M60050.001348

M60050.001348
MCAS EL TORO
SSIC # 5090.3

Bechtel

Vest A Street
10
Di CA 92101-7905

CLEAN II Program
Bechtel Job No. 22214
Contract N68711-92-D-4670
File Code: 0222

IN REPLY/REFERENCE: CTO-0080/0041

June 9, 1995

Department of the Navy - Southwest Division
Naval Facilities Engineering Command
Environmental Division
1220 Pacific Highway, RM 1832.JJ
San Diego, CA 92132-5181

Attention: Joseph Joyce, MCAS El Toro

Subject: Technical Review Comments on (Draft) RI/FS Evaluation of Background Concentrations of Inorganic Constituents in Groundwater Phase II RI/FS, MCAS El Toro, CTO-0145.

We have reviewed the subject document and have focused on two technical issues: the pyrite oxidation model and the statistical approach to defining background. For each topic we have identified key issues which appear to seriously affect the utility of this document. As always, there may be reasonable explanations for what seems to be erroneous; however, for the moment the text does not provide adequate support.

. ..ched are extensive comments on the proposed geochemical model for the development of groundwater inorganic populations at MCAS El Toro. It is our opinion that the pyrite oxidation model is not supportable based on the data collected at the station. Further, we question the need for a model which lacks corroborative data when the apparent purpose of the effort was to develop numeric background levels within groundwater.

We believe that the emphasis in this report should be on the statistical approach rather than the geochemical model which appears incorrect. Our statistical review identified what appears to be a significant error in the fundamental approach. The censoring of values below detection limits is discussed in detail in our comments. This problem results in background levels which are substantially greater than the sample population. This issue requires closer scrutiny.

If I can be of any assistance please call me in Bechtel's San Diego office at (619) 687-8780.

Best personal regards,

BECHTEL NATIONAL, INC.

Dante J. Tedaldi, Ph.D., P.E.
Technical Quality Assurance MCAS El Toro

cc:

Larry Vitale, Remedial Project Manager
California Regional Water Quality Control Board - Santa Ana Region
2010 Iowa Avenue, Suite 100
Riverside, CA 92507-2409

Juan Jimenez, RPM Base Closure Branch
State of California Environmental Protection Agency
Department of Toxic Substances Control
245 West Broadway
Suite 350
Long Beach, CA 90802-4444

Bonnie Arthur, RPM
U. S. Environmental Protection Agency Region IX
Hazardous Waste Management Division, H-9-2
75 Hawthorne Street
San Francisco, CA 94105-3901

Attachments

1. Statistical Approach

1.1 General Comments

The approach appears to be flawed due to the censoring of data below detection limits. This is a significant issue and should be addressed prior to the completion of this report which may require recalculation of all background values. Other comments on the statistical approach provided below are not as critical but should be considered.

1.2 Values Less Than Detection Limits

The "below detection limits" values were excluded from the statistical analysis (See page 2-2, last bullet). We do not concur with the current approach and believe that below detection limit values should be included for estimates of the background concentration.

A review of the data indicates that for many metals the number of nondetects is exceptionally large, often exceeding 50 percent of the population. Under these conditions, censoring these data by excluding nondetects from the database provides an artificially high background concentration. Below detection limits values are usually censored by simple substitution using one half the detection limit, not removal from the data set. Other, more complex treatments are available and their use depends on the size of the data set and the percentage of nondetects.

The typical approach of using one half of the detection limit will likely lower the background value for almost all metals at MCAS El Toro. The degree to which this change will affect the conclusion of the draft report is not clear and can only be evaluated after the recalculations are performed.

It is commonly accepted that "below detection limits" values not be ignored (Helsel, 1990). In fact, SWDIV has recommended (D. Askvig personal communication, 1995) using one half the detection limit and USEPA has issued guidance recommending the use of one half the detection limit (EPA, 1989). This approach is also used in other regions, for example, the default method recommended by the Washington State Department of Ecology (1992) is the substitution of one half the detection limit.

Table 2 for major ions is misleading because a complementary table is not provided for other inorganics including heavy metals. The creation of such a table would clearly indicate that there was an exceptionally large number of nondetects that were erroneously removed from the data set.

1.3 Normalization Techniques

An explanation is needed about the selection of the normalization procedure (see page 4-12). Explain why the maximum value was used to "normalize" instead of the common approach of estimating the "standard normal score" or expressing the values as percentage of their mean. In a normal score the deviation from the mean is measured.

Other than being expressed as percentages of the maximum observed values it is not clear what the use of the normalized values is. Provide more discussion of the interpretation of the normalized values. The total normalized scores indicate rank only and can be used only to identify wells that have the highest concentrations in total or to estimate correlation between chemicals. This should be mentioned in the text.

On page 4-12 in the first paragraph it is stated that "Normalizing the data by dividing all the concentrations by the corresponding maximum...often 'transform' the data into populations that generally fit a normal distribution". This statement is unclear because of the word "...often...," please clarify. Also explain the term "...near normal..." distribution used on page 4-12.

1.4 95th Percentile Values

What method was used for estimating the background concentration (95th percentile)? For example the value for background concentration for nickel in Table A-9b agrees with the estimate for the Upper Tolerance Limit of the 95th percentile; however, other estimates do not. Please include the formula.

On page 4-18 lognormal populations are mentioned and it is not clear if the arithmetic values of concentrations or the logarithms were used for estimating the background concentrations.. Are the background concentrations the exponents of the 95th percentile of the logarithms or the 95th percentile of the arithmetic values?

1.5 Normal Probability Plots

Only the normal probability plots of the logarithms are included in Appendix D. The normal probability plot of the arithmetic values should be also included. In general, Appendix D is unacceptable in its present format. A table should be created to explain the undefined features of the graphs and tables.

2. Geochemical Data and Proposed Models

2.1 General Comments

The technical memorandum presents a complicated conceptual model for the possible geochemical reactions in the vicinity of the site. However, the conceptual model is insupportable and presents explanations beyond the limitations of data currently available. Many of these deficiencies were identified in previously submitted comments on the Draft MCAS El Toro OU-1 Remedial Investigation Report 1 July 1994. Of most concern is that there are no data presented in either report to support: 1) the presence of iron sulfide minerals (i.e., pyrite and marcasite) in the bedrock and subsurface sediments, and 2) the presence of the high redox potential in subsurface environments.

For example, although the site has no redox potential (Eh) or dissolved oxygen (DO) measurements, geochemical reactions dependent upon an understanding of these data were presented in this document. In the absence of these measurements there is likely to

degree of uncertainty in the geochemical conceptual model involving species t dox conditions. The proposed pyrite oxidation model is only weakly d and there are other equally if not more supportable hypotheses which can be .

on, data used were based on only two sampling events, which may not be to provide the information needed for a sophisticated geochemical model. For seasonal changes in the solubility of certain oxides and metals can occur, y in shallow groundwater and these cannot be accounted for with the present (Montgomery et al., 1987). The limitations of data should be noted in the t.

ite Oxidation Model

nical memorandum indicates that pyrite oxidation is the important geochemical occurring in the area. However, the document does not discuss in which zone tion occurs. Most likely, the oxidation of pyrite would occur in the surface to subsurface soils because of the availability of oxygen. In the saturated zone, the n of pyrite, if it occurs, would not be as significant as the reaction in the vadose s due to the low dissolved oxygen as compared to the atmospheric oxygen.

or any physical evidence are presented to confirm the presence of sulfide in subsurface environments at MCAS EL Toro. Even if the presence of sulfides me e deep subsurface environments would not enhance the oxidation process of lack of sufficient quantities of dissolved oxygen in the water and the of certain type of microorganisms which work as a catalyst for the oxidation

ides oxidation in soils is a biogeochemical process that requires both high redox and presence of certain microorganisms (Thiobacillus Ferrooxidans) which as a catalyst. This redox reaction is extremely slow in the absence of these ganisms (Stumm and Morgan, 1981; Williams et al., 1979). Oxidation of sulfides considerable amounts of sulfuric acid which dissolves surrounding minerals and tied metals and drops sharply the pH of the system. Within a deep subsurface nent the presence of highly oxidizing conditions is possible but not likely. r, microorganisms such as Thiobacillus Ferrooxidans are not known to be n sufficient numbers in deep subsurface environments .

hypothesizes that the acid generated by the oxidation of iron sulfides causes the on of iron and manganese hydroxides and thus releases the adsorbed trace However, most metal exceedances are seen from monitoring wells located within line of the Station or within the contaminant plumes within or downgradient of on. As a result, there is no compelling evidence to indicate that all of the metal ces are caused by one mechanism.

2.3 Geochemical Model

Under highly acidic conditions generated by sulfide oxidation it is likely that released iron and manganese ions will interact with sulfate ions which are present at a very high concentration. Thus, the products in these highly acidic environments are expected to be iron and manganese sulfate and not the hydroxide minerals described in the draft report. Under neutral and alkaline conditions, oxyhydroxides of iron, manganese, and aluminum may be initially present as soil components but they would not be due to sulfide oxidation.

Colloidal oxyhydroxide minerals have specific (physicochemical) surface properties. Under acidic conditions (similar to those conditions generated by sulfide oxidation), oxyhydroxide surfaces have positive charges and can adsorb only anions such as selenite, arsenate, and phosphate. Metal cations such as lead, cobalt, nickel, copper, zinc, and cadmium are not adsorbed on oxyhydroxides in acidic environments.

The technical memorandum repeatedly suggests that the remobilization of metals by dissolution of iron and manganese hydroxides is caused by pyrite oxidation in groundwater in the region. However, based on information presented on Figure 3, there appears to be a pattern that the exceedances of most redox sensitive species are from wells and from within the plume located either within the MCAS El Toro fence line or downgradient of the Station. These species include iron and manganese plus those that are commonly associated with iron and manganese hydroxides such as arsenic, chromium, nickel, barium, and selenium. These exceedances were not observed in monitoring wells 18_BGMW02 and 18_BGMW17 that are located upgradient of the Station. The geochemical reactions presented in the technical memorandum suggested that pyrite oxidation and other processes are responsible for these exceedances. The document should address the possibility that the elevated metals may be derived from changes in the redox levels within the contaminant plumes, which can cause iron and manganese hydroxides to dissolve.

2.4 Relationship of TDS and Bicarbonate

The discussion on page 4-6 2nd paragraph of the direct relationship between the TDS and bicarbonate concentration is incorrect. The bicarbonate ion concentration is controlled by: 1) partial pressure of CO2 (gas), 2) activity of calcium ions, and 3) activity of hydrogen ions (pH). The text should be corrected. The reference to Hem, 1985 is missing from the draft document. We have used it and included it in our list of references.

2.5 Aluminum Mobility

The discussion on page 4-8 4th paragraph of the limited mobility of aluminum due to precipitation as aluminum silicate mineral (kaolinite) is entirely without basis. Formation of aluminum silicates (clay minerals) in soil system is very complex and it is not known to form under the circumstances described in this geochemical concept

.6 Organic Matter in the Subsurface

T scussion of the effect of pH and organic matter on adsorption (page 4-9, and 4-10) insupportable. Natural fulvic and humic acids are the major organic substances that dsorb and complex metals in soil and groundwater systems. These natural substances are ot known to be anthropogenic. The presentation of surface effects of natural organic natter on adsorption is confusing mixed with discussions about petroleum releases. It is ot clear if the intent was to propose that the release of petroleum resulted in competitive dsorption for sites or if the microbial degradation of the petroleum would result in educing conditions which would enhance the release of inorganics. This section should e revised accordingly.

.7 Evapotranspiration Effects on TDS Levels

he text on page 4-7 1st paragraph states that marine sediments are probably responsible or part of the increase in TDS because low TDS groundwater can also be relatively high n sodium and chloride. However, it also indicates that marine sediment dissolution is the rincipal source of chloride. Please clarify and explain how low TDS groundwater can ave high sodium and chloride concentrations. Furthermore, there are no calculations resented which support the assertion that evapotranspiration of agricultural return water vould be sufficient to significantly alter the TDS levels observed in groundwater.

.8 Ion Exchange

t i ted on page 4-7 2nd paragraph that calcium concentrations are more strongly ssociated with chloride than sodium because some of the sodium is exchanged for alcium in the soils and sediments.. If indeed ion exchange occurs between sodium and alcium, more likely there should be an inverse correlation between calcium and sodium oncentrations. The presentation is misleading because the concentration terms should be onverted to milliequivalents prior to making assessments of associations.

.9 Irrigation Return Waters

he text on pages 4-7 and 4-8 indicates that the irrigation water is similar to the mixed roundwater chemistry; therefore, the source of calcium and sulfate in groundwater ppears to be due to the oxidation of sulfide minerals. Sulfate may not be the dominant nion in the irrigation water; however, it is highly likely that irrigation water will dissolve ulfates in the surface soils and transport the sulfate to the saturated zone. Even the draft ocument strongly supports this mechanism on page 4-6. The document indicates that oth calcium and sulfate ions concentration appeared to be controlled by the solubility of hydrous calcium sulfate mineral (gypsum).

s previously mentioned, the technical memorandum repeatedly indicates that pyrite idation is the important geochemical process occurring in the area. However, the ocument does not discuss in which zone this reaction occurs. Most likely, the oxidation pyrite would occur in the surface to shallow subsurface soils because of the availability

of oxygen. In the saturated zone, the oxidation of pyrite, if it occurs, would not be as significant as the reaction in the vadose zone soils due to the low dissolved oxygen as compared to the atmospheric oxygen.

2.10 Microbial Interactions

The text on page 4-10, 3rd paragraph indicates that aerobic bacteria catalyze the oxidation, thereby increasing the production of sulfuric acid which in turn causes increased metals transport. However, in the same paragraph, it states that since the organic content of groundwater at MCAS El Toro is low, the bacterial effects are considered to be negligible. If so, the oxidation of pyrite that is suggested throughout the document is called into question. The oxidation of pyrite is a reaction mediated by microorganisms. Also, microorganisms play an important role in the oxidation and reduction of iron and manganese.

2.11 Presence of Dissolved Barium

The relatively high values of barium are attributed to acidic attack on the aluminosilicates. See page 4-21, 3rd paragraph and page 4-23, 3rd paragraph. However, the draft report does defend this hypothesis using site-specific groundwater pH measurements to support the generation of sulfuric acid. Thus, this hypothesis is highly questionable. Dissolved barium concentrations in groundwater more likely are controlled by the solubility of barium sulfate and adsorption to manganese oxides. In fact, from Tables A-3a and A-3b, the majority of barium concentrations seems to vary in a narrow range, which is an indication that solubility control may be a more appropriate cause for the barium concentrations (Hem, 1985).

In addition, the barium exceedances were mostly reported from wells located within the triangular shaped source area and Site 3 (Original Landfill) within the Station (see Figure 3). Based on Figure 3, it appears that the elevated barium concentrations may be caused by redox changes within or near the contamination source areas due to organic contaminants discharged to the subsurface, which can lead to the dissolution of manganese oxides.

2.12 Redox Conditions of Groundwater

The discussion on page 4-24 of the redox conditions of groundwater indicates that on the average the groundwater is under oxidizing conditions because of the relatively low percentage of detected iron concentrations. In the same paragraph, it also states that "as suggested by the relatively high 95th percentile concentrations of iron, manganese and nickel, such oxidizing conditions probably involve some pyrite oxidation." It seems to suggest that the oxidizing conditions due to pyrite oxidation is the cause for the high 95th percentile concentrations for these three metals. The oxidation of pyrite will result in depletion of oxygen at depths, which leads to an anaerobic, reducing condition. The same paragraph then states that relatively high iron concentrations can remain in solution

where sufficiently reducing conditions exits in the aquifer. Apparently, there is some inconsistency. Please clarify.

In addition, please explain how pyrite oxidation can be occurring to the extent proposed and yet there be no corresponding significant increase in soluble iron concentrations and significant decreases in pH.

2.13 Sulfate Dissolution

On page 4-25, 1st paragraph the variations in iron and other metal concentrations between the two sampling rounds are attributed to pyrite oxidation. Sulfate in groundwater is not necessarily related to pyrite oxidation; it also can be derived from recharge of irrigation water which contains sulfate from surface soils. The draft document notes this on page 4-6. If indeed sulfate is from the oxidation of pyrite in the groundwater, there is no explanation for the increase of sulfate concentrations between two sampling events. In groundwater containing high values of TDS and sulfates it is possible that the concentrations of both calcium and sulfate ions are controlled by the solubility of gypsum.

In addition, the document does not mention if the observed variations can be caused by turbid samples. A review of the turbidity values between the two sampling events may provide some information.

Another possibility is that the variations may be due to temporal variability of data reflecting the fact that the data are from only two sampling events.

2.14 Atypical Conditions at Sites 13 and 15

The text on page 5-5, 4th paragraph indicates that the available evidence shows that the elevated concentrations of major ions and trace metals in the area of Site 13 and 15 are at least partly due to isolated groundwater flow conditions. To substantiate this statement, please provide physical hydrogeologic data to support the so-called "isolated groundwater flow conditions."

Also, the text indicates that this area is impacted by natural processes such as evapotranspiration, dissolution of minerals in marine deposits and pyrite oxidation, as well as by agricultural activities. These natural processes occur throughout the entire region. It is not clear why these natural processes at Sites 13 and 15 would be different from other areas. Considering the historical uses of these sites, it would be logical to include and discuss the potential for anthropogenic impacts.

3. References

Askvig, D. 1995. Personal communication--comments from CLEAN I/II RPM and PjM Meeting on 15 February in San Diego, CA.

Francis, A. J. and Dodge, C. 1990. "Anaerobic Microbial Remobilization of Toxic Metals Coprecipitated with Iron Oxide." Environmental Science & Technology. 24: 373-378.

Helsel, D.R. 1990. "Less Than Obvious-Statistical Treatment of Data Below the Detection Limit." Environmental Science & Technology. 24(12):1766-1774.

Hem, J. D., 1985. "Study and Interpretation of the Chemical Characteristics of Natural Water." 3rd. Ed., U.S. Geological Survey Water-Supply Paper 2254.

Mongomery, R.H., Loftis, J. C., and Harris, J. 1987. "Statistical Characteristics of Ground-Water Quality Variables." Ground Water. 25(2): 176-184.

Stumm, W. and Morgan, J.J. 1981. "Aquatic Chemistry, 2nd Edition." John Wiley & Sons, New York, NY.

United States Environmental Protection Agency. 1989. "Methods for Evaluating the Attainment of Cleanup Standards." Office of Policy, Planning, and Evaluation, Washington, D.C. EPA/230/02-89-042.

Washington State Department of Ecology. 1992. "Statistical Guidance for Ecology Site Managers." Toxics Cleanup Program, Olympia, WA.

Williams, R.E., Baldwin, J., and Ralston, D.R. 1979. "Coping with Mine Drainage Regulations." In: Mine Drainage, Proceedings of the first International Mine Drainage Symposium. Ed. by Argall, G.O. and Brawner, C.O., Denver, CO.