO_3$	2	12	metal oxides
EDTA/H_2O_2	47	26	organics

It should be noted that Triay and Loge did not determine the speciation of the leached Pu and Am: their study was of limited scope and focused on bench-scale treatability issues. Leaching studies were also performed on dried and sieved soil isolated with markedly disrupted soil fabrics. Only leached radionuclides in a operationally-defined 'dissolved' fraction were analyzed (by centrifugation: 1 h at 28K relative centripital force). However, these experiments demonstrate that significant fractions (2 to 50%) of RFETS soil Pu and Am may be available to be mobilized under the appropriate environmental conditions (e.g., long contact times with soil pore waters). While the fraction mobilized in real time under *in situ* conditions may be small, the inventory of available, but kinetically hindered, material may be significant.

Study #2): Harnish and co-workers (1994, 1995) used tangential flow ultrafiltration techniques to determine Pu and Am associations with 'dissolved'-phase (< 5 μm) colloidal material in groundwater and seeps. Although ultrafiltration techniques are not without problems (e.g., Buesseler *et al.,* 1995; Guo and Santschi, 1995; Wen *et al.,* 1995), with proper calibration (i.e., determination of mass balances, wall losses, etc.) ultrafiltration methods can provide reasonably accurate estimates of molecular weight associations of radionuclides. 'Dissolved' (< 10K daltons) Pu was found to constitute up to 35% of Well 1587 groundwater activity and ca. 85% of the 'dissolved' Pu was in the form of fulvic materials (400 - 2,000 MW). It should be noted, though, that total dissolved activities were quite low: 1.2×10^{-2} pCi L^{-1}.

Study #3): A study of plutonium in Pond C-2 waters (Efurd *et al.,* 1993) strongly suggests that the environmental behavior of Pu at RFETS is regulated by local environmental conditions such as E_H (pe) and the behavior of dissolved organic carbon. While the C-2 site is a different setting than

the area around the 903 pad, the C-2 data shows that Pu is present at RFETS in 'environmental' forms.

Figure 1a shows 'dissolved' and particulate Pu activities which are associated with the pit studies. Dissolved values were taken from 'A Soil Monitoring System...,' Table 1, and are the mean values; particulate values were estimated from soil activity profiles ('Fate and Transport....,' Figure 2). Figure 1b is a plot of the estimated distribution coefficient (L/kg^{-1}) as a function of depth. The value of the K_d is low compared to what one might expect (10^3 to 10^4 L kg^{-1}: Sanchez *et al.,* 1985); however, a significant fraction of the bulk soil is likely unimportant in affecting actinide migration and the calculated K_d is 'diluted' by the unreactive material. However, Figure 1b suggests that Pu is becoming more mobile with depth: the higher the K_d value, the more highly retarded by soil materials is the Pu. The observation that K_d values are decreasing with depth in the soil supports the notion that Pu speciation is changing throughout the soil column.

It is important in this discussion to recognize that some of the Pu and Am may be migrating downward through particle mixing rather than the migration of soluble species [LANL]:

> Particle migration and chemical migration can occur simultaneously. On the short term, particle migration, particularly immediately after a disturbance (such as a rainfall event or biological intrusion), will be the major mode of Pu transport. On the long term, small amounts of Pu will solubilize no matter what the solid form and will be transported by water in the soil. Depending on the stability of the Pu species created, the migration could be some distance before the speciation is changed and Pu is deposited on the matrix material.
>
> It should be noted that there is an indication that freshly-deposited Pu quickly redistributes into the soil profile, perhaps within the first year or rainy season. Subsequent redistribution appears to occur at a much slower rate thereafter (except for major disturbances).
>
> Particles bearing Pu or Am can be mixed downward in the soil profile. Any kind of biointrusion (e.g., burrowing) or physical disturbance (e.g., raindrop impact) may dislodge particles that can redistribute in the soil. Animal burrowing does redistribute soil materials; talus resulting from the burrowing can bury surface deposits containing Pu. Over the years the soil surface heals and those original deposits now appear to be buried.
>
> Expansion/contraction cycles can easily allow surface or near surface particles to redistribute into the soil profile. These cyclic effects are generally limited to the near surface, perhaps within the top 6-18 inches depending on the freeze depth and on the clay content of the soil(and on the depth of any clay-enriched layer). Flushing of newly-created macropores would allow particulates to redistribute but would seem that after a period of time the walls of the pore would heal and subsequent release of particles would decrease.

While discussions of the effect of biota on Pu and Am migration have largely been restricted to bioturbation (physical mixing), the relative effect of particle ingestion on the mobilization of Pu

and Am is unclear. Earthworm activity has clearly been documented by Dr. Litaor and, in areas of heavy earthworm activity, a significant fraction of the soil is processed through the guts of earthworms. Since most of the earthworm activity occurs in the upper reaches of the soil column, and this is coincident with the bulk of the radionuclides, it is possible that repackaging of soil particles by earthworms is a dominant factor in the soil biogeochemistry of actinides.

A conceptual model of Pu environmental chemistry in RFETS soils by the review Technical Lead: Pu entered the soils as metallic Pu in a reactive organic 'soup'. Pu was relatively quickly transformed to a suite of oxide and metal-organic forms, species which, given the soil environment, exist in a transient state. Such transience is due to thermodynamic instability or the episodic movement of fluids through the soil environment. Plutonium oxide particles are subject to attack by a host of soil organic and inorganic ligands. In addition, plutonium may disproportionate under environmental conditions yielding mixed oxidation states (Guillaumont and Adloff, 1992). Brainard *et al.* (1992) showed that microbial siderophores (substances which form strong complexes with metal ions) can dissolve Pu oxide. Functional groups found in natural organic matter are capable of dissolving metal oxides through ligand-promoted dissolution (e.g., Furrer and Stumm, 1986); the similarity in redox potentials between PuO_2 and iron oxides suggests that natural organic matter may effectively dissolve Pu oxides. Natural organic matter may also stabilize Pu in 'soluble' colloidal forms (Nelson *et al.,* 1985) through the formation of strong Pu/natural organic matter complexes (e.g., Guillaumont and Adloff, 1992). Wahlgren and Orlandini (1982) found an inverse linear function between dissolved organic carbon concentrations and the particle/solution distribution coefficient for Pu(IV): the greater the concentration of dissolved organic matter in soil water, the more mobile the Pu. Dissolved inorganic carbon can also mobilize sorbed Pu through the formation of solution-phase carbonato complexes (e.g., Sanchez and Murray, 1985) or the carbonate-promoted dissolution of metal oxides (e.g., Bruno *et al.,* 1992). Local 'micro-environments' may exist with conditions which foster radionuclide mobilization; such environments include zones of low E_H (pe) or high P_{CO2} and may the result of microbial activity. For example, $PuO_2(s)$ can be reductively-dissolved by iron-reducing bacteria under relatively moderate reducing potentials (i.e., similar to those for the reduction of α-FeOOH; Rusin *et al.,* 1994).

The consequence of the above processes is an 'aging' of soil-associated Pu from early metallic forms to complexed and mobile species. The studies over the last several years have only provided a poor 'snapshot' of plutonium behavior. Predicting future behavior requires understanding plutonium speciation.

B. Soil physics/hydrology.

The general assessment of the water movement program by the review group is that the implementation, that is, the data gathering, of the studies was good. The conclusions of the work by Dr. Litaor and co-workers that macropore transport of fluids is dominant is consistent with the published literature as is the general conclusion that Pu and Am are highly retarded by soils materials. In other words, while water is rapidly transported through the vadose zone during rain events, Pu and Am, however, are strongly held back through their associations with soil particles. Only a small fraction of the soil Pu inventory ($< 2.5 \times 10^{-3}$ percent) migrates with the soil water

during each rain event.

> The papers indicate very small amounts of plutonium are moving with the water and at a very slow speed relative to the water flow. However, the studies do not indicate where the groundwater exits to a point of exposure. Does the water flow out to the local streams and drainage channels? To complete a risk assessment from this pathway requires determination of a point of exposure to the water.
>
> The rapid subsurface flow of water experiments indicate some very small amounts of plutonium and americium is moving deeper into the soil. The studies are silent on the amount of time needed for the movement to a point of exposure. The movement is so small that estimates of time based on the data presented would give estimates of time of arrival of significant concentrations at the water table are in the 1,000 to 10,000 year range.
>
> The above studies do not address the chemical forms of plutonium and americium in the soils, in the soil water or the potential for colloid transport. There are many reports on the importance of colloid-facilitated transport, and leaching of soluble plutonium through soil under certain conditions. The questions surrounding groundwater contamination will not be adequately characterized until speciation and colloid formation of plutonium are known. A risk assessment of the significance of this route of transport, even if present, will likely indicate a small risk increment compared to the air transported plutonium and americium because of the low adsorption of these elements in the intestine. [LANL]

The review documents do not address the issue of system calibration. The calibration question fundamentally deals with the applicability of the results garnered from a disturbed system (the pits) to undisturbed areas. While the reviewers acknowledge the difficulty of understanding vadose zone transport through *in situ* monitoring schemes, Dr. Litaor provides no evidence as to the existence or extent of artifacts created by the invasive monitoring procedures. Backfilled pits are unlikely to retain much of the original undisturbed structure of hydraulic characteristics. There is ample evidence that disruption of the soil fabric during manipulations (e.g., ASAE, 1995), such as the emplacement of monitoring devices, introduces experimental artifacts which make the quantitative assessment of soil transport difficult. For example, hydraulic conductivity has a scale length which must be considered when designing sampling systems. The appropriate scale length depends on the soil material (e.g., Jenssen, 1990 and references, therein) and cross-correlation of methods should a fundamental part of the research program. The pit scaling criteria employed by Dr. Litaor is not evident; if the pits or placement of the samplers and tensiometers is not at the appropriate scale for RFETS soils then estimates of hydraulic conductivity are suspect. In other words, the value of the hydraulic conductivity determined by experiment depends, to a certain extent, on the size of the experimental system. For example, hydraulic conductivity determined using a 1 dm^3 sample of soil may not be applicable to understanding a 30 m^3 system. Similarly, the validity of applying hydraulic conductivity determined from the RFETS experimental pits to undisturbed soils of a different scale length should be established.

The technical documents reviewed by the LANL and CSM team provided no information on the calibration of sampling devices or estimations of the magnitude of emplacement artifacts.

There are four concerns with the experimental setup (described in "*Soil Water Monitoring* ...") that bear on the conclusions drawn: 1) vacuum on the TS, 2) adsorption on or in the TS, 3) filtration outside the TS, and 4) hydrophobicity of the PTFE. Let's assume that no hindrance of solute collection occurred with the ZTS.

1. Vacuum: Page 19 indicates that "... vacuum was applied for most of the drying periods ...". There are two ways that vacuum can be applied. First, quick evacuation of the TS and sealing the sampler and then repeating the process for subsequent samples. Second, continuous pumping on the TS to maintain a high vacuum. In the first case the possibility of evaporating water from the TS is minimal. In the second case evaporation of water from the TS continues as long as the vacuum pump operates venting to the atmosphere, essentially boiling some of the water out of the TS. This can be exacerbated if the porous material of the sampler is not kept wet. If it is allowed to dry, continuous pumping will draw air into and through the TS and sweep even more of the water vapor from the TS (may also be the reason for poor recoveries of water). If significant evaporation is allowed the solute contents of the TS will increase; this may also explain the elevated conductivity and alkalinity results compared to the ZTS (pH tends also to be higher but not significantly).

2. Adsorption: Although PTFE is known to be inert and not a significant medium for sorption of solutes, surface effects can occur on the inside surface of the TS as solution is drawn in. If evaporation is allowed to occur inside the TS, particularly with a solution that is close to saturation (or supersaturated) with mineral-forming solutes, a film of mineral-like materials can form that can sorb solutes such as Pu and Am (this phenomenon is observed in water sampling operations hence the use of acid to maintain solubility of the desired solute species). This would lead to the observed reduced Pu and Am in the TS samples compared to those from the ZTS. Pu and Am solubility are very low at the pH level of the soil solution but the effect can be exacerbated by the increase in pH of the TS samples and the higher concentration of solutes.

3. Filtration: Perhaps the most likely effect on Pu and Am concentrations in the TS is the formation of a filter bed on the outside of the TS surface. During implantation of the TS the soil is disturbed, reducing structural integrity, and allowing movement of particles of a wide range in sizes toward the TS. This material will pack around the TS creating a filter bed primarily of fines. This bed can filter colloidal or larger particles containing Pu and Am. Compared to the Pu and Am contained in the particle load of the ZTS samples, the Pu and Am concentrations in samples from the TS will likely be considerably lower reflecting the absence of the larger particles even of clay size and perhaps a different distribution of soluble species. It would be informative to recover several of the TS and attempt to analyze both the outer filter bed and the inner surfaces for Pu and Am; any significant concentrations of Pu or Am on the inside of the TS would be evidence that the samplers did not function as assumed.

4. Hydrophobicity: The PTFE that I am familiar with is highly hydrophobic. Considerably higher tension (vacuum) is required to overcome the internal resistance to water entry created by the lack of wetting of the PTFE surfaces. Could this be a reason for the reduced water production by the TS? **[LANL].**

Two additional concerns are extant:

1) The placement of tension samplers and tensiometers and the effect of the disruption on the soil fabric in the immediate vicinity of the device. The existence of wall effects is clearly documented for a variety of flow evaluation systems. Effects include channeling (i.e., preferential flow; ASAE, 1995) and marked modifications to soil density (e.g., Jenssen and Heyerdahl, 1988). Tensiometers in this study were emplaced in pit walls 'immediately upslope from the pits in undisturbed soil...' In addition to tensiometer/soil boundary wall effects, the method of backfilling the pits will have had a significant effect on the interpretation of tensiometer results. For example, a loosely backfilled pit would produce a different effect than would a pit that was packed. In addition, the fabric of the pit soils, themselves, are expected to change with time, e.g., due to burrowing, freeze/thaw, altering the baseline calibration of the tensiometers.

2) The observation that the volumes of collected water collected were 'comparable...regardless of the antecedent moisture, duration, frequency and intensity of the simulated and natural rain'. The implication is that all rain events are equally efficient at flushing the vadose zone. This is a result which is anti-intuitive. The data shown in Figures 5 and 6 of '*A Soil Monitoring...*' indicate that the initial, simulated rain event of the study increased soil moisture in the pits from relatively low 'background' values to a markedly higher levels and such elevated soil moisture conditions were maintained throughout the entire experimental period. Because the pit soils were not allowed to dry to background levels between rain events, the soil was in effect 'primed' for the next application of water. It is possible that the observation that there exists a lack of correlation between rain events and water collected is the consequence of artificial experimental conditions rather than 'normal' soil behavior. If this is the case, then the radionuclide flux data is also suspect.

C. Spatial distribution of Pu and Am:

The spatial distribution work was undertaken to increase the number of samples for geostatistical analysis and to reprocess the data set using geostatistical procedures. This study is valuable in that it created a much larger data set from which to evaluate radionuclide fate and transport. The general conclusions of the work seem valid but, as with the other tasks in the overall soils work, there are questions of the details:

1. A critical issue in low level environmental work involves the details of the analytical procedures: it is not possible to evaluate them from the review documents. In addition, Dr. Litaor and co-workers used data from earlier sampling programs which employed CDPHE protocols but which did not include 'formal' QA/QC documentation. It seems that a study

placing such a high weight on determining 'uncertainty' should provide an estimate of data quality for the historical data sets. This is particularly troublesome when a significant fraction of the data base is composed of data of uncertain (undocumented) quality.

2. Including Krey's data with those of the RFETS and CDH may generate improper spatial distributions. The microwave digestion/HF + HNO_3 leach of the RFETS/CDH study is more aggressive in removing Pu and Am than is the nitric acid leach of Krey *et al.*

4. The means by which background was included in the calculations is not clear nor is the effect of using an upper-range value 2.96 Bq/kg, or a global fallout mean of 1.29 Bq/kg, in risk estimates. Dr. Litaor states that, 'This uncertainty must be taken into account ...,' in evaluating health risks, yet it is not clear as to how it is included. A recent study by LANL (Efurd *et al.,* 1995) employed thermal ionization mass spectrometry (TIMS) to distinguish between RFETS environmental plutonium and that from global fallout (by examining isotopic ratios). This study, commissioned by DOE/RFETS, and running concurrently with Dr. Litaor's program, provides important information for resolving the background issue and should be incorporated into the Pu spatial analysis study.

5. Knowing the speciation of an element is crucial to the evaluation of risk. Because speciation is unknown, it is unclear as to how the ultimate goals of this portion of the work will be met.

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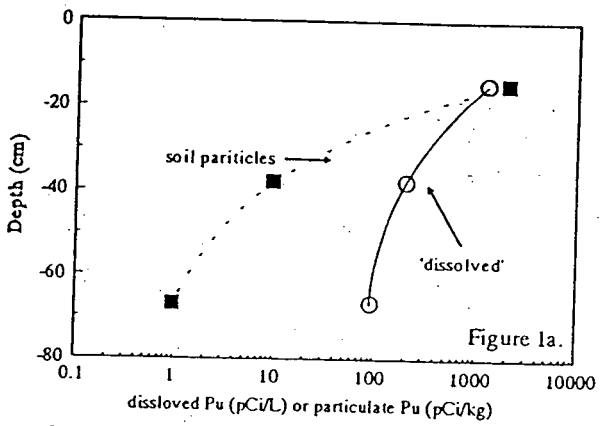

Figure 1a.

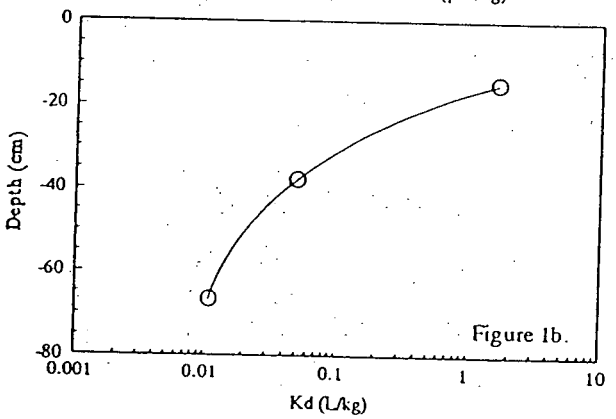

Figure 1b.

Review Team Biographies:

Bruce D. Honeyman, Ph.D., is an Associate Professor of Environmental Science and Engineering at the Colorado School of Mines. His major areas of research are the environmental physical chemistry of radionuclides, surface and colloid chemistry, and remediation of radionuclide-contaminated media. He received his B.S. in Applied Earth Sciences and his M.S. and Ph.D. degrees from Stanford University in Environmental Engineering. Before joining the Colorado School of Mines faculty in 1992, Dr. Honeyman conducted research at the University of Washington's Institute for the Study of Atmospheres and Oceans (1984-1985), the Swiss Federal Institute for Water Resources and Water Pollution Control in the Isotope Geochemistry Laboratory (1986-1988), at Stanford University (1989-1990) and Texas A & M (1991) in the marine radioecology laboratory. He has authored or co-authored 30 peer-reviewed publications and has over 50 published abstracts. He is the Principle Investigator (P.I.) or co-P.I. on over $2.4 M in sponsored research. He has served on the National Science Foundation Oceanography Program Review Panel (1994-1995), the EPA Office of Exploratory Research Review Panel (1993-1994), the DOE Subsurface Science Program Review Panel (1993) and is currently on the WIPP Site Actinide Source Term Technical Committee- Colloid Sub-Group.

Wayne Hansen has been involved in human health and ecological risk assessment activities since 1967. His experience includes both managerial, consultative and hands on experience in evaluating environmental pathways for radioactivity and chemicals. At Los Alamos National Laboratory he has provided leadership in environmental research, environmental monitoring, waste management and interpretation of monitoring and research data. He is currently Group Leader of the Environmental Science Group in the Earth and Environmental Sciences Division. The group is involved in ecological risk research and applications, hydrological transport of contaminants studies, human and ecological risk assessment of depleted uranium, and global change studies. Dr. Hansen receive a B.S. in chemistry from the University of Wisconsin in chemistry in 1961, an M.S. in Radiation biophysics fro the University of Kansas in 1963, and earned his Ph.D. in Radiation biology form Colorado State University in 1971. Dr. Hansen is a Fellow of the American Association for the Advancement of Science. He has served on numerous State and Federal Review Panels.

Edward Essington received a M.S. degree from the University of California, Los Angeles in Plant Science in 1964 and a B.S. in Soil Science from the California State Polytechnic University in 1958. Mr. Essington has been employed at Los Alamos National Laboratory since 1973 in the Waste Management Group developing analytical procedures for the analysis of plutonium and other constituents in environmental matrixes and determining the inventory and distribution of plutonium and other radionuclides dispersed in environmental media. Mr. Essington has been involved in contaminant movement and distribution studies at various sites including Mortendad Canyon, at the Nevada Test Site as a member of the Nevada Applied Ecology Group, the Maxcey Flats Low Level Waste Burial Site and the Yucca Mountain C-Wells.

Appendix A: Review of Rocky Flats Colloid Programs by Dr. John McCarthy, ORNL (1992).

This review, completed in 1992, focused on the colloid and actinide characterization programs of the U.S. Geological Survey, Los Alamos National Laboratory and EG&G, Rocky Flats, Inc. It represents a formal review by a leading expert in the field of colloid-facilitated transport of radionuclides.

TECHNICAL REVIEW OF COLLOID-RELATED ACTIVITIES AT ROCKY FLATS

I have reviewed the colloid related activities at Rocky Flats, as you have requested. My comments are based on both the written documentation provided to me by Scott Grace, as well as the oral presentations on February 24, 1992.

USGS "Colloidal and Solution-Phase Transport of Am and Pu

Drs. McKnight and Harnish did an excellent job of outlining a reasonable program to address this issue. It was clear that they had constructively modified some of their original approaches based on their preliminary sampling. Their willingness to greatly increase the extent and difficulty of the field sampling in response to the low levels of radionuclides speaks well for their intellectual and scientific commitment to provide quality results. They demonstrated an awareness of the difficulties and issues in sampling and characterizing groundwater colloids. They were able to quickly propose alternative approaches and reasonable solutions to several "what-if" scenarios. Their sampling protocols were very thorough and included measurement of a very complete suit of chemical parameters that will aid in interpretation of their results.

My only concern about this project centers on a general issue of terminology. The real issue that Rocky Flats (and DOE in general) need to address is not *colloids* per se, but rather the potential impact of *facilitated transport* of contaminants. The term *colloid* is simply a size-cut definition. Low-molecular-weight natural organic solutes may bind Am or Pu. Under such circumstances, the transport of the radionuclides may be altered even though "colloidal" size material is not involved. In a number of studies in Germany's Gorleben aquifer, for example, virtually all the Am was complexed with natural humic and fulvic acids. From this perspective, this issue should be considered within the context of 3 questions:

1. *Is the Pu and Am in the groundwater or surface water present as dissolved (aquo-) ions or inorganic complexes of these ions?* If so, then conventional speciation models and transport models are designed to address those transport issues.
2. *Are the Pu and Am sorbed to colloidal-size particles (either inorganic particles, organically-coated inorganic particles, or very large macromolecular aggregates of natural organic matter [NOM])?* If so, then the Pu and Am will be transported by mechanisms described in colloid and polymer theory, and factors such as the size and surface potential of the particles will be important for understanding and predicting the extent of radionuclide transport. Likewise, remediation technologies can be formulated based on fundamental understanding of colloid behavior.
3. *Are Pu and Am sorbed to lower-molecular-weight components of NOM?* Under such circumstances, the transport of the radionuclides may still be considerably altered, but the transport predictions and remedial alternatives must be based on quite different theory than that appropriate for colloids.

As currently defined, the USGS project focuses on the fist two questions, but appears to be somewhat tentative in addressing the third question. Dr. McKnight and many other researchers at the Denver USGS are internationally known for their expertise in humic and fulvic acids, and are well qualified to extend their research to consider the association of

radionuclides with NOM if results indicate this avenue should be addressed. Dr. McKnight should be cautioned to consider *all the components of NOM, not just the fulvic and humic components.* In DOE's Subsurface Science Program, the mobility of NOM is being examined, and results clearly indicate that the non-humic component of NOM is considerably more mobile in aquifers and soils than is the humic component. Considerably less is known about the non-humic component of NOM, including its capacity to sorb radionuclides. However, new methods for isolating the non-humic, hydrophilic-acid components of NOM have been developed at the USGS, and are well-suited for examining this issue at Rocky Flats.

In summary, the USGS project is scientifically and technically strong, and is headed in the right directions. They should be given freedom to pursue the significance of complexation of Pu and Am to NOM if results of the size fractionation indicate this as a potential transport vector (DOE basic research in the Subsurface Science Program (Environmental Sciences Division, OHER) can contribute to predictions of transport of colloid- or NOM-bound radionuclides, if association of radionuclides with these materials is demonstrated). The USGS project has an excellent chance of contributing substantially to determining the extent and mechanisms of Pu and Am transport in groundwater and surface water at Rocky Flats, and will contribute directly to developing and implementing appropriate remediation technologies.

Soil Colloid Characterization Studies

Dr. Litor has devised an excellent and comprehensive study to describe water transport within the vadose zone at Rocky Flats. His sampling design considers issues of spatial heterogeneity as well as the implications to colloid transport of the relative flow through large and fine pores. His plans to track both natural storm events, as well as to simulate large storm events is commendable and very relevant to safety assessment and to decisions on additional remedial action at the site. However, two concerns should be addressed, one relatively minor worry, and one very substantive issue:

1. Being a student of Murphy, and having conducted a number of field exercises that have confirmed and extended his Law, I have some reservations about the high-tech automated telemetry-driven technology Dr. Litor is implementing. Clearly, Dr. Litor is knowledgeable in this area, and the use of these technologies is useful and appropriate because of difficulties in accessing the contaminated sites. Nevertheless, a well-developed and detailed contingency plan is required to assure uninterrupted collection of data and samples in the (inevitable?) event of breakdowns. What is a reasonable failure rate on the automated data collection and reporting units, how will these failures be detected, what are the consequences (long- and short-term) of the loss of these data, what can be done to repair/replace malfunctioning units and/or can manual data and sample collection replace the automated links??? If such "critical path" analyses reveal major concerns, perhaps some redundancy can be built into the system.
2. More substantively, there is a concern that Dr. Litor's meticulous approach to soil

physics is not balanced by adequate attention to the equally important aspect of soil chemistry and characterization of mobile sorbents. For example, the proposed work will only differentiate between material in 3 size fractions: >450 nm, 100-450 nm, and <100 nm. This size fractionation fails to consider the potentially critical importance in material that can sorb and cotransport Pu and Am, but that is <100 nm. In Los Alamos, radionuclides in groundwater were associated with material between 25-450 nm, and in Gorleben aquifer in Germany, Am was complexed with small fulvic acids. Furthermore, Dr. Litor proposes to distinguish radionuclides associated with different size fractions based on retention on Millipore filters configured in a cross-flow filtration mode. This kind of filtration is subject to a number of limitations, including pore clogging (which alters the size of material retained) and ion retention; the extent of these effects varies with the load of filterable solids in the sample. For example, Puls (USEPA 1991) documented errors in determination of cation concentrations in filtrates of groundwater due to sorption of dissolved cations on filter cakes of colloids. Finally, the protocols did not include enough measurements of key chemical parameters that would permit the "reasonableness" of results to be evaluated (for example, evidence that results are not artifacts, evidence that the colloid phase would be insoluble under groundwater conditions, use independent methods to cross-check the nature and abundance of particle-bound radionuclides retained on filters).

Given the magnitude and importance of Dr. Litor's project, it is strongly recommended that a chemist be brought into the project to balance the detailed flow physics with equally rigorous consideration of the chemical aspects of transport. The types of protocols and analyses presented in the USGS project could serve as a model. The recommended participation needs to involve more than simply letting the USGS or other contractor use a wider range of filter sizes; rather, a substantive re-evaluation is required of the entire issue of what chemical measurements are needed to interpret a reasonable set of transport hypotheses. These comments are in no way intended as criticism of Dr. Litor's project, his approach, or his considerable expertise. Rather, these recommendations recognize that such an exemplary study of vadose zone transport field research *demands* integration of chemical aspects of transport to realize the full importance and impact of the research to environmental assessment and remediation at Rock Flats. These recommendations would, incidently, be equally strident in demanding the participation of a soil physicist or hydrologist if a chemist were proposing work on transport along a flow path. Dr. Litor's project must be supplemented significantly with respect to the chemistry of radionuclide transport and the potential for facilitated transport of contaminants. One possible approach is to involve McKnight and Harnish of the USGS with this project so that the soil solutions can be analyzed in a manner similar to the work they're doing in surface- and ground waters.

In summary, this project is an important study that, if supplemented with appropriate balance of soil physics and soil chemistry, will contribute directly to evaluation of the

potential for radionuclide transport and to evaluation of remedial alternatives.

Filtration Treatability Studies

The oral presentations on this topic were very general and provided little information useful to evaluating the projects. The following comments are, therefore, based only on the written document entitled "Microfiltration/Ultrafiltration Treatability Study Work Plan" (Draft Final, January 1992). In general, the plan duplicates the more detailed and fundamental study of the seep water already in progress by the USGS. The only novel aspects of the treatability study were the isotope spike experiment and the determination of Pu oxidation states. In addition to being duplicative, the treatability study is technically weaker than the USGS study in a number of areas:

1. Sample processing will occur at a remote laboratory (Los Alamos), with an undetermined delay in sample filtration. Potential for alteration of the colloidal phase upon storage is well-documented. Even very careful sampling cannot really overcome this concern.
2. Inadequate attention appears to be given to the unique chemistry of samples taken from different locations and at different times. No mention is made of field measurements of key chemical parameters (pH, temperature, turbidity, major cations and anions), or of hydrological parameters (rain events, antecedent moisture content of soil, possible wind-driven deposition shortly before sampling, etc.). In the absence of such basic information, differences in success of treatments will be empirical and anecdotal, and insufficient to develop a reliable and reproducible treatment technology.

   This concern is not limited to the treatability study on the seeps, but extend to consideration of treatment of retention pond water. Seasonal patterns of productivity, phytoplankton succession, thermal stratification and mixing and other limnological processes need to be considered in developing a consistent and reliable treatment methodology. It is strongly recommended that these studies include experts in limnology and ecology who can contribute to developing rational and flexible changes in treatment technologies that respond to the pattern of changes in pond-water chemistry.

The general discussion by the representative of this project proposed that characterization of colloids is essential before a rational treatment technology can be developed and tested. This is an excellent and valid point. However, since that colloid characterization of the seep waters is already being done by the USGS, it is recommended that the treatability study described in the work plan document be substantially reduced and limited to the isotope spike and oxidation state characterization, using samples provided by the USGS from their sampling. Additional resources may be required to permit the USGS to gather enough material for this additional characterization. If results warrant, the second phase of the treatability study, development and testing of flocculation or other technologies, can then proceed in the future.

Summary — In general, the colloid-related activities at Rocky Flats are impressive with respect to the scope and technical depth of studies on the potential role of facilitated transport of contaminants in surface-, soil-, and ground waters at Rocky Flats. Primary recommendations are limited to the following:

1. Do not ignore the potential role of low-molecular-weight NOM in enhancing the transport contaminants. The issue is *geochemical transport processes* affecting Pu and Am, not colloids per se.
2. Assure that all projects are integrated, multidisciplinary efforts that consider both the physical and chemical aspects of transport.
3. Develop and test remedial technologies in the context of understanding of basic mechanisms rather than empirical engineering. Avoid redundancy in efforts to develop fundamental characterization of phases that sorb radionuclides, but involve experts who can help focus and guide remediation based on established understanding of basic mechanisms responsible for chemical and physical differences in sorbent phases over time.

REPORT SUBMITTED BY

John F. McCarthy, Ph.D.
Environmental Sciences Division
Oak Ridge National Laboratory
February 28, 1992

Appendix B: Text of the Los Alamos National Laboratory Technical Review

Los Alamos National Laboratory Review August 18, 1995

Reviewers:
David L. Clark, Plutonium Chemistry
Edward H. Essington, Soil Chemistry and Sampling
Wayne R. Hansen, Radioecology and Environmental Health Physics
Bradford P. Wilcox, Hydrology

Review of the following documents was carried out to evaluate whether the fate and transport of plutonium at the Rocky Flats Site has been adequately characterized and studied. The documents provided for review included:

1. "Spacial Analysis of Plutonium-239/240 and Americium-241 in Soils Around Rocky Flats, Colorado"

2. "A Soil Water Monitoring System for Assessing Fate and Transport of Contaminants: Case Study for Pu-239/240 and Am-241"

3. "Fate and Transport of Pu-239+240 and Am-241 in the Soil of Rocky Flats, Colorado"

4. "Comprehensive Appraisal of Plutonium 239+240 in Soils of Colorado: A Basis for Risk Assessment"

5. "Soil Monitoring", M. Iggy Litaor

6. "OU3 Remedial Investigation Pu-239+240 Isoplot with Exhaustive Surface Soil Sampling Locations"

Conclusions of the reviewers are as follows:

The above information contains enough analysis to start planning alternative remediation methods for specific land use scenarios. The extent and distribution of surface plutonium and americium isotopes has a large variability and new surface samples would not add much new information. Rather, the existing data can be used to plan specific sampling programs with well defined goals. These goals should be set by a preliminary risk assessment of the surface radioactivity and the remediation alternatives.

The hydrological studies of water movement to the water table are well designed, and indicate rapid subsurface flow. The papers indicate very small amounts of plutonium are moving with the water and at a very slow speed relative to the water flow. However, the studies do not indicate where the groundwater exits to a point of exposure. Does the water flow out to the local streams and drainage channels? To complete a risk assessment from this pathway requires determination of a point of exposure to the water.

The rapid subsurface flow of water experiments indicate some very small amount of plutonium and americium is moving deeper into the soil. The studies are silent on the amount of time needed for the movement to a point of exposure. The movement is so small that estimates of time based on the data presented would give estimates of time of arrival of significant concentrations at the water table are in the 1000 to 10,000 year range.

The above studies do not address the chemical forms of plutonium and americium in the soils, in the soil water, or the potential for colloid transport. There are many reports on the importance of colloid-facilitated transport, and leaching of soluble plutonium through soil under certain conditions. The questions surrounding groundwater contamination will not be adequately characterized until speciation and colloid formation of plutonium are known. A risk assessment of the significance of this route of transport, even if present will likely indicate a small risk increment compared to the air transported plutonium and americium because of the low adsorption of these elements in the intestine.

The results of this review indicate the areas that need evaluation for further work are:

- The fate and transport of plutonium and americium slowly moving downward with water flow.

- The chemical form of the species moving with the downward water flow.

Specific comments on the above paper have been supplemented by added references on plutonium and americium chemistry and behavior of these elements in the environment. The reference list is at the end of the following specific comments.

The documents addressing the transport and fate of plutonium at Rocky Flats, Colorado concentrate on potential for movement to the water table. The likely mechanisms of transport include resuspension of plutonium and americium on soil particles, surface water movement of soil particles, and movement verticly downward in the soils. Reports such a Webb, *et al.* studied the surface erosion of the Rocky Flats soils and conclude such a mechanism is possible in the movement of plutonium and americium. The original spread of plutonium and americium from the 903 pad is thought to be by wind erosion and resuspension of soil particles. All three mechanisms will need to be addressed in risk assessments to evaluate alternative methods of dealing with the soils at Rocky Flats.

The distribution curves drawn on maps of the Rocky Flats, Colorado area appear to include data bases from several sampling programs with different goals. Based on the above papers, the combination of the samples from Rocky Flats programs and the Colorado Department of Environment and Health, (CDH) is demonstrated to be combining similar results. Including data from Krey, *et al.* may introduce more uncertainty because the methods used for extraction of the plutonium from the soil samples differed. Krey, *et al.* uses a nitric acid leach that removes "available" plutonium whereas the rest use a HF plus nitric acid digestion which is more robust and releases plutonium trapped in the matrix. This may be the reason Krey's data appear to be lower in plutonium concentration than the rest. The effect is pronounced in attempting to dissolve plutonium oxides and silicate particles with trapped Pu. The use of Krey's data with other data would generate improper spacial distributions.

Evaluation of the hydrological studies conducted would indicate fast subsurface flow. The experiments appear to be well designed and complete. The observations reported on fast subsurface flow through channels is being observed in soils on the western part of Los Alamos National Laboratory. In the case of Los Alamos experiments, the water exits the soil horizons downslope where the interface between the soil and bedrock thins to become a surface flow. However, based on the review of the plutonium and americium data from these experiments, the sampling methods may have disturbed the distribution of plutonium and americium adsorbed on particles enough to introduce important errors.

There are four concerns with the experimental setup (described in "Soil Water Monitoring ...") that bear on the conclusions drawn, vacuum on the TS, adsorption on or in the TS, filtration outside the TS, and hydrophobicity of the PTFE. Let's assume that no hindrance of solute collection occurred with the ZTS.

1. Vacuum Page 19 indicates that "... vacuum was applied for most of the drying periods ...". There are two ways that vacuum can be applied. First, quick evacuation of the TS and sealing the sampler and then repeating the process for subsequent samples. Second, continuous pumping on the TS to maintain a high vacuum. In the first case the possibility of evaporating water from the TS is minimal. In the second case evaporation of water from the TS continues as long as the vacuum pump operates venting to the atmosphere, essentially boiling some of the water out of the TS. This can be excerbated if the porous material of the sampler is not kept wet. If it is allowed to dry, continuous pumping will draw air into and through the TS and sweep even more of the water vapor from the TS (may also be the reason for poor recoveries of water). If significant evaporation is allowed the solute contents of the TS will increase; this may also explain the elevated conductivity and alkalinity results compared to the ZTS (pH tends also to be higher but not significantly).

2. Adsorption: Although PTFE is known to be inert and not a significant medium for sorption of solutes, surface effects can occur on the inside surface of the TS as solution is drawn in. If evaporation is allowed to occur inside the TS, particularly with a solution that is close to saturation (or supersaturated) with mineral-forming solutes, a film of mineral-like materials can form that can sorb solutes such as Pu and Am (this phenomenon is observed in water sampling operations hence the use of acid to maintain solubility of the desired solute species). This would lead to the observed reduced Pu and Am in the TS samples compared to those from the ZTS. Pu and Am solubility are very low at the pH level of the soil solution but the effect can be exacerbated by the increase in pH of the TS samples and the higher concentration of solutes.

3. Filtration: Perhaps the most likely effect on Pu and Am concentrations in the TS is the formation of a filter bed on the outside of the TS surface. During implantation of the TS the soil is disturbed, reducing structural integrity, and allowing movement of particles of a wide range in sizes toward the TS. This material will pack around the TS creating a filter bed primarily of fines. This bed can filter colloidal or larger particles containing Pu and Am. Compared to the Pu and Am contained in the particle load of the ZTS samples, the Pu and Am concentrations in samples from the TS will likely be considerably lower reflecting the absence of the larger particles even of clay size and perhaps a different distribution of soluble species. It would be informative to recover several of the TS and attempt to analyze both the outer filter bed and the inner surfaces for Pu and Am; any significant concentrations of Pu or Am on the inside of the TS would be evidence that the samplers did not function as assumed.

4. The PTFE that I am familiar with is highly hydrophobic. Considerably higher tension (vacuum) is required to overcome the internal resistance to water entry created by the lack of wetting of the PTFE surfaces. Could this be a reason for the reduced water production by the TS?

   Page 19, line 15: The limited amount of water extracted by the TS was more likely due to air bleeding. My experience with "biological filters" (early models of TS) was that, except for deflocculated clay suspensions, dewatering of clay suspensions was not a serious problem, although somewhat slower than soil suspensions low in clay content, so long as the entire filter surface was covered with a film of fine soil particles.

Additional documents from the open literature.

7. Litaor, M. Iggy, "Spatial analysis of plutonium-239+240 and americium-241 in soils around Rocky Flats, Colorado," J. Environ. Qual. (1995), 24 (3), 506-16.

8. Litaor, M. Iggy; Thompson, M. L.; Barth, G. R.; Molzer, P.C., "Plutonium-239+240 and americium-241 in soil east of Rocky Flats, Colorado," J. Environ. Qual. (1994), 23(6), 1231-9.

Comments on above documents.

Document number 1 provided by LATO was nearly identical to document number 7 that I obtained from the literature with a few exceptions, most notably in the discussion of the actinide analyses. The open literature document number 8 contained information that overlapped with some of the documents provided by LATO. The open literature documents are attached.

The experimental section of the documents 1-6 were somewhat detailed on the monitoring apparatus, but were very poorly documented regarding the analytical chemistry, making it difficult to judge the quality of the chemical analyses. For example, in document 2, only a brief section (page 14, top) states that "specific conductance, temperature, pH, and alkalinity of the water were also measured in the field." There is no mention of how these experimental parameters were measured, with what instruments, how they were calibrated, etc. These data are used to support claims made in the documents, but there is no way to judge their accuracy or precision. This leads to the next critical question of actinide concentrations. The data are widely scattered, as might be expected, and observation of higher mean concentrations in the upper layers of soil is believable, but again, there is no way to judge the analytical result. Using document 2 as the example, a single sentence is provided that "activities ... were measured by alpha spectroscopy in a commercial laboratory following a modified procedure..." (page 14). What instruments were used, what commercial lab, what level of QA, etc. are not given. This is extremely frustrating, and makes the scientific review of the analytical chemistry results extremely difficult. Document number 1 is the only document with a detailed explanation of how actinide samples were prepared for analysis. The discussion in that document provides enough detail to ascertain that samples were prepared using established procedures. The details of the actual actinide analyses are still unclear, other than the fact that analyses were performed by alpha spectroscopy by a commercial lab.

Discussion

The objective of the review is to determine of the fate and transport of plutonium at the Rocky Flats Sites has been adequately characterized and studied. From reading documents 1-8 it appears as though a very extensive monitoring program has been underway from some time at the Site. It is quite evident that there is plutonium-239/240 and Am-241 present in the soils and that the relative concentrations of these isotopes decrease with depth and distance from the Site. This data will undoubtedly be valuable for risk assessment activities. However, this reviewer believes that there are still key pieces of data needed for making accurate risk assessment regarding the future fate and transport of the actinides at the Site. In particular, the chemical from of the plutonium in soils and ground water is still unclear, and the mechanism of transport has not been determined. The introductory remarks in most of these documents argue that the uniform depth of the Pu found at the Site is consistent with wind transport of Pu bound to soil particles, and that surface soils were probably contaminated during cleanup operations of the 903 Drum Storage Site. This

may be the case, but the soil water monitoring program provides data which assert that other processes can facilitate transport at the Site. In this regard, it would be extremely useful to know the chemical form of Pu at the Site. The assertion is that chemical form is plutonium dioxide.

I looked into the history of the site, to see if there were enough information to back up the claim that Pu is in the form of an oxide. This history is provided for the other team members below. From the site history, the exact chemical form and speciation of plutonium in soil and groundwater remains uncertain. From a consideration of kinetics and thermodynamics, it is unlikely that metallic Pu still exists at the site. The reactions of plutonium metal with soil water should produce one of several oxide phases, which should limit migration due to the extremely low solubility of the plutonium oxides in aqueous solutions. The soil and groundwater chemistry will play a role in potential migration at the site. In view of the large quantities of organics that were originally present at the 903 Storage Site, there is potential for Pu complexation. The soil water monitoring program seemed to indicate Pu migration was not affected by the volume of interstitial waters, soil moisture conditions, or intensity of rain. However, there are many reports on the importance of colloid-facilitated transport, and leaching of soluble Pu through soil under certain conditions that should not be ignored. I do not believe that the fate and transport of Pu at the site is adequately characterized until the speciation of Pu is known.

Background on the 903 Drum Storage Site

The following information is an abridged version of data presented in the Final Phase II RCRA Facility Investigation/Feasibility Study Work Plan.[1] From October 1958 to January 1967 the 903 Drum Storage Site at Rocky Flats was used to store drums containing waste machine cutting oil that was radioactively contaminated.[1] Approximately 75% of the drums were plutonium-contaminated, while the majority of the remaining 25% contained uranium. (Has uranium also been released? Could be used as a tracer if enriched or depleted uranium.) Most of the plutonium-containing drums held waste lathe coolant consisting of a high molecular weight straight-chain hydrocarbon oil (Shell Vitrea) and carbon tetrachloride in diverse proportions. An unknown number of drums contained other waste liquids such as hydraulic oils, vacuum pump oils, trichloroethylene, tetrachloroethylene, silicone oils, acetone, still bottoms, etc. Leakage of the oil was recognized early, and in 1959 ethanolamine was added to the oil to reduce the corrosion rate of the steel drums.

During drum handling operations in 1964, drum leakage was noted at the 903 Drum Storage Site, and the contents of leaking drums were transferred to new drums and the entire area was fenced to restrict access.[1] It is estimated that a total of 5,000 gallons of waste oil leaked from drums onto the ground at the Drum Storage Site. Based on oil samples taken from drums, the average plutonium concentration was 4.54 milligrams per Liter (280 mCi/L). Thus, approximately 86 g (5.3 Ci) of plutonium were released into soils at the 903 Drum Storage Site.[1] An asphalt cap was applied in October 1969, and in February 1970 additional road base course material was applied to soils directly east and south of the asphalt pad due to soil contamination.[1]

Several years after the asphalt cover was applied, Navratil et al. examined soils beneath the 903 Pad to determine the extent and distribution of plutonium and americium. This study indicated that plutonium-239 (ranging from 427 - 20,455 pCi/g) and americium-241 (ranging from 282 - 2,273 pCi/g) contamination was indeed present in the soil beneath the 903 Pad, and appeared to be restricted to shallow depths below the original ground surface.[2] It was estimated that 18,000 tons of contaminated soil was present beneath the asphalt cover.

Phase I Remedial Investigations of environmental media demonstrated that volatile organic contamination exists in soils, surface water, and ground water in areas adjacent to the 903 Pad, as well as under the Pad itself.[1] Ground water samples were found to contain carbon tetrachloride in significant quantities with concentrations of several hundred to several thousand mg/L. Tetrachlorethylene was detected in wells ranging from a few mg/L to 528,000 mg/L, and trichloroethylene was detected in wells with an upper concentration of 12,1000 mg/L. Significantly lower concentrations of other volatile organic compounds including vinyl chloride, 1,1-dichloroethylene, 1,1-dichloroethane, chloroform, dichloromethane, and acetone were found. Radionuclides were also found in groundwater sampled at the 903 Pad, although concentrations were below 1 pCi/L.[1]

The above data and discussion indicates that there is uranium, plutonium, americium, and volatile organic contaminants in the soils under the 903 Pad. Since only trace amounts of uranium, plutonium, and americium were found in groundwater samples at that time, the radionuclide contaminants appeared to be confined to the soil beneath the Pad.[1] This raises important questions concerning the chemical form of actinide elements in the soils at the present time.

The Chemical Form of Plutonium in Soils

When the plutonium leaked into the soil it was in the form of metal in machining oils. However, plutonium is a very reactive metal that oxidizes readily when exposed to oxygen or water vapor, and a number of studies on the oxidation of plutonium have been conducted.[3-11] Micobalance studies of the oxidation of plutonium in water vapor show different kinetics of pure plutonium and plutonium alloyed with 1 wt. % gallium. Characterization data (XRD, XPS, EDS, metallography) shows that water vapor reactions with unalloyed plutonium produces a diverse mixture of products depending on temperature. These oxidations products include PuO_2, Pu_2O_3, and a monoxide monohydride, HPuO.[10]

The kinetics of the reaction of plutonium with liquid phases is found to be much different than that observed for gaseous reactions. The primary difference appears to be that in liquid water and carbon tetrachloride reactions, the corrosive liquid is able to diffuse through the oxide coating with an end result of complete oxidation. There have been several reports on the corrosion of plutonium by liquid water from the domestic supply at Rocky Flats,[3] synthetic seawater,[11] and salt solutions.[4] The reactions of alpha and delta plutonium (2.9% Ga) in water and 1 molar salt solutions were studied by measuring the production of hydrogen gas formed by a sequence of hydrolysis reactions.[3] In contrast to reactions between plutonium metal and gaseous oxygen that form a protective oxide layer, liquid water is extremely corrosive to plutonium. In liquid water reactions, plutonium metal was found to convert quantitatively to a fine black powder which was identified as plutonium monoxide monohydridge, HPuO, by means of TGA, XRD, and XPS studies. Other hydrolysis products were also identified in aqueous hydrolysis media such as a second hydride, $H_3Pu_7O_9$, and a series of oxides Pu_2O_3, Pu_7O_{12}, Pu_9O_{16}, $Pu_{10}O_{18}$, $Pu_{12}O_{22}$, and PuO_2. Kinetic studies on the liquid water reaction with plutonium reveals that the reaction is catalyzed by salt.[4] If submerged in seawater at 25°C, a 1-mm thick sheet of plutonium metal will be converted to HPuO powder in approximately 16 days. From the kinetics of the oxidation of plutonium,[3] it can be shown that the lifetime of a 100 micron plutonium particle is only 8.4 days in liquid water, and 4 minutes in a carbon tetrachloride-methanol mixture.[9] From these discussions one can ultimately conclude that the plutonium in the soil is no longer metallic, but the chemical form of the product is uncertain.

References

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12) S. B. Webb, S. A. Ibrahim, and F. W. Whicker, "A Study of Plutonium in Soil and Vegetation at the Rocky Flats Plant," In Environmental Health Physics. Proceedings of the Twenty Sixth Midyear Topical Meeting of the Health Physics Society, R. L. Katherine, et al., Eds., January 24-28, 1993, Cored d'Alene, I.D. (1993).

Appendix C: Estimation of actinide transport rates through the vadose zone.

Plutonium soil inventories were estimated from the soil activity data derived from the pit studies (*'Fate and transport...'*). All pit data for Pu shows an exponential decrease in Pu activities with depth. It is remarkable that all pits, regardless of the maximum surface activity, show a Pu attenuation rate of ca. 0.19 cm^{-1}. This attenuation rate appears to be valid for all pits to a depth of ca. 50 cm in spite of changes in soil horizons. The Pu inventory in each pit was determined by integration of a first-order attenuation rate equation. A bulk soil density of 2.2 kg dm^3 was assumed. From these calculations, a column of soil 10 cm square in cross section and extending to 'infinite' depth has an inventory of about 2.3×10^4 Bq, assuming a surface activity of 2.0×10^4 Bq kg^{-1}.

The center of the plutonium soil column inventory, regardless of the surface activity, resides at ca. 4.5 cm: 50% of the activity is, therefore, in the top 4.5 cm of the soil. This has several implications. First, in the 30 or so years since the beginning of drum leakage, the center of Pu soil activity has only moved to 4 -5 cm deep within the soil. However, 10% of the inventory has moved to below 15 cm. of soil depth.

Elusive Pu: The fraction of the Pu soil inventory which is rapidly moving through the soil is more difficult to estimate. It is not apparent that Dr. Litaor established the volume of soil that was in contact with the water collected in the samplers; this could be done, for example, through the use of a tracer (e.g., LiBr). As a consequence, it is not possible to be certain of the fraction of inventoried Pu leaving the soil through pore water movement. However, an estimate can be made, for each sampling depth, based on the cross-section of the zero tension samplers and an estimated probable volume of soil flushed (Table C-1). In the calculations below, the fraction of soil Pu which is 'elusive' is estimated using a 200 ml average collection volume (*qq.v.*, Fig. 5, *'A soil monitoring system...'*; note that the volume of collected water was determined to be independent of the magnitude of the rain event, although the observed behavior may be an artifact of the experimental design: Section IIB).

While the percent of Pu appearing at the lower levels of the soil column during each rain event is small, the accumulated effect of multiple, 'normal' rain events may be significant at transferring Pu from the soil column. [Based on the water infiltration work, however, it is unclear as to whether a threshold rain event exists for the appearance of water, and Pu, in the lower soil horizons.]

Table C-1: Estimation of the fraction of Pu removed from the upper soil column during rain events.

Zero Tension Sampler (ZTS) depth (cm)	Soil inventory flushed[1]	Percent of soil Pu removed per rain event[2]
30	1.1×10^4 Bq (424 pCi)	9.4×10^{-4} - 19
45	6.9×10^5 Bq (2.6×10^4 pCi)	7.4×10^{-4} - 4.0×10^{-2}
80	2.3×10^6 Bq (8.5×10^4 pCi)	3.0×10^{-5} - 2.5×10^{-3}

Example calculations:

[1]The estimated soil volume times the integrated inventory in that volume. The ZTS have a cross-section of 450 cm^2. The ZTS at 30 cm depth likely collects water from a ca. 500 cm^2 cross-section soil column, extending to 30 cm. The Pu inventory in the column equals approximately 1.1×10^4 Bq (424 pCi).

[2]The range of Pu activities collected is 0.02 - 413 pCi L^{-1} (Table 1, '*A soil monitoring...*'). Given a 200 ml collection volume, the activity range of the collected waters was 4×10^{-3} - 83 pCi. The range in the fraction of the overlying Pu inventory removed is 9.4×10^{-6} to 0.19 (9.4×10^{-4} % to 19%).