Department of Energy

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FEB 25 1998

98-DOE-03309

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

Dear Mr. Moore,

We are in receipt of your letter to Jessie Roberson, Manager of the Department of Energy Rocky Flats Field Office (DOE-RFFO), dated February 11, 1998. We appreciate the comments from Dr. Litaor on the Actinide Migration Final Fiscal Year 1997 (FY97) Report that were attached to your letter. Dr. Litaor raises some important issues related to Actinide Migration at Rocky Flats. We have considered Dr. Liator's comments during the finalization of the FY98 Actinide Migration work scope. One of the important hypotheses brought forth by Dr. Litaor is that under certain environmental conditions, the potential exists for both physical as well as colloidal or dissolved transport of actinides; the FY98 work scope planning has included a strong focus on examining this hypothesis. Attached are the responses to Dr. Litaor's comments prepared by the Actinide Migration Studies Group.

I appreciate your interest in ensuring that Dr. Litaor routinely receives reports on actinide migration at Rocky Flats. Dr. Litaor is welcome to review all reports and relevant information on the Actinide Migration Investigation and I will make sure that he receives future reports. The Actinide Studies are intended to foster an open exchange of information and ideas that will help develop the best possible approach to the successful closure of Rocky Flats. Accordingly, we are interested in obtaining recent reports on Rocky Flats data authored by Dr. Litaor. The Rocky Flats Environmental Technology Site has never received any draft reports for review and several of these reports either have been or are about to be published in journals (per Dr. Litaor's reference section to his comments). Any assistance you can provide in seeing that Dr. Litaor's reports and data are made available to me would be most appreciated.

Please feel free to contact me at 966-9692 if you have any additional questions or concerns.

Sincerely,

Russell McCallister

Russell McCallister
Regulatory Liaison Group

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cc:
Steve Gunderson, CDPHE
Tim Rehder, EPA
Mike Konczal, CED, RFFO
Chris Dayton, K-H
Dave Shelton, K-H

Actinide Migration Studies Response to Comment Letter from
Dr. M. Iggy Litaor of Tel-Hai College, Upper Galilee, Israel,
dated January 11, 1998

Comment I. The executive summary claims that reducing agents solubilized 0.1% to 5% of Pu compared with 20% to 40% suggested by Litaor and Ibrahim (1996). There is a basic difference in the experimental design between the two studies, which may have significant environmental implications for the site (see below).

Response I. Provided under Comment #III.

Comment II. The authors of the report provided qualified conclusion that may lead the reader to the importance of this Pu-sesquioxides fraction by saying that some of the water quality exceedances observed in RFP can be explained by redox change in the soil system (aerobic ⇒ anaerobic) that induced higher solubility of Pu. I am grateful to the members of the Actinides Migration Panel that they finally came to this realization especially in the light of previous work that promoted this view (e.g., Litaor and Ibrahim, 1996; Litaor et al. 1998; Litaor et al. in review).

Response II. In our opinion, the important hypothesis brought forth by Dr. Litaor is that under certain environmental conditions, such as redox changes, that the potential exists for both physical as well as colloidal or dissolved transport of actinides. The fiscal year 1997 (FY97) investigations and the FY98 work scope planning has included a strong focus on examining this hypothesis and evaluating the potential consequences/implications on remedial actions (also see Comment #3).

Comment III. The differences in the reported Pu-sesquioxides fraction resulted from different extraction techniques employed and vastly different sampling scheme. In Page 3, the report describes the protocol of extracting Pu in the following order: exchangeable, carbonates, sesquioxides, organic matter, and residual. Litaor and Ibrahim (1996) employed different sequence: soluble, exchangeable, carbonates, organic matter, sesquioxides, and residual. I suspect that the destruction of organic matter before the dissolution of sesquioxides may released some of the Fe-Al-Mn-oxides and hydroxides bound together with organic matter. In the work by Litaor and Ibrahim (1996) this fraction was probably dissolved by the CBD extraction resulted in higher percentage of Pu-sesquioxides content. The sequence described by Litaor and Ibrahim is more appropriate sequence to the problem at hand, especially in light of the increased Pu activity in colloidal and dissolved forms during the wet spring and summer of 1995. This increase is due to dissolution of sesquioxides, sesquioxide-Pu-organic matter humate, and even Pu solid phase (Litaor et al. in review).

In Page 3, the Final Report describes the location of the soil samples. Their approximate locations were also sketched in Figure 1 and their organic carbon content was given in Appendix 6. The soil samples were not taken by the authors of the report but provided by a subcontractor. The area they described is highly disturbed due to past RFP activities. The topsoil of the area from which the soil samples 1 to 5 were collected was partially scraped in the past and does not

exhibit a mollic eppipdon like the A horizon described by Litaor and Ibrahim (1996). The mollic horizon exhibits organic matter that varies between 4 % to 16 % unlike the highly disturbed samples described in the Final Report which exhibited organic matter values that ranged between 0.99% to 2.39%. The report did not provide additional information regarding the soil samples such as CEC, sesquioxides content, mineralogy, and other edaphic factors essential for a meaningful comparison between the two studies. We walked the site numerous times using old and new air photographs to delineate the disturbed areas before picking up our sampling sites. We have conducted a GPR survey to locate the sites which may provide the highest potential for Pu transport due to lateral discontinuity (Litaor et al., 1994; Litaor et al., 1996). The haphazard sampling protocol described in the Final Report is additional cause for the apparent differences between the studies.

Response III. Dr. Litaor has highlighted some important issues with respect to the selective extraction approach both generally and relative to Litaor and Imbrahim (1996): (1) the use of different extraction techniques; and (2) a different sampling scheme. As pointed out by Litaor, both issues will yield differences between the results reported by Honeyman and Santschi (1997) and Litaor and Imbrahim (1996).

Although it was not pointed out by Dr. Litaor, the selective extraction technique, irrespective of the specific extraction scheme, is an operational technique that cannot be uniquely tuned to a general set of components in complex systems such as soils, even without inclusion of multi-component actinide chemical processes. It has often been pointed out in the literature, and Dr. Litaor acknowledges it in his paper, that the extracted 'phases' are conditional upon the chemical attack used as well as the order of the extraction. In the case of the FY97 study, the selection sequence followed, and the extractants were selected, to address the hypothesis forwarded by Dr. Litaor, (that under reducing conditions plutonium (Pu) and americium (Am) are released through sesquioxide reductive dissolution). We felt that destruction of the organic matter before the destruction of the sesquioxides might have underestimated the magnitude of Pu release during reductive dissolution. However, efforts this fiscal year will include: (1) analysis of a small suite of samples for comparative Pu/Am extraction, further focusing the extraction information on the question of particulate transport engendered in the hypothesis; (2) the K_d task will include substantial focus on evaluating the mobility of Pu and Am, including reducing conditions which are better representatives of potential environmental conditions. The comparison between the sequential extraction experiments and the mobility experiments is one of total inventory versus accessible Pu and Am, respectively. In both cases, information will be gained on the form of the mobile components.

With respect to the soil sampling locations, the samples were not collected in a haphazard fashion. Ms. Annette Primrose of RMRS, who has been involved with activities associated with the 903 Pad and Lip Area since 1990, led the FY97 soil sampling activities (and was in the field with the samplers). The five sampling locations mentioned in Dr. Litaor's comments were collected from undisturbed areas in the plateau region. RMRS believes Dr. Litaor may be referring to the disturbed area around the old shooting range; the CSM samples were taken upslope of that area. Ms. Primrose stated that the area that was sampled has not been scraped and exhibited the cobbly surface common to soils on the plateau area.

The sampling question is clearly important for sample representation and heterogeneity. Sample selection at the site was limited by the budget. The issue of the scale-length of heterogeneity, which Dr. Litaor acknowledged in some of his published work, requires further analysis.

Comment IV. The experimental protocol of the Distribution Coefficients (K_d) described in page 5 and results presented in Pages 13 to 16 is inappropriate. The need for K_d values stem from the required input to solve the advection-dispersion equation for transport of reactive constituents. It is successfully used in groundwater contaminant problems and to a lesser degree in vadose zone cases. One of the fundamental flaw in the experimental design described in the Final Report is the implicit assumption that the entire soil matrix is wet, thus 5 gram of sieved soil was submerged in 0.5 L of water. This condition never occurred in the field except during the flooding of 1995. There is a large body of literature that describes preferential flow conditions in soils of RFP. In general, only small fraction (< 10%) of the soil is wetted during 'normal' snowmelt and rainfall events monitored between 1992 to 1995 and the flow is largely confined to macropores at high velocity which facilitated the transport of particulate material (Litaor et al., 1996, Litaor et al., 1998, Litaor et al., in review; Nachabe et al., 1995; Ryan et al., 1998). We found that under aerobic conditions up to 97% of the Pu is restricted to the fraction greater than 0.45 μm (see Litaor et al., 1998). Hence, the K_d experimental protocol as described by this report has little merit in the real soil environment. Failure to understand this fundamental point will result in erroneous conclusions regarding the main goal of this report, namely 'to provide information as a foundation for assessing whether additional soil cleanup goals must be established, or further institutional controls that may be needed, for the protection of surface water'.

To further illuminate the problems with the simplistic K_d approach I call the authors' attention to the following findings. During the wet spring and summer of 1995 we observed significant shift in the fractionation (termed speciation by the authors) of Pu during the prolonged saturation period probably because of the change in redox potential. Up to 64% of the observed Pu was in colloidal (0.45μm > X > 10kD) or dissolved form (< 1 nm) (Litaor et al., in review), compared with less than 17% in aerobic conditions (Litaor et al., 1998). It should be emphasized that most of the colloidal and dissolved fraction during the aerobic conditions of the monitoring period (1992 to 1995) were around 1% to 2%. From the comment above, it is clear that the K_ds values described by the author will not provide the necessary information for vadose zone modeling because of the sampling and experimental flaws as well as large spatial and temporal variations.

In 1996, the Colorado Department of Public Health and the Environment (CDPHE) asked me to provide some Kd values from my studies. The values were given to Dr. N. Morin of CDPHE with a clear reservation as far as the usefulness of this approach (Attachment I).

Response IV. It is our opinion that K_d values derived experimentally under controlled conditions, ranging from oxic to anoxic, can be very useful in defining the potential range of values that may occur in the environment, and are a required input parameter into the RESRAD model. The

preliminary K_d determinations described in the Final FY97 Report were intentionally designed to provide the upper range of K_d values for oxic conditions. Time and resources did not permit the affects of other conditions on the K_d values to be investigated during FY97. Further experiments are currently planned for FY98 to look at K_d values under varying redox conditions.

We would like to request the methodology used to determine the K_d values provided in Tables 1 and 2 of Dr. Litaor's comments. We suspect that these were measured from data which were collected in-situ They are in close agreement with those shown in Table 7 of the Final FY97 Report. This appears to confirm that ex-situ laboratory experiments can provide useful data for interpretation of the behavior of Pu in the environment, especially when confirmed by in-situ data.

The K_d values, required by the RESRAD model, do not focused on advection-diffusion processes in watershed transport, but instead on potential health effects. For example, the available actinides following ingestion of soil is a solution saturated process. It is recognized that the K_d values measured during the FY97 work were representative of saturated oxidizing conditions. Part of the work scope for FY98 is to extend these measurements to suboxic conditions, directly focusing on evaluating the conceptual model hypothesis that changing redox conditions within the soils due to saturation will change the amounts of Pu and Am available for transport.

Comment V. The section describing the Pu activity in Ponds especially in C-2 has a fundamental flaw in their approach. The authors assume that all flow reached the settling pond. This is far from the truth. Most of the near-surface and surface flow from the 903 lip area is collected by the South Interception Ditch (SID) that diverts the flow from the contaminated slopes around the 903 Lip area into C-2 Pond. Large amount of sediment is trapped in the SID that never reached the Pond. Hence, the computation of the Pu flux on the basis of cumulative deposition over time is a gross underestimation of the amount of Pu that has been remobilized by vadose-zone flow and surface flow over the years. During the flooding incident on May 17, 1995 we observed numerous areas of seepage on the downhill side of the SID. This observation suggests that some Pu may bypass the SID on its way to Woman Creek and subsequently offsite! Moreover, during the wet summer of 1995, we observed that the intensity of subsurface flow decreased downslope. We believe that much of the flow did not even reach the SID but have ceased somewhere downhill above the SID. The existence of hot spots along the contiguous slope from the 903 Lip area towards the SID, strongly supports this assertion (Litaor unpublished document). Hence, the proposed computational approach does not provide the information regarding the potential of Pu remobilization during normal and/or extreme events.

Response V. The primary objectives of the pond core analyses were: 1) to inventory the Pu that has accumulated in the pond sediments over time; and 2) to assess Pu transported to the ponds as a consequence of storm events and site activities. It is recognized that not all sediment that may be moved from the 903 Pad and Lip Area by overland flow toward the SID actually reaches Pond C-2. Deposition of entrained sediment occurs on the hill slope and a portion of sediment reaching the SID will settle out in the channel before reaching Pond C-2. In order to inventory the total amount of sediment reaching the SID/C-2 drainage system, the SID sediments would

also have to be sampled to determine the depth of sediments and Pu accumulation. Objective one was met and estimates of the Pu inventory in three ponds were presented. Although Pu activities were determined by depth for two ponds, objective two was not met due to the inability to date the sediments by the ^{137}Cs method. The Final FY97 Report states that the pond inventory calculations provided a lower bounds to Woman Creek basin erosion and an order of magnitude estimate for yearly erosion rates.

In addition, in our opinion, Pu is transported in near-surface groundwater is "cut-off" by the SID because the SID is dug several feet below ground surface. Any Pu -contaminated groundwater would be in the top few feet and be captured by the SID.

Comment VI. The authors suggested that 'mechanical erosion' is the dominant process in transporting Pu downhill. I was thrilled to see that some members of the Actinides Migration Panel have finally came to the realization that the physical processes and not the geochemical ones govern the Pu transport downslope via near-surface and to a lesser extent surface flow. However, it points to an internal flaw in their argument for further geochemical work. In any event, our original conceptual design was based around the physical processes concept, hence we tried in our studies to quantify the processes such as vadose zone flow (Litaor et al., 1996; Litaor et al., 1998); surface flow (Zika, 1996); evapotranspiration (Daniels, 1996); snowmelt processes (Moffitt, 1996); colloidal transport (Ryan et al., 1998); water velocity and macropores (Nachabe et al., 1995).

Response VI. We agree that physical transport is the dominant process affecting Pu movement at the RFETS, but are not convinced that near-surface processes are more dominant than surface processes under "normal" environmental conditions, though our opinion is based upon transport length and may change under anoxic conditions. It is assumed that Dr. Litaor is referring to his work that showed vertical transport via macropores and other hydrologic processes. However, we are less concerned with slow vertical movement than rapid, event-related surface flow processes which have been shown to affect surface water quality.

As Dr. Litaor notes in Comment IV, Pu may have moved during the Spring 1995 in colloidal or dissolved form as a result of changes in redox conditions of the environment. It is this potentially important range in transport behavior that the geochemical work will address. Future geochemical studies will attempt to clarify whether changes in redox conditions can significantly affect the solubility of Pu. This will be conducted through interpretation of existing data, potential collection of additional data, and geochemical modeling.

Comment VII. In general, the report is riddled with citing inaccuracies. For example, in Page 9, the authors claim that Litaor and Ibrahim (1996) took five soil cores from an area NW of SW 51. In fact, Litaor and Ibrahim (1996) took five soil samples by diagnostic horizons from five open pits NW of SW 53. In page 10, the authors mentioned Marty et al (1996). In fact, it is Marty et al (1997). There are other several errors of that kind. The authors should be more careful in citing other people work.

Response VII. The comment is noted.

Comment VIII. The work by Marty et al. (1997) has added nothing new to the problems involved with the operationally defined sequential experiment. In any event, a detailed reply was submitted to the Journal of Environmental Quality (Litaor, 1997) (Attachment II).

Response VIII. The comment is noted.

Comment XIX. Page 17. The desorption kinetics results support my assertion that K_d values have little usefulness in predicting the fate and transport of Pu in the vadose zone of RFP. On the basis of the 1995 wet spring and summer we have presented our conceptual flow model and remediation approach that was based on five years of studies by numerous researchers. Our approach was ignored and we never received the opportunity to write it up in a report form. I wish we could get the chance to finish that document and present our ideas and thinking to the regulatory agencies as well as DOE.

Response XIX. Although it is difficult to extrapolate from the analytical results of three samples with no duplicates, the desorption data presented in Figure 3 is consistent with past results and indicates that under aerobic conditions there may be an initial partitioning of Pu to the solution phase with a repartitioning to the solid phase over time. The effect appears to be slight and cannot be confirmed by the data presented in the Final FY97 Report.

The initial partitioning to the solution phase could be an artifact of the K_d method given in the Final FY97 Report. The soil samples were air-dried and dry-sieved before determination, and thus there may have been a release to solution upon rewetting, which could be responsible for the observed effect. This data may indicate that under the aerobic soil conditions, which are commonly present at the Site, there may be a small flush of Pu released during each wetting cycle that may be available for transport with infiltrating water. Over time this could be a mechanism for redistribution of Pu in the soil profile and warrants further investigation.

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