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June 26, 2002

Fernald Environmental Management Project
Letter No. C:ARWWP:2002-0012

Mr. Johnny Reising
Department of Energy
Fernald Environmental Management Project
P. O. Box 538705
Cincinnati, Ohio 45253-8705

Dear Mr. Reising:

**CONTRACT DE-AC24-01OH20115, RESPONSES TO US EPA AND OHIO EPA COMMENTS
ON THE PROJECT SPECIFIC PLAN FOR THE ANALYSIS OF HOW URANIUM IS SORBED
AND PARTITIONED ON GREAT MIAMI AQUIFER MATRIX SEDIMENTS**

- Reference: 1) Letter from Mr. James A. Saric, USEPA to Mr. Johnny W. Reising,
US DOE, "Uranium Sorption and Partitioning of GMA PSP," dated
May 14, 2002.
- 2) Letter from Mr. Thomas A. Schneider, Ohio EPA to Mr. Johnny Reising,
US DOE, "Comments on PSP for Uranium Partitioning of GMA Sediments,"
dated May 22, 2002.

Enclosed please find responses to the referenced comments for your review and forwarding on to EPA and Ohio EPA. A revised PSP is not included since the comment responses will be included in the PSP file and noted actions resulting in changes to the protocols identified in the PSP will be implemented as appropriate. Should you have questions regarding this transmittal please contact me at 648-5814 or Bill Hertel at 648-3894.

Sincerely,



David J. Brettschneider, Project Manager
Aquifer Restoration/Wastewater Project

DJB:BH:ldt
Enclosure

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**RESPONSES TO U.S. EPA AND OEPA
TECHNICAL REVIEW COMMENTS ON THE
PROJECT SPECIFIC PLAN FOR THE
ANALYSIS OF HOW URANIUM IS SORBED AND
PARTITIONED ON GREAT MIAMI AQUIFER MATRIX
SEDIMENTS**

**FERNALD ENVIRONMENTAL MANAGEMENT PROJECT
FERNALD, OHIO**

JUNE 2002

U.S. DEPARTMENT OF ENERGY

These four items are addressed as follows:

- 1) Why the proposed study is required: As stated in the first sentence of the comment, the proposed study is required to improve the accuracy of cleanup predictions. As explained below, the best case groundwater cleanup time predictions made in 1997 are not being borne out. It is anticipated that results of this study will provide information to better understand the model limitations and a better understanding of the aquifer/uranium geochemistry.
- 2) Provide more information showing that the actual cleanup results are significantly different from predictions and that these differences (modeled versus actual) are due to the absence of equilibrium conditions in the aquifer: As noted in the text of the PSP, the actual versus modeled cleanup results *may* be due to the absence of equilibrium conditions. Some other reasons why the actual versus modeled cleanup results differ are: The actual source terms in the aquifer may be larger than modeled; groundwater injection rates being less than what was modeled; and water table variation with contaminant being potentially fixed above the water table during parts of the year or during periods of lower regional water levels. Regarding the equilibrium question, the Baseline Remedial Strategy Report (BRSR) (DOE 1997) predicted remediation of the aquifer would be complete by 2006 under a piecewise continuous equilibrium assumption (e.g., a K_d value of 1.78 L/kg during the early years and a K_d value of 17.8 L/kg during the out years). These BRSR model scenarios predicted total uranium concentrations in the off site portion of the plume (South Plume) would be below 20 $\mu\text{g/L}$ by 2003. These scenarios also predicted the South Field portion of the plume would require 10 additional wells in the Southern Waste Units (SWU) area to complete the aquifer remediation by 2006. Operational experience with the remediation system since publication of the BRSR has shown that the off site portion of the plume (South Plume) is being remediated at a slower rate than predicted, with total uranium concentrations remaining above 100 $\mu\text{g/L}$ in the aquifer in 2002. Under the SWU area, total uranium concentrations in the aquifer have decreased from over 2000 $\mu\text{g/L}$ to under 500 $\mu\text{g/L}$ indicating that remediation in this area is proceeding at a faster rate than predicted and that 10 additional extraction wells will not be required in this area. A detailed discussion of the modeling approach and the justification is contained in Appendix A of the BRSR.
- 3) Provide a step-by-step description of how the results obtained from each of the eight steps associated with the extraction study will be used to determine chemisorption and desorption coefficients and how these coefficients will be used to improve the current cleanup model: The steps in the selective extraction procedure will provide the following information:

Steps 1 & 2 – exchangeable uranium. Step 1, the wash with $\text{Mg}(\text{NO}_3)_2$, measures the exchangeable cationic species. Mg concentrations of 0.1 M to 1.0 M are commonly used--the lower concentrations simulate more natural conditions (Yong et al., 1993). Schultz et al. (1998) suggest a concentration of 0.4 M to maximize the effect of the exchange, and Table 1 (attached) will be changed to reflect this recommendation. Step 2, the exchangeable anionic species wash with $\text{Na}_2(\text{SO}_4)$, was added to evaluate mobile, anionic forms of uranium. Although the NO_3^- will be present at a concentration of 0.8 M in Step 1, it is such a weakly complexing anion that a second rinse with SO_4^{2-} was deemed necessary. Uranium associated with the extraction fluids used in these steps is assumed to be highly mobile, and results will provide an estimate of the uranium fraction that is available for desorption.

Step 3 – digestion of carbonate grains. This step provides information on the mass fraction of uranium that is partitioned into carbonate minerals. Yanase et al. (1991) showed that a significant fraction of the total uranium (20-30 percent) in soil from Koongara, Australia was carbonate-bound. Sodium acetate solution is commonly used

to extract the carbonate fraction. Approximately 10 percent of this mass may contribute to the chemisorption load present in the sediment. The remaining uranium mass is considered background.

Steps 4 & 5 – digestion of amorphous oxides and organic material. Most of the chemisorbed uranium will be released during the digestion of the noted materials. Step 4 extracts poorly crystalline and amorphous iron oxides. Several different solutions have been used for this step, but Tamm’s reagent (0.175 M ammonium oxalate—0.1 M oxalic acid) is the standard (Chao and Zhou, 1983). Step 5 extracts organically bound uranium. Acidified H₂O₂ solution is commonly recommended (Tessier et al., 1979, Rauret et al., 1989, Schultz et al., 1998). Uranium (IV) associated with these materials could be released by changes in the redox conditions in the sediments. Steps 3, 6 & 7 will also contribute some uranium to the chemisorption load.

Step 6 – digestion of crystalline Fe oxides and oxyhydroxides. Step 6 uses dithionite to dissolve well-crystallized ferric iron oxides and oxyhydroxides. This step provides information on the mass fraction of uranium that is partitioned into crystalline iron oxide and oxyhydroxide minerals. Approximately 10 percent of this mass may contribute to the chemisorption load present in the sediment. The remaining uranium mass is considered background.

Step 7 – digestion of clays and U-oxide rims. Step 7, the strong acid leach, breaks down clays, phosphates, and some other oxide and silicate phases. This fraction is mostly uranium released from clays (Yanase, 1991) and is not generally considered part of the labile uranium, but any U oxides that survived the oxalate and dithionate washes will be removed in this step. Some fraction of the released uranium would be considered part of the chemisorption load.

Step 8 – digestion of residual phases. Step 8 is whole rock digestion of the remaining refractory phases. The uranium released during this extraction is part of the background load (zircon, monazite, etc.), and will not participate in transport.

Currently a constant, linear equilibrium isotherm assumption is made when running the VAM3D transport model, with a single value for K_d of 1.78 L/kg. The VAM3D transport model has capabilities for modeling non-linear (Freundlich) equilibrium isotherms, variable K_d values, or non-equilibrium kinetics. The study results will be used with the VAM3D transport code to improve transport model predictions of remedy performance. For example, results from Steps 1 and 2 and the groundwater uranium concentration will be used to estimate desorption coefficients, and the calculated values may be used to assign variable K_d values to different zones of the aquifer. Alternatively, the results may indicate a more complex approach is warranted, where a range of kinetic reaction rates for chemisorption will be used with the data fusion model to estimate the transport parameters. The chemisorption rates will be estimated using the appropriate uranium mass fractions from Steps 4 through 7 and 35 years as the time period over which the physically adsorbed uranium became chemically bonded to the sediment. An initial range for the reaction rates can be obtained using the results from the sequential extraction tests and this range can be the starting point for initial runs of the data fusion model, with successive iterations converging on possible solutions.

- 4) Explain why the study is identified as semi-qualitative and how semi-qualitative results will be used to meet the study’s primary objective: The phrase semi-qualitative is incorrect. Analytical results provided by this study will be quantitative. That is, laboratory QA/QC controls will be implemented with respect to test duplicates, analytical duplicates, matrix spikes, and laboratory control standards. Conclusions drawn from the use of the quantitative data will be considered reasonable estimates of

the dynamic geochemical processes active within the aquifer. A robust estimation of the range in chemisorption and desorption coefficients is the desired objective, because it is not possible to measure the results against a known true value to evaluate the accuracy of the results. The chemisorption rate will be normalized to the appropriate time period in the transport model to estimate the mass fraction of physically absorbed uranium that is permanently bound and is not available for desorption.

Action: As stated in response.

TABLE 1
SELECTIVE EXTRACTION REAGENTS AND DETAILS

Solid to Solution	Reagent	U fraction measured	Details
2g to 40 ml	0.4 M Mg(NO ₃) ₂ @ neutral pH	Exchangeable cationic species	Agitate for one hour at room temp.
Wash 15 minutes with 20 ml DI water, centrifuge and add to Mg nitrate extract			
2g to 40 ml	0.1 M Na ₂ (SO ₄) @ neutral pH	Exchangeable anionic species	Agitate for one hour at room temp.
Wash 15 minutes with 20 ml DI water, centrifuge and add to sulfate extract			
2g to 40 ml	1 M NaOAc adjusted to pH=5 with acetic acid	Carbonate Minerals	Agitate for four hours at room temp. Shouldn't release Fe, Al, or Mn. If it does, then dissolution of amorphous oxides may have occurred.
Wash 15 minutes with 20 ml DI water, centrifuge and add to acetate extract			
2 g to 200 ml	0.1 M oxalic acid + 0.175 M amm. Oxalate	Amorphous Fe, Al, Mn, Si oxides	Agitate in the dark for four hours at room temp.
Wash 15 minutes with 30 ml DI water, centrifuge and add to oxalate extract.			
2g to 40 ml	Mix 15 ml of 0.02 M nitric acid and 25 ml of 30% H ₂ O ₂ later add ammonium acetate/nitric acid	Organics	Heat to 85°C for two hours, add 25 ml more of 30% H ₂ O ₂ and heat to 85 C for three hours. Add 40 ml of 1 M ammonium acetate/nitric acid to pH = 2, shake for 30 minutes, and extract.
Wash 15 minutes with 30 ml DI water, centrifuge and add to peroxide extract			
2 g to 200 ml	Mix 0.3 M trisodium citrate, 0.2 M NaHCO ₃ , 1 g/g sample sodium dithionite; pH ~8.3 to keep from dissolving Mn.	Crystalline ferric iron oxides, oxyhydroxides	Stir for 30 minutes at 85°C; repeat extraction (total 2 times combine leachate)
Wash 15 minutes with 60 ml DI water, centrifuge and add to dithionite extract			
2g to ~50 ml	8 M HNO ₃	Clays, U oxides	Add 50 ml of 8 M HNO ₃ , mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO ₃ , replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO ₃ , repeat this step (addition of 5 ml of conc. HNO ₃) until no brown fumes are given off by the sample indicating the complete reaction. Allow the solution to evaporate to approximately 25 ml without boiling or heat at 95°C ± 5°C without boiling for two hours. Remove the acid extract after solids settle.
Wash 15 minutes with 15 ml DI and add to nitric acid extract			
0.2 g in 10 ml 1:1 HNO ₃ , 15 ml HF.	HF plus HNO ₃	Residuals (quartz, zircon, etc)	Oven dry to get wt. Crush, digest in 15 ml conc. HF plus 10 ml 1:1 HNO ₃ . Allow to go to near dryness, redissolve in 1 M HCl for analysis.

RESPONSES TO OEPA REVIEW COMMENTS ON THE PROJECT SPECIFIC PLAN FOR THE ANALYSIS OF HOW URANIUM IS SORBED AND PARTITIONED ON GREAT MIAMI AQUIFER MATRIX SEDIMENTS

5. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc. Section#: 1.0 Pg.#: 1 Line#: 26 Code: C Original Comment# 1 Comment: The last paragraph states that Kd is related to the kinetic terms alpha_c and alpha_D. This statement assumes that a linear sorption model is the appropriate model for relating soil and water concentrations. The PSP will help provide information on whether this is a valid assumption, but the validity of a linear sorption model should not be assumed before the study is completed. Previous reports have discussed differences in Kd under sorption and desorption conditions, suggesting that linear sorption concepts are not valid. We believe that data from the study will help in understanding the controls on uranium transport, but it is premature to conclude that a kinetic sorption/desorption approach will work. Further, this study does not provide any information on the kinetics of the reactions. Response: The U.S. Department of Energy (DOE) agrees that it is premature to conclude that a kinetic/desorption approach will work. The study will provide information on where uranium is located on sediment grains. This knowledge should improve our understanding on the kinetics of the reactions. Action: No action required.

6. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc. Section#: 3 Pg.#: 4 Line#: 15 Code: C Original Comment# 2 Comment: The use of archived samples for this study may produce results that are not consistent with newly collected samples. If the uranium is associated with iron oxyhydroxides, then aging and crystallization of the oxyhydroxides may impact the results. We have not performed any literature review to determine whether drying of samples affects the crystallinity of the oxyhydroxides, assuming that the archived samples have been allowed to dry. On the other hand, if the samples are still moist, what is the effect of possible microbial growth? These questions should be evaluated with respect to use of the archived samples. Response: Given the logistics associated with sample collection, it was necessary to archive some of the samples for short periods of time. It is more cost effective to run all of the analyses in batch than it is to piecemeal the work. Step 5 of the leaching process (Table 1 of the PSP) targets organics. We are not expecting a high amount of organics. If significant bacterial growth occurs, then results from Step 5 will reflect it by being biased high. This possibility will be considered as results are interpreted. Action: As stated in response.

7. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc. Section#: 3 Pg.#: 4 Line#: 18 Code: C Original Comment# 3 Comment: The four locations are associated with uranium plumes. If background concentrations are high enough to provide measurable concentrations in the extracts, collection of samples from background areas should be considered. Response: DOE agrees with the comment. Background areas were considered. It was decided to focus on areas in the uranium plume to maximize the probability of measuring uranium on the sediments. Background areas can be considered at a later date should it be deemed necessary. Action: No action required.

OEPA REFERENCES

- Schultz, M.K., Biegalski, S.R., Inn, K.G.W., Yu, L., Burnett, W.C., Thomas, J.L.W., and Smith, G. E., 1999. Optimizing the removal of carbon phases in soils and sediments for sequential chemical extractions by coulometry. *J. Environ. Monit.*, v. 1, p. 183-190.
- Schultz, M.K., Inn, K.G.W., Lin, Z.C., Burnett, W.C., Smith, G.E., Biegalski, S.R., and Filliben, J. 1998a, *Appl. Radioat. Isot.*, v. 49, p. 1289.
- Schultz, J.K., Burnett, W.C., and Inn, K.G.W. 1998b. *J. Environ. Radioact.*, v. 40, p. 155.
- Tessier, A., Campbell, P., and Bisson, 1979. *Anal. Chem.*, v. 51, p. 844.