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NSY PORTSMOUTH
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LETTER AND COMMENTS FROM U S NAVY REGARDING EVALUATION OF HEAVY METAL MIGRATION WITH GEOCHEMICAL MODELING NSY PORTSMOUTH ME
6/19/1998
NAVFAC NORTHERN

DEPARTMENT OF THE NAVY
NORTHERN DIVISION
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY
MAIL STOP, #82
LESTER, PA 19113-2090

IN REPLY REFER TO

5090
Code 1823/FE

19 JUN 1998

Mr. Iver McLeod
Maine Department of Environmental Protection
State House Station 17
Augusta, ME 04333-0017

Subj: EVALUATION OF HEAVY METAL MIGRATION AT THE PORTSMOUTH NAVAL SHIPYARD WITH GEOCHEMICAL MODELING, DECEMBER 31, 1997

Dear Mr. McLeod:

The Navy has reviewed the document titled "EVALUATION OF HEAVY METAL MIGRATION AT THE PORTSMOUTH NAVAL SHIPYARD" dated November 1997. Our comments on the above-referenced document are provided in Enclosure I of this letter.

If you have any questions regarding these comments, please contact me at (610) 595-0567.

Sincerely,

FREDERICK J. EVANS, P.E.
Remedial Project Manager
By direction of the
Commanding Officer

Copy to:
USEPA Region 1 (M. Cassidy)
US Fish & Wildlife Service (K. Munney)
NH Fish & Game (J. Nelson)
Mr. Doug Bogen
Ms. Michele Dionne
Ms. Mary Marshall
Mr. Jack McKenna
Mr. Onil Roy
Ms. Carolyn Lepage
PNS (Code 106.3R, M. Raymond)
NOAA (K. Finkelstein)
ME Dept. of Marine Resources (D. Card)
Ms. Juanita Bell
Mr. Jeff Clifford
Ms. Eileen Foley
Mr. Phil McCarthy
Mr. Guy Petty
Mr. Peter Vandermark
PNS Code 100PAO w/o encl
COMSUBGRU TWO (R. Jones)
Brown and Root Environmental (L. Klink, B. Horne)

Tetra Tech NUS, Inc. reviewed the report entitled "Evaluation of heavy metal migration at the Portsmouth Naval Shipyard with geochemical modeling" dated December 31, 1997, and generated the attached comments.

STATE OF MAINE
CHARLES D. HACE
243
CERTIFIED GEOLOGIST

Review Comments on

EVALUATION OF HEAVY METAL MIGRATION AT THE PORTSMOUTH NAVAL SHIPYARD WITH GEOCHEMICAL MODELING by Andrew Reeve, Dated December 31, 1997.

Comments by Brown & Root Environmental

GENERAL COMMENTS

1) The geochemical modeling report does not adequately draw conclusions in relationship with what is physically occurring at the site (e.g., is lead migrating to the off-shore environment). Also it is unclear if the geochemical modeling supports the Navy's fate and transport model developed by Brown & Root Environmental for OU2 and OU3 at Portsmouth Naval Shipyard (PNS). For example, does the geochemical model confirm the Navy's model is conservative or if it is adequately matching the chemical characteristics at PNS. For instance, Figure 13 shows that the concentration of lead decreases sharply from the source area. Is the interpretation of this that lead is not very mobile in the groundwater and is not moving toward the shoreline? Would this correspond to a relatively high soil/water partitioning coefficient used in the Navy's model? If conclusions such as these can not be drawn from the geochemical model, it should be indicated in the geochemical modeling report.

2) Since the simulated groundwater concentrations do not match well with the measured groundwater concentrations (some predicted concentrations are much higher than measured [approximately 50 times for mercury] and some concentrations are much lower than measured [7 orders of magnitude for copper], an uncertainty analysis or evaluation should be included to help in evaluating how realistic the geochemical modeling results are.

3) It would be helpful to the reader, if a brief conceptual model could be presented that summarizes the input, and boundary conditions for the transport model. A map would be useful showing the location of the contaminant source, groundwater flow directions, monitoring wells, and the superposition of the 1-D model grid with cell numbers identified.

SPECIFIC COMMENTS

1) Section 2

Several rounds of groundwater data have been collected at PNS using various sampling techniques. The monitoring well(s), sampling depths, sampling round, sampling technique, and dates of the chemical analyses and field measurements of pH, Eh, temperature, etc. from groundwater samples, that were used to develop the figures and input to the model should be documented in the report.

2) Section 2 Figure 1

The interpretation of the Piper plot (as stated is a representation of the major ion chemistry) is that the fresh-water and salt-water mixing is a dominant control on the general geochemistry of the groundwater. The first sentence of the conclusion sections states "Geochemical modeling indicates that the addition of salts from mixing of sea water with the fresh groundwater lens will not have a large impact due to changes in ionic strength of solutions" Are these two statements contradictory?

3) Section 2 Figure 1

It would be helpful to describe how the general mixing line was developed on Figure 1.

4) Section 2 Figure 2

For the layman, please describe why box and whisker plots were selected to show the metals concentrations, and the basis for concluding the concentrations of metals in filtered and unfiltered samples are similar. Is the conclusion based on visual comparison of the two graphs? Was a statistical analysis performed?

5) Section 3.2, First paragraph

Please describe the basis for selecting the PHREEQC model. There are several geochemical models available, why was PHREEQC selected? What are the model assumptions? What is the basis for selection of the model? Are the reaction rates rapid relative to groundwater movement? Are kinetic factors important or can equilibrium be assumed?

6) Section 3.2, First paragraph

The following statements casts considerable doubt on the modeling results: "Many of the parameters required by the model have been estimated from data presented in the Phase I report..." Furthermore, "In some cases a large amount of uncertainty is associated with these estimates." A considerable amount of time and money have been spent collecting and evaluating data from PNS. Why is it felt that there is a large amount of uncertainty? How was uncertainty determined?

7) Section 3.2, Third paragraph

Why were 2 modeling approaches used?

8) Section 3.2, Third paragraph

The modeling approach for the saturation index (SI) series of model simulations states that surface processes and organic compounds were not included. Why were surface processes and organic compounds excluded from the SI simulations? Will this modeling approach present a significant limitation to the modeling results?

9) Table 1

(a) How were the input values presented in Table 1 selected (e.g., are the input values based on maximum, average, or UCL concentrations of sample data). Please identify the sampling locations, dates, and analytical methods.

(b) Using the column name "Input Solution" conflicts with continuous input that is given in the text. Similarly, the "Initial Solution" conflicts with initial concentration.

(c) Why is the "Fresh Water End Member" concentrations different from the continuous source input concentrations and the initial concentrations input to the transport model?

(d) Why were the organic compounds selected as input to the transport model? Are these compounds surrogates for other organic compounds found at the site?

(e) Why were solutions equilibrated with mineral phases prior to input to the model?

(f) Why is alkalinity based on two different parameters for the two different simulations?

9) Table 2

(a) Why were salts added to cells 1to 10 and 21 to 30?

(b) Surface complexation sites were lowered in run 3 to evaluate the importance of this variable on the migration of lead. What was the purpose of the other runs?

10) Section 3.2, Page 6

(a) Based on the discussion on page 6, there are a significant number of assumptions which were made to perform the geochemical modeling. An uncertainty analysis or evaluation may be appropriate to ascertain the significance of these assumptions.

(b) A clay content of 10% was assumed. What is the basis for this assumption? Is this clay content representative? Furthermore, what clay minerals were assumed to be present? Are the surface properties of the clay minerals in the model representative of the clay minerals expected at the site?

(c) How valid is the equilibrium assumption?

(d) Please cite studies, preferably in coastal New England, that have shown that hydrous ferric oxides are primarily responsible for surface complexation in groundwater?

(e) Why was the surface complexation sites characterized with the weak binding site parameter? Furthermore, It is not understood what the basis for the 1.05 moles/liter Fe with 1% as hydrous ferric oxides?

(f) In regard to the discussion of adding the salts to the model cells, if 1% sea water is added to each of ten cells in the model, wouldn't the overall sea water content still be 1% in all ten cells and not 10%? Is the mixing process in the model representative of the mixing that actually occurs at the site? Groundwater mixes with seawater only in the vicinity of the shoreline. Is seawater added to model cells located in the vicinity of the shoreline?

(g) It is assumed that the waste sites are approximately 600 feet from the estuary. At the OU3 the waste material is located a maximum of about 700 feet from the shoreline and extends to the shoreline. This would seem to contradict the assumption in the geochemical model. Will this have a significant effect on the geochemical modeling results (.i.e, doe the geochemical model assume 600 feet of uncontaminated material between the source and the estuary which would not match the physical characteristics of the site)?

(h) The groundwater flow velocity (2 ft/day) used in the model is representative of Profile A (Fig. 6.4) in the Phase I Modeling Report. The velocity along other profiles is an order of magnitude lower. How does variation in the flow velocity affect the results of the geochemical modeling?

11) Section 4, Page 11

What minerals are heavy metals in equilibrium with and is it likely that those minerals are present at the Site? How will the absence of gibbsite and other minerals affect the results of

the modeling?

12) Section 4, Page 19

(a) The results indicated the model output concentrations of Hg, Pb and Ni were higher than observed at the Site. What groundwater samples were being compared?

(b) The results indicated the surface complexation sites (SCS) removes Pb from groundwater. Further, the low concentration of SCS specified in the model may partly explain the difference between the simulated and observed concentrations of Hg, Pb and Ni. Is there site data that supports the concentration of SCS sites in the model?

(c) Concentrations of Fe, Mn, Al, Ag, and Cu are higher in groundwater than predicted by the geochemical model. This was attributed to inclusion of solid particulates, colloids or organic complexes in the groundwater samples with high turbidity. The discussion of the whisker plots in Figure 2 indicates that filtered and unfiltered data are similar when low-flow groundwater data is used. Since the concentrations are the similar between the filtered and unfiltered data, it would indicate that suspended solids are not present in the groundwater and that colloidal transport is not significant transport mechanism.

(d) How would variation in some of the other input parameters affect the results? What would you expect theoretically, without running the model? How would seasonal changes in temperature and recharge affect the results?

(e) How do impurities in the mineral structure affect the SI?

(f) Please identify the thermodynamic database that was selected. How does variation of thermodynamic data affect the results?

(g) How does the process of hydrodynamic dispersion affect the results?

13) Section 5, Page 20, Paragraph 2

The Navy's contaminant Fate and transport model developed by Brown & Root Environmental is based on steady state simulation, however, the Navy disagrees with the statement that retardation would not be important in the flux of contaminants. Under steady state conditions, the retardation factor will not affect the groundwater concentration, however, it will affect the flux of contaminants (mass per time).

The retardation factor relates the contaminant velocity to the velocity of the groundwater. The velocity of the contaminant will effect the flux of the contaminant. The flux of contaminant is important to the calculation of surface water concentrations since the contaminant is mixed with a certain volume of surface water over a specific time period (related to the surface water flow rate). Also in the Navy's model, the sediment concentration is based on the surface water concentration, the groundwater concentration, and the sediment distribution coefficient (Kd). The retardation factor will also effect the estimated sediment concentration.

The retardation factor is estimated based on the distribution coefficient (Kd), therefore the Kd value is very important to the Navy's contaminant fate and transport model.

14) Section 5, Page 20, Paragraph 3-4.

It is unclear if the author is discussing the Navy's contaminant fate and transport model developed by Brown & Root Environmental or the geochemical model. This point is unclear

because the Navy's model does not calculate source terms based on measured concentrations in the sediment, rather, the Navy's model attempts to estimate a surface water and sediment concentrations based on measured (source) soil and groundwater concentrations.