Shaw Environmental, Inc.

312 Directors Drive
Knoxville, TN 37923
865.690.3211
Fax 865.690.3626

Shaw™ Shaw Environmental, Inc.

March 14, 2005

SHAW-MC-CK11-0323
Project No. 800486

Mr. Lee Coker
U.S. Army Corps of Engineers, Mobile District
Attn: EN-GE/Lee Coker
109 St. Joseph Street
Mobile, Alabama 36602

Contract: **DACA21-96-D-0018, Task Order CK11**
Fort McClellan, Alabama

Subject: **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 3**

Dear Mr. Coker:

Attached is the revised memorandum *Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC.* This document describes the protocol for site-to-background comparisons performed to select site-related chemicals at Fort McClellan. The memo was revised to reflect agreements reached during the meeting to resolve lingering EPA issues in Atlanta on January 25, 2005. It represents modifications to the original background screening protocol set forth in technical memoranda dated April 28, 2003, and June 24, 2003.

At your request, I have distributed copies of this document as indicated below. If you have questions, or need further information, please contact me at (865) 694-7361.

Sincerely,

J. Troy Winton for

Stephen G. Moran, P.G.
Project Manager

Attachments

Distribution: Mike Kelly, USAEC
Ron Levy, FTMC
Lisa Holstein, FTMC
Doyle Brittain, EPA Region 4
Julie Corkran, EPA Region 4
Sharon Thoms, EPA Region 4
Ted Simon, EPA Region 4
Shana Decker, ADEM
LaBarron Rudolph, ADEM
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Dave Erickson, Matrix Environmental
Steven Young, Matrix Environmental
Michelle Beekman, Matrix Environmental
Greg Schank, Matrix Environmental

Shaw Environmental & Infrastructure, Inc.

Shaw The Shaw Group Inc.™

312 Directors Drive
Knoxville, TN 37923-4799
Phone: 865-690-3211
Fax: 865-690-3626

Memorandum

Date: 14 March 2005

To: Ft. McClellan Project File

From: Karen Thorbjornsen, Jonathan Myers, and Paul Goetchius

RE: Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 3

This memo describes the protocol for site-to-background comparisons performed to select site-related chemicals at Fort McClellan (FTMC). It represents modifications to the original protocol set forth in the 28 April 2003 and 24 June 2003 technical memos.

Background screening is performed to differentiate between elements that have elevated concentrations due to natural processes versus elements that have elevated concentrations due to releases from site activities. The original protocol, which used the Slippage test, has been shown to provide an unacceptably high false-negative error rate due to the highly right-skewed nature of trace element distributions in many FTMC site data sets. The identification of exactly which site samples exhibit anomalously high elemental ratios on geochemical correlation plots was also an issue of concern. This memo reflects agreement reached between the Army (via USACE and Shaw E & I) and EPA Region 4 during the project meeting on 25 January 2005 in Atlanta, Georgia. The modifications to the methodology include the substitution of the hot measurement test for the Slippage test during the Tier 2 evaluation, and the addition of ratio plots to identify samples with anomalously high elemental ratios during the Tier 3 evaluation. The ratio plots are used in conjunction with the correlation plots when conducting the Tier 3 evaluation.

Background screening will be performed as a multi-tiered process, as follows:

Tier 1: *(Tier 1 remains unchanged from the 28 April 2003 memo.)* The maximum detected concentration (MDC) of site data is compared with the background screening criterion (BSC). Chemicals for which the MDC of site data does not exceed the BSC are considered to be present at background concentrations, are not selected as site-related chemicals and are not considered further in the risk assessment. Chemicals for which the MDC of site data exceeds the BSC are carried forward to Tier 2.

Tier 2: Tier 2 consists of two complementary statistical tests: (a) The hot measurement test is performed as the test of upper tails. This test consists of comparison of the site MDC to the background 95 UTL (for lognormally and normally distributed analytes) or the background 95th percentile (for nonparametric distributions). (b) The Wilcoxon rank sum test is performed to compare the central tendencies of the site and background distributions, for those analytes with less than 50 percent nondetects in both the site and background data sets. The background data are provided in the installation-wide background study report (SAIC, 1998). Metals that fail either of these statistical tests are then subjected to the Tier 3 evaluation. "Failure" of a statistical test means that the site data are shown to be elevated with respect to background.

Tier 3: Tier 3 consists of a geochemical evaluation to determine whether concentrations of site metals are naturally occurring or elevated due to contamination. Geochemical evaluations are based on the natural association between a trace element and one or more specific soil-forming minerals that concentrate that trace element. The correlation of the trace element of interest with a major element representing the abundance of the specific mineral that concentrates the trace element is evaluated. The selection of the major reference element is dependent on a number of general and site-specific factors as discussed below.

Some elements, under certain environmental conditions, display exclusive associations with specific reference elements. For instance, in oxic, neutral-pH soils, arsenic, selenium, and vanadium are almost exclusively associated with iron oxides, so iron is usually used as a reference element for these trace elements (Bowell, 1994; Schiff and Weisberg, 1997). The reason for this association is well understood, and is based on aqueous speciation and surface chemistry effects. These three elements are present in oxic soil pore fluid as negatively charged oxyanions ($HAsO_4^{-2}$, $HSeO_3^-$, $H_2VO_4^-$) (Pourbaix, 1974; EPRI, 1986; Brookins, 1988). Iron oxides maintain a positive surface charge that strongly attracts these oxyanions, resulting in the observed linear correlations (Bowell, 1994).

Cadmium, nickel, lead, and zinc exist in the pore fluid of most soils as positively charged divalent cations (Cd^{+2}, Ni^{+2}, Pb^{+2}, Zn^{+2}) (Brookins, 1988; Pourbaix, 1974). These trace elements have a strong affinity to adsorb on clay minerals which maintain a negative surface charge (EPRI, 1984). These elements are usually evaluated against aluminum, which is a major component of all clay minerals.

Chromium can be present in soil pore fluid as a mixture of aqueous species with different charges such as $Cr(OH)_2^+$, $Cr(OH)_3^o$, and $Cr(OH)_4^-$, depending on the pH of the pore fluid (EPRI, 1984). The positive, neutral, and negative charges on these species result in the distribution of chromium on several different types of sorptive surfaces, including clay and iron oxide minerals. Higher soil pH conditions will favor the anionic Cr species which adsorb on iron oxides, and lower soil pH conditions will favor the cationic Cr species which preferentially adsorb on clay minerals.

Manganese oxides have a specific affinity to adsorb barium, cobalt, and lead (Kabata-Pendias, 2001). In most soils, the manganese concentrations are too low for it to form discrete manganese oxide minerals. However, in oxic, manganese-rich soils, minerals such as pyrolusite (MnO_2) and nsutite ($MnO_{1.9}$) will form that strongly adsorb Ba, Co, and Pb. Under reducing, low CO_2

conditions, the minerals MnO•OH, Mn_2O_3 and Mn_3O_4 will form, which also concentrate these trace elements. Under reducing, high CO_2 conditions however, Mn will be present as rhodochrosite ($MnCO_3$) which does not have as strong adsorptive properties as the Mn-oxides (EPRI, 1984).

Soils that contain fragments of limestone often show linear correlations between barium, cadmium, cobalt, nickel, strontium, lead, and zinc versus calcium. This is because these divalent metals readily substitute for calcium in calcite ($CaCO_3$) and dolomite [$(Ca,Mg)CO_3$], which are the major minerals present in limestone. This association is also common in arid regions where the divalent metals co-precipitate with calcite and gypsum ($CaSO_4 \bullet 2H_2O$) in caliche horizons.

Arkosic soils that contain unweathered fragments of feldspar have very different trace/major element associations, reflecting the mineralogy of the primary igneous or metamorphic source material. For instance, beryllium is associated with alkali feldspars which all contain sodium, potassium and aluminum, so the correlations of beryllium versus those major elements would be evaluated.

Total organic carbon is a good reference element for mercury, which has a strong affinity for adsorption on natural organic material. Mercury often shows better correlations with total organic carbon than with inorganic reference elements.

In reducing environments such as swamps, bogs, and wetlands where organic content is high, anaerobic sulfate-reducing conditions can become established. Under these conditions, trace elements such as arsenic, cadmium, nickel, lead, and zinc will co-precipitate with iron as sulfide minerals. These trace metals in this environment would be expected to be correlated with iron and sulfide in soil samples.

Care must be taken in the selection of reference elements to ensure that those elements are themselves not directly or indirectly impacted by contamination. Aluminum is usually a good reference element because it is not sensitive to redox conditions, and direct aluminum contamination is rare. A further advantage of aluminum is its low solubility over the neutral pH range, but it does become soluble at pH conditions below 4 and above 9. The release of strong acids or bases will leach aluminum from soil and solubilize aluminum in groundwater, so evaluation of the pH conditions is important.

Examining the correlation between iron versus aluminum in soil is an important tool in geochemical evaluations. Both elements tend to concentrate in the finer grain size fractions as oxide and clay minerals, respectively. Concentrations of iron and aluminum may vary from sample to sample by orders of magnitude reflecting differences in grain size, but they are usually present at a fixed ratio. Site samples that plot off of the trend established by the background samples and exhibit anomalously high Fe/Al ratios, may have some excess component of iron, suggesting contamination from rust, machine shop sweepings, ferric chloride sludge, etc. If iron contamination is identified in some samples, then those samples should be identified as such and removed from the evaluation, or an alternate reference element should be selected.

Iron and manganese in groundwater are subject to reductive dissolution effects which should be evaluated before they are used as reference elements. The release of organic contaminants such as hydrocarbon fuels or chlorinated solvents can establish local reducing environments caused by anaerobic microbial degradation of the organic compounds. The establishment of local reducing conditions can drive the dissolution of iron and manganese oxides, which become soluble as the redox potential drops below a threshold value. Dissolution of these oxide minerals can mobilize the trace elements that were adsorbed on the oxide surfaces, which is a process termed "reductive dissolution." Several investigations have documented the mobilization of arsenic, selenium, and other trace elements under locally reducing redox conditions (Sullivan and Aller, 1996; Nickson, et al., 2000; Belzile, et al., 2000).

Evidence for reductive dissolution would be a correlation between elevated trace elements (arsenic, selenium, and vanadium in particular) versus lower redox conditions. Low redox conditions can be identified in groundwater by local depressions in oxidation-reduction potential or dissolved oxygen measurements; the presence of detectable ferrous iron; or the presence of reducing gases such as hydrogen, methane, ethane, or ethene. Anaerobic microbes can also reduce sulfate to sulfide and nitrate to ammonia, resulting in local depressions in sulfate and nitrate concentrations, and local detections of sulfide and ammonia. In areas impacted by chlorinated solvents, additional evidence for the establishment of anaerobic reducing conditions is the presence of dichloroethene and/or vinyl chloride, which are reductive dechlorination products resulting from the microbial degradation of trichloroethene or tetrachloroethene under anaerobic conditions.

An additional technique that is used to identify the presence of local reducing conditions in groundwater is a correlation plot of iron versus aluminum. These two elements are usually highly correlated in oxic groundwater because they are both insoluble and tend to be present as suspended particulates at a fairly constant ratio. If local reducing conditions are present, then samples from those areas will have a higher Fe/Al ratio than oxic areas because iron becomes soluble under reducing conditions but aluminum does not. Results can be independently confirmed by evaluating manganese versus aluminum because manganese and iron have similar redox behavior.

All available laboratory and field data are examined to determine if there is a local reducing environment that is driving the dissolution of iron and manganese oxides, as this effect may cause erroneous geochemical evaluation results if this process is not taken into account. Field measurements of oxidation-reduction potential, and concentrations of dissolved oxygen, ferrous iron, and sulfide are useful in identifying natural or contaminant-induced changes in redox conditions that may alter elemental ratios. Data are also evaluated for pH anomalies and the presence of organic contaminants that may alter the geochemical environment.

Ratio Plots. Site samples with a trace element present as a contaminant will exhibit anomalously high trace-versus-major element ratios compared to background trace-versus-major element ratios. These elevated ratios may not always be apparent in log-log correlation plots, especially at the upper range of concentrations. Therefore, ratio plots – which depict trace element concentrations on the y-axis and trace/major element ratios on the x-axis – are employed in conjunction with correlation plots in those cases where it is not immediately apparent which site samples have anomalously high elemental ratios on the correlation plots. The ratio plots permit easy identification of samples with anomalously high elemental ratios relative to background, and they have high resolution over the entire concentration range.

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Sullivan, K. A. and R. C. Aller, 1996, "Diagenetic cycling of arsenic in Amazon Shelf sediments," *Geochimica et Cosmochimica Acta*, Vol. 60, No. 9, pp. 1465-1477.

ADEM

ALABAMA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
POST OFFICE BOX 301463 36130-1463 ◆ 1400 COLISEUM BLVD. 36110-2059
MONTGOMERY, ALABAMA
WWW.ADEM.STATE.AL.US
(334) 271-7700

ONIS "TREY" GLENN, III, P.E.
DIRECTOR

BOB RILEY
GOVERNOR

Facsimiles: (334)
Administration: 271-7950
General Counsel: 394-4332
Communication: 394-4383
Air: 279-3044
Land: 279-3050
Water: 279-3051
Groundwater: 270-5631
Field Operations: 272-8131
Laboratory: 277-6718
Mining: 394-4326

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March 31, 2005

Ronald M. Levy
BRAC Environmental Coordinator
Environmental Office, 291 Jimmy Parks Blvd.
US Army Garrison
Fort McClellan, Alabama 36205

RE: ADEM Notice of Concurrence: *Selected Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 3.* Document dated March 14, 2005
Fort McClellan, Calhoun County, Alabama
EPA ID No. AL4210020562 DSMOA Site ID 2535-223-0445

Dear Mr. Levy:

The Alabama Department of Environmental Management (ADEM or the Department) has reviewed the subject risk assessment submittal for Fort McClellan.

The Army, EPA, and ADEM met at EPA headquarters in Atlanta on January 25, 2005 to discuss risk assessment issues at Fort McClellan. ADEM representatives Frederick L. Rudolph and Shana Decker were in attendance at this meeting. The subject document is a Memorandum from Shaw Environmental & Infrastructure, Inc. describing the protocols suggested and proposed at the meeting. The purpose of the memorandum is reportedly to formally update the protocol for the multi-tiered screening process that Fort McClellan intends to use to identify site-related chemicals. ADEM's understanding of the revised protocol is as follows.

Tier 1 of the background screening process is unchanged. Tier 2 was changed by removing the use of the slippage test, which reportedly provided a high false-negative error rate. The Army and EPA agreed to use the hot measurement test as a replacement for the Slippage test. Tier 3, the geochemical evaluation, was also revised at the request of EPA. The geochemical correlation plots used in Tier 3 will now be accompanied by ratio plots, a tool to supposedly avoid anomalously high elemental ratios during the evaluation. The memorandum also provides a description of several trace elements, with information supporting the natural association of the trace elements with different soil types and relatively ubiquitous elements. It also provides a qualitative explanation of some of the conditions that affect trace element correlations.

Birmingham Branch
110 Vulcan Road
Birmingham, Alabama 35209-4702
(205) 942-6168
(205) 941-1603 [Fax]

Decatur Branch
2715 Sandlin Road, S.W.
Decatur, Alabama 35603-1333
(256) 353-1713
(256) 340-9359 [Fax]

Mobile Branch
2204 Perimeter Road
Mobile, Alabama 36615-1131
(251) 450-3400
(251) 479-2593 [Fax]

Mobile - Coastal
4171 Commanders Drive
Mobile, Alabama 36615-1421
(251) 432-6533
(251) 432-6598 [Fax]

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The Department concurs with the proposed changes to the process as outlined in the Memorandum. However, ADEM will continue to evaluate the application of the three-tiered screening process on a case-by-case basis.

For any questions or concerns regarding this matter, please contact Ms. Shana Decker via email at sdecker@adem.state.al.us or at (334)-270-5684.

Sincerely,

Stephen A. Cobb, Chief
Governmental Hazardous Waste Branch
Land Division

SAC/JWG/SD/mal

cc: Mr. Doyle Brittain/EPA Region 4
Mr. Lee Coker/USA COE, Mobile District
Mr. Jim Grassiano/ADEM
Ms. Brandi Little/ADEM
Mr. Steve Moran/Shaw
Mr. Frederick L. Rudolph/ADEM
Ms. Miki Schneider/JPA

File:Land Div/Hazardous Waste/Fort McClellan/AL4210020562/Correspondence/2005

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
ATLANTA FEDERAL CENTER
61 FORSYTH STREET
ATLANTA, GEORGIA 30303-8960

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November 20, 2007

<u>EMAIL & US MAIL</u>

4WD-FFB

Lisa Holstein
BRAC Environmental Coordinator
U.S. Army Transition Force, Fort McClellan
P.O. Box 5022
Anniston, AL 36205-5000

SUBJ: Memorandum, Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 3, March 14, 2005; Fort McClellan, Alabama

Dear Ms. Holstein:

The Environmental Protection Agency (EPA) has reviewed the subject document and agrees with it as written. Therefore, EPA approves the subject document. If you have any questions, please call me at (404) 562-8549.

Sincerely,

Doyle T. Brittain

Doyle T. Brittain
Senior Remedial Project Manager

cc: Michael Kelly, US Army AEC
Brandi Little, ADEM
Lee Coker, USA/COE
Steve Moran, Shaw Environmental
Daniel Copeland, CEHNC-OE-DC
Bernie Case, ALANG
Miki Schneider, JPA
Wayne Sartwell, ALANG
Pete Tuttle, USF&WS