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**13. SUPPLEMENTARY NOTES**

None.

**14. ABSTRACT**

The Final Work Plan for the Geochemical Evaluation of Metals in Groundwater at Ravenna Army Ammunition Plant, Ravenna, Ohio summarizes the technical approach, data analysis procedures, reporting requirements, and management for the execution of work under this project. It was prepared in accordance with the requirements included in the contract award.

**15. SUBJECT TERMS**

Final Work Plan for the Geochemical Evaluation of Metals in Groundwater at Ravenna Army Ammunition Plant, Ravenna, Ohio

| 16. SECURITY CLASSIFICATION OF: a. REPORT | b. ABSTRACT | c. THIS PAGE | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| Unclassified | Unclassified | Unclassified | UL | 64 | David Cobb |
| | | | | | **19b. TELEPHONE NUMBER** *(Include area code)* 617.589.5561 |

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**17. LIMITATION OF ABSTRACT.** This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

# Final Work Plan for the Geochemical Evaluation of Metals in Groundwater at Ravenna Army Ammunition Plant, Ravenna, Ohio
**Version 1.0**
**Ravenna Army Ammunition Plant**
**Ravenna, Ohio**

**Contract No. W912QR-08-D-0013**
**Delivery Order 0006**

**Prepared for:**

US Army Corps of Engineers ®
Louisville District
**600 Martin Luther King, Jr. Place**
**Louisville, Kentucky 40202**

**Prepared by:**

**Shaw Environmental & Infrastructure, Inc.**
**100 Technology Center Drive**
**Stoughton, MA 02072**

**March 25, 2010**

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| National Guard Bureau | 0 | 1 |
| OHARNG Environmental Specialist | 1 | 1 |
| Ohio EPA Facility Manager | 2 | 2 |
| USACE – Louisville District Project Manager | 3 | 3 |
| USAEC – Program Manager | 0 | 1 |
| Shaw Project Manager | 3 | 3 |

BRAC – Base Realignment and Closure
OHARNG – Ohio Army National Guard
Ohio EPA – Ohio Environmental Protection Agency
RVAAP – Ravenna Army Ammunition Plant
Shaw – Shaw Environmental & Infrastructure, Inc.
USACE – U.S. Army Corps of Engineers – Louisville District

## CONTRACTOR'S STATEMENT OF INDEPENDENT TECHNICAL REVIEW

Shaw Environmental & Infrastructure, Inc. has completed the *Final Work Plan for the Geochemical Evaluation of Metals in Groundwater at Ravenna Army Ammunition Plant, Ravenna, Ohio*. Notice is hereby given that an independent technical review has been conducted that is appropriate to the level of risk and complexity inherent in the project. During the independent technical review, compliance with established policy, principles, and procedures, utilizing justified and valid assumptions, was verified. This included review of technical assumptions; methods, procedures and materials to be used; and whether the product meets customer's needs consistent with law and existing Corps policy.

Reviewed/Approved by: ____________________ Date: 03/25/2010

David Cobb
Project/Program Manager

Reviewed/Approved by: ____________________ Date: 03/25/2010

Jonathan Myers, PhD.
Senior Environmental Engineer

# *Table of Contents*

## List of Figures



## List of Tables



## List of Appendices

# *Acronyms and Abbreviations*

| | |
|---|---|
| DFFO | Director's Final Findings and Orders (Ohio EPA) |
| EPA | Environmental Protection Agency (United States) |
| Ohio EPA | Ohio Environmental Protection Agency |
| POC | Point of Contact |
| RAB | Restoration Advisory Board |
| RVAAP | Ravenna Army Ammunition Plant |
| Shaw | Shaw Environmental & Infrastructure, Inc. |
| SOW | Scope of Work |
| USACE | U.S. Army Corps of Engineers |

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# 1.0 Introduction

Under Contract No. W912QR-08-D-0013, Delivery Order 0006, the Louisville District, U.S. Army Corps of Engineers (USACE) contracted Shaw Environmental & Infrastructure, Inc., (Shaw) to conduct a geochemical evaluation of metals in groundwater at the Ravenna Army Ammunition Plant (RVAAP), Ravenna, Ohio. The geochemical evaluation is necessary to determine if elevated concentrations of detected metals in groundwater are naturally occurring or chemicals of concern. This Scope of Work (SOW) identifies specific requirements that will be completed by the Contractor.

## 1.1 Project Objective

The objective of this project is to characterize the naturally occurring background distributions of 23 elements in groundwater at RVAAP on a facility-wide basis. In addition, the site-specific geochemical and hydrogeological processes controlling the concentrations of elements in groundwater at the facility will be identified. This information will be useful in future groundwater investigations for properly distinguishing between naturally occurring concentrations versus impact from contamination-related to site activities. The approach is based on screening and evaluating Army-provided laboratory analytical results from previously conducted comprehensive site-wide groundwater sampling events involving at least 237 wells.

## 1.2 Document Organization

The balance of this document is organized as follows:

- Section 2.0 – Data Evaluation Methodology
- Section 3.0 – Geochemical Evaluation Report
- Section 4.0 – Project Management
- Section 5.0 – Schedule
- Section 6.0 – References

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# 2.0 Data Evaluation Methodology

The primary source of data for the background characterization will be an October 2009 sampling event that will obtain filtered (0.45 micron) and unfiltered pairs of samples from 237 existing groundwater monitoring wells. All samples will be analyzed for the United States Environmental Protection Agency (EPA) 23-element Target Analyte List. In addition, standard field parameters (temperature, turbidity, specific conductivity, pH, dissolved oxygen, and oxidation-reduction potential) will be collected from each well. Analyses of additional samples from deep wells and/or results from older sampling events may also be used in the evaluation. All sampling and data validation activities will be conducted by the Army. Following validation and preparation of the data, the information will be provided to Shaw by the Army in Microsoft® Access® database format.

It is anticipated that some of the samples will be representative of natural background conditions, and others will be impacted by current and/or historic activities performed at the facility. The analytical results from each well will thus need to be carefully screened to identify and remove any impacted samples from the candidate background data set so that the final data set is truly representative of background conditions. The background data screening process includes multiple procedures based on statistics and geochemistry that are designed to identify and remove potentially contaminated samples from the data sets, such that the remaining samples contain only naturally occurring concentrations of metals.

Prior to screening, the laboratory and field data will be transformed from a Microsoft® Access® database "record" format to a "cross-tab" spreadsheet format to facilitate evaluation. A cross-tab format contains all of the results from a given sample on the same row, with all of the results for an individual analyte or field parameter in the same column.

Following this data transformation, all of the analytical data will be screened using the following steps, which will be performed sequentially, although some iteration between steps may be necessary:

1. Screen data for completeness and acceptable quality, considering analytical methods, method reporting limits, quantitation limits, and presence of laboratory qualifiers and field parameters.
2. Perform a statistical outlier test for each analyte. Examine outliers to determine whether they reflect site-related contamination (see Step 6), transcription errors, etc., and eliminate as appropriate.
3. Eliminate "high nondetects" (nondetect results with reporting limits that are in the upper 10 percent of the distribution). Removal of these results ensures that the

background screening values are not biased high due to the presence of nondetect results with elevated reporting limits.

4. Eliminate samples that exhibit impacts from the presence of organic contaminants. The presence of high concentrations of organic constituents in groundwater can, under certain conditions, depress the local redox potential of the aquifer. Local redox depression can cause the dissolution of naturally occurring iron and manganese oxide minerals within the reduced zone of the aquifer. These minerals have very strong affinities to adsorb certain elements including antimony, arsenic, molybdenum, selenium, and vanadium; which can become mobilized when the oxide minerals dissolve. This "reductive dissolution" effect can be easily identified in impacted groundwater samples because they will have low dissolved oxygen and redox potential; and elevated dissolved concentrations of iron, manganese, and associated trace elements. Unfiltered aluminum/iron ratios, and filtered/unfiltered ratios for iron and manganese are accurate independent redox indicators, and will also be evaluated during this step.

5. Prepare probability plots of metal concentrations to identify the presence of multiple distributions and statistical outliers. Examine outliers to determine whether they reflect site-related contamination (see Step 6) and eliminate as appropriate.

6. Perform geochemical evaluations to determine whether metal concentrations are naturally occurring. This step involves graphically examining selected trace versus major element ratios to identify samples with anomalously high ratios, which is an indicator of potential contamination. A large number of exploratory correlation and ratio plots are generated at this step to identify the site-specific elemental associations. Ratios of concentrations in filtered versus unfiltered samples, and correlations between element concentrations versus selected field parameters will also be evaluated. Samples exhibiting anomalous trace versus major element ratios will be considered suspect and be eliminated from the candidate background data set. The advantage of the geochemical evaluation step is that it distinguishes anomalously high metal concentrations from naturally elevated concentrations in groundwater samples with elevated turbidity. Samples with elevated turbidity will be retained if no evidence of contamination is observed; this allows the background groundwater data set to reflect the full range of concentrations that are likely to be observed in future site investigation data sets, thus avoiding a low bias in the background screening values. For reference, the theory and application of geochemical evaluation of groundwater can be found in publications by Thorbjornsen and Myers (2007, 2008).

7. Spatial relationships will be considered during the screening process to determine whether subpopulations are present in the background data sets. Groundwater samples obtained from different hydrostratigraphic units or from different watersheds may show different distributions of concentrations. Likewise, groundwater from naturally reducing wetland environments may show different distributions than samples from toxic environments. Statistical tests such as the Wilcoxon Rank Sum test along with probability plots and geochemical relationships will be used to identify significant differences in subpopulations. If evidence for subpopulations exists, then these data

will be subdivided into groups, and separate background distributions will be defined for each group.

Data that survive the multi-step screening process will be regarded as representative of background metal concentrations at Ravenna, and will be used to calculate background summary statistics. These statistics will include the number of samples, percent of nondetects, distribution shape (normal, lognormal, nonparametric) minimum, median, arithmetic mean, 95th upper confidence limit of the mean, 95th upper tolerance limit, and the maximum concentration. The Upper Concentration Limits and Upper Tolerance Limits will be calculated using nonparametric bootstrap methods to maintain consistency and avoid bias (EPA, 1997 and 2009).

These statistics provide a complete description of the distributions that can be used for future site-to-background comparisons. The screened data will also be provided for use in nonparametric site-to-background comparison tests such as the Wilcoxon rank sum test, which requires the actual data rather than summary statistics such as the mean and standard deviation.

Additional information related to the approach associated with the geochemical evaluation was presented by Shaw during a meeting at RVAAP on 9 February 2010. A copy of the slideshow presentation has been included in Appendix A.

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# 3.0 Geochemical Evaluation Report

Documentation of the methodology and results of the evaluation will be provided in a written report that will include the following information:

- A description of the statistical and geochemical screening and evaluation methodologies, including the theoretical basis for the geochemical methods will be provided. Literature references to the theory, previous applications, and case studies will be included.
- Narratives for each element will be provided that will include probability, correlation, and ratio plots (as applicable) to graphically illustrate the screening process and results. If a significant proportion of samples are rejected during the screening process, then plots of pre-screened and post-screened data may be provided in the report for comparison.
- Complete statistical descriptions of the fully screened background distributions will be provided for each element as described in Section 2.0 above. The screened analytical data will also be provided in electronic format.
- The site-specific geochemical and hydrogeological processes controlling the concentrations of elements in groundwater at the facility will be identified. This information will be useful in future groundwater investigations for properly interpreting the results of future groundwater sampling events and distinguishing between naturally high concentrations versus contamination.
- A discussion of the occurrences of inorganic contamination in the rejected samples will be included. This discussion may be useful to form the basis for a petition to eliminate certain elements and/or wells from long-term monitoring programs or future remediation programs at the facility if it can be demonstrated that some elements are not contaminants or if no contamination is present at some wells.
- A general discussion of effective remediation methods for specific inorganic contaminants of interest in groundwater at the facility will be provided.

The Preliminary Draft Report will be submitted on or before 30 May 2010. Upon receipt of Army comments and resolution of those comments, Shaw will prepare and submit a Draft Report for stakeholder review and approval. Shaw will submit the Final Report within 30 calendar days of receipt of Ohio EPA comments. Schedules specified by the Ohio EPA will take precedence over the USACE schedule. The number and distribution list for the versions of the report are in Table 3-1, "Document Distribution List."

**Table 3-1**
**Document Distribution List**

| Document / Recipient | Paper Copies | Electronic Copies |
|---|---|---|
| ***Preliminary Draft Report*** | | |
| USACE –Louisville District | 3 | 3 |
| RVAAP Project Manager | 2 | 2 |
| National Guard Bureau | 0 | 1 |
| Ohio Army National Guard (OHARNG) | 1 | 1 |
| ***Draft Report*** | | |
| USACE – Louisville District | 2 | 3 |
| RVAAP Project Manager | 2 | 1 |
| National Guard Bureau | 0 | 1 |
| OHARNG | 1 | 1 |
| Ohio EPA | 2 | 2 |
| USAEC Program Manager | 0 | 1 |
| ***Final Report*** | | |
| USACE – Louisville District | 2 | 3 |
| RVAAP Project Manager | 2 | 1 |
| National Guard Bureau | 0 | 1 |
| OHARNG | 1 | 1 |
| Ohio EPA | 2 | 2 |
| USAEC Program Manager | 0 | 1 |

*Ohio EPA = Ohio Environmental Protection Agency*
*RVAAP = Ravenna Army Ammunition Plant*
*USACE = U.S. Army Corps of Engineers*
*USAEC = U.S. Army Environmental Command*

Shaw will ensure that review and response periods are consistent with the applicable regulatory drivers (see Director's Final Findings and Orders [DFFO]) (Ohio EPA, 2004). It is understood that Ohio EPA, per the DFFO, requires a minimum of 45 calendar days to review and comment on each submittal provided for this project. The included project schedule (Appendix B, "Project Schedule") accounts for a 45 day review period for each document to be provided to regulators. To the extent possible, Shaw will work with regulators in an effort to expedite turnaround times based on the Ohio EPA's available resources. Shaw will ensure that the USACE will be present during, or will have prior knowledge of, all correspondence with EPA regulators.

With the exception of the Quality Control Plan, each document under this contract (reports, work plans, etc.) will be identified as Draft until completion of Stakeholder coordination. Each document will only be issued as Final after Stakeholder's comments have been completely addressed and concurrence has been received from each Stakeholder. The report will be submitted in electronic and printed format in accordance with the latest version of the *Ravenna Army Ammunition Plant Submission Document Format Guidelines* (Vista Sciences Corporation, 2009). Per the SOW, the Quality Control Plan will be issued as Draft and Final for review and approval by the USACE only.

The Final Report will be provided in electronic format for posting to the Ravenna Environmental Information Management System. The final electronic document will be a text-searchable Adobe® Acrobat® Portable Document Format (PDF) file and will be accompanied by defined metadata for upload into the Army Repository of Environmental Documents. The Final Report will also be submitted on Compact Disc/Digital Versatile Disc in Microsoft® Word® and Microsoft® Excel®.

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# 4.0 Project Management

Shaw has assigned Mr. David Cobb as Project Manager for this project. Mr. Cobb is qualified to oversee all work described in the SOW and will serve as the single point of contact (POC) and liaison for all work required.

The following activities and deliverables will be performed in support of this project:

- Monthly Progress Reports with schedule update
- Records of Conversations
- Teleconference Progress Updates
- Meeting Minutes Documentation
- Public Involvement/Restoration Advisory Board (RAB) Meetings

The above activities will be conducted by Shaw to achieve project execution, and maintain communication with the USACE. These activities are discussed in further detail below.

## 4.1 Monthly Progress Reports

Shaw will submit monthly written progress reports to the USACE POC for every month by the fifth day of the following month. The monthly reports will include an accurate and current account of all work completed and deliverables furnished to the Ravenna stakeholders. An example of the monthly report and its content is presented as Figure 4-1, "Example Monthly Progress Report."

## 4.2 Records of Conversations

Shaw will prepare and maintain records of telephone conversations and significant verbal conversations conducted in support of this project. These records will be forwarded with monthly progress reports.

## 4.3 Teleconference Progress Updates

Mr. Cobb currently attends biweekly teleconference progress meetings with the USACE. The purpose of the meetings is to provide project status updates on various RVAAP projects. A brief update on this project's status will be provided as part of the calls.

## 4.4 Meeting Minutes Documentation

Shaw will take minutes at all meetings held in support of this project. Meeting minutes will be typed, and distributed to the USACE and respective POCs within seven calendar days following the meeting.

## 4.5 Public Involvement/Restoration Advisory Board Meetings

The RVAAP has an active RAB. Shaw will present the findings of the geochemical evaluation during one or more of the RAB meetings if requested by the USACE.

**Figure 4-1**
**Example Monthly Progress Report**

**DEVIATION IN SCHEDULE (with explanation):**

**INVESTIGATIVE DERIVED WASTE:**

**REMARKS:**

PROJECT REPRESENTATIVE: ____________________ SIGNATURE ______________________________

SHAW PROJECT MANAGER: ____________________ SIGNATURE ______________________________

# 5.0 Schedule

A resource loaded project schedule has been prepared and is presented in Appendix B. The schedule will be updated on a monthly basis to reflect the most current project conditions. The updated schedule will be submitted as an attachment to the Monthly Progress Report (Section 4.1). Shaw will notify the USACE and Ohio EPA in the event of any significant schedule variations and in accordance with the provisions of the DFFO (Ohio EPA, 2004). At present, the above SOW is contractually scheduled to end no later than 30 September 2009.

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# 6.0 References

Ohio Environmental Protection Agency (Ohio EPA), 2004, *Director's Final Findings and Orders, Ravenna Army Ammunition Plant*, June 10.

Thorbjornsen, K. and J. Myers, 2007, "Identifying Metals Contamination in Groundwater Using Geochemical Correlation Evaluation," *Environmental Forensics*, Vol. 8, Nos. 1-2, pp. 25-35.

Thorbjornsen, K. and J. Myers, 2008, "Geochemical Evaluation of Metals in Groundwater at Long-Term Monitoring Sites and Active Remediation Sites," *Remediation*, Vol. 18, Issue 2, pp. 99-114.

U.S. Environmental Protection Agency (EPA), 1997, *The Lognormal Distribution in Environmental Applications, Technical Support Center Issue*, EPA/600/R-97/006.

U.S. Environmental Protection Agency (EPA), 2009, *ProUCL Version 4.00.04, Technical Guide*, EPA/600/R-07/041, February.

Vista Sciences Corporation, 2009, *Ravenna Army Ammunition Plant Submission Document Format Guidelines*, Version 17.0, Ravenna, Ohio, September 18.

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# *APPENDIX A*
# *GEOCHEMICAL EVALUATION APPROACH*

# Geochemical Evaluations of Metals in Groundwater:

*Distinguishing Naturally Elevated Concentrations from Contamination*

**Jonathan Myers Ph.D.**
**Shaw Environmental, Inc.**

**February 9th, 2010**
**On Site RVAAP Meeting Presentation**

1-1

## Geochemical Evaluation

- Considers observed interrelationships between element concentrations.
- Evaluates observations based on known geochemical behaviors of the elements in the site-specific environment.
- Not a statistical method.
- Distinguishes between contamination versus naturally high background concentrations.
- Identifies natural and anthropogenic processes controlling concentrations.
- Can identify sources of contaminants when properly performed. Good forensic technique.

2

# Presentation Outline

1. Standard statistical approaches and limitations
2. Geochemical mechanisms controlling trace element concentrations in groundwater and surface water
3. Case studies
4. Additional applications

3

# Standard Statistical Approach: Bright Line Comparison

| Statistic | Comment |
|---|---|
| Max BG | Value tends to increase as *n* increases |
| 2x mean | No statistical validity, does not consider variance or skewness |
| 3x median | " |
| mean+2$\sigma$ | Considers $\sigma$ (good), assumes normality (bad) |
| mean+3$\sigma$ | Similar to mean+2$\sigma$ but less conservative |
| 95$^{th}$ percentile | Only representative of population if *n* is large |
| 95$^{th}$ UTL | Slightly larger than 95$^{th}$ percentile to extrapolate to population |
| Quartile | [1.5 x IQR] + 75$^{th}$ percentile, needs accurate 25$^{th}$ %ile |
| 95$^{th}$ UPL | Only valid for *k* future observations, not practical for multipurpose BG study |

4

# Standard Statistical Approach: Two-Sample Comparisons

**Parametric**

*t*-test - Normality assumed

*F*-test - Test of variance

**Nonparametric**

Wilcoxon Rank Sum (WRS; a.k.a. Mann Whitney) test – Comparison of medians

Gehan test – WRS with mixed reporting limits (RLs)

Quantile test – Upper tails

Rosenbaum (a.k.a Slippage) test – Upper tails; high false-negative error rate

5

# Limitations of Statistical Approach

- Trace element concentrations span wide range (3 to 4 orders of magnitude)
  - Large range requires more samples to characterize
  - Valid $n$ proportional to $\sigma^2$
- Distributions are highly right-skewed (lognormal)
  - Skewness requires even more samples to characterize upper range
- Insufficient number of background samples
- Unequal sample sizes ($n_{Site} >> n_{BG}$) and variances

6

# Limitations of Statistical Approach
(continued)

- Representativeness of facility-wide background data set
- Presence of estimated (J-flagged) concentrations
  - High analytical uncertainty increases test error rates
- Presence of nondetects
  - Substitution (RL, ½RL, MDL, ½MDL, 0), Kaplan Meier, Survival, etc.
  - All options for treatment of nondetects cause problems
- Differences in labs, reporting limits, sampling methods, etc.

- 95 % confidence level = 5 % false-positive error rate:
  - Minimum rate
  - Only achieved with ideal data

7

# Problems With Standard Approach
(continued)

- **Result:** Lots of apparent background exceedances

- **Consequence**: Lots of unnecessary activities:
  - Declaration of contamination
  - Additional sampling and analysis
  - Risk assessments
  - RI/FS activities
  - Remedial actions!

- **Solution:** Integration of geochemical evaluation in data analysis

8

# Reasons for Elevated Metals in Groundwater and Surface Water

- Suspended particulates
- pH effects
- Natural redox effects
- Reductive dissolution
- Total dissolves solids effects
- Complexation effects ($Cl^-$, $F^-$, $CO_3^{2-}$)
- Evaporation (concentration), cooling water
- Contamination

9

# Geochemical Mechanisms Controlling Trace Element Concentrations in Groundwater and Surface Water

- Adsorption on surfaces of suspended particulates
  - Most important process for trace elements at most sites
- Redox effects
  - Mn and Fe soluble at low redox
  - U, Pu and Tc soluble at high redox
  - $As^{+3}$ has lower $K_d$ (mobile at low redox)

1-10

## Geochemical Mechanisms Controlling Trace Element Concentrations in Groundwater and Surface Water

- pH effects
  - Amphoteric "U" shaped solubility curve
    - $OH^-$ complexes form at high pH
    - $H^+$ complexes form at low pH
  - Sorption competition from $H^+$ and $OH^-$ at low and high pH

11

## Geochemical Mechanisms Controlling Trace Element Concentrations in Groundwater and Surface Water

- Total dissolved solids effects
  - Competition for sorption sites
  - Concentrated cooling water, brine discharge
- Complexation effects
  - Chloride increases solubilities of Cd, Cu, Pb
  - Fluoride increases solubility of Al
  - Halogens increase solubility of Hg
  - Carbonate increases solubility of U, Pu

12

## Effects of Suspended Particulates

- Most common suspended particulates in groundwater are clay minerals, hydrous aluminum oxides, aluminum hydroxides; and iron oxides, iron hydroxides, iron oxyhydroxides
- In neutral-pH water, Al concentrations > 1 mg/L indicate suspended Al-bearing minerals (clays)

  *(–) surface charge*

- In neutral-pH, moderate to oxidizing redox conditions, Fe concentrations > 1 mg/L indicate suspended iron oxides

  *(+) surface charge*

- Filtered samples can have suspended particulates too
  - Suspended range is 100 to 0.001 micron
  - 0.45 micron filter allows some particulates through

13

## Effects of Suspended Particulates

- Trace elements are associated with specific suspended particulates, yielding good correlations for trace-vs.-reference element concentrations in uncontaminated samples
- Oxyanionic elements – negatively charged speciation under oxidizing conditions

Arsenic (V): $HAsO_4^{2-}$, $H_2AsO_4^{-}$
Antimony (V): $Sb(OH)_6^{-}$
Selenium (VI): $SeO_4^{2-}$
Vanadium (V): $H_2VO_4^{-}$, $HVO_4^{2-}$

} Iron oxides (Fe)

14

# Effects of Suspended Particulates

- Cationic elements – positively charged speciation

| | | |
|---|---|---|
| Barium: | $Ba^{2+}$ | Clays (Al) and/or manganese oxides (Mn) |
| Lead: | $Pb^{2+}$ | |
| Nickel: | $Ni^{2+}$ | |
| Zinc: | $Zn^{2+}$ | |

- Mixed elements – multiple charges at equilibrium

Chromium (III): $Cr(OH)_2^+$, $Cr(OH)_3^o$, $Cr(OH)_4^-$

15

# Effects of Suspended Particulates

- Graphically evaluate correlations between trace elements vs. selected reference elements (Al, Fe, Mn).
- Naturally occurring trace elements have consistent trace/reference ratios.
- Impacted samples have elevated trace/reference ratios.

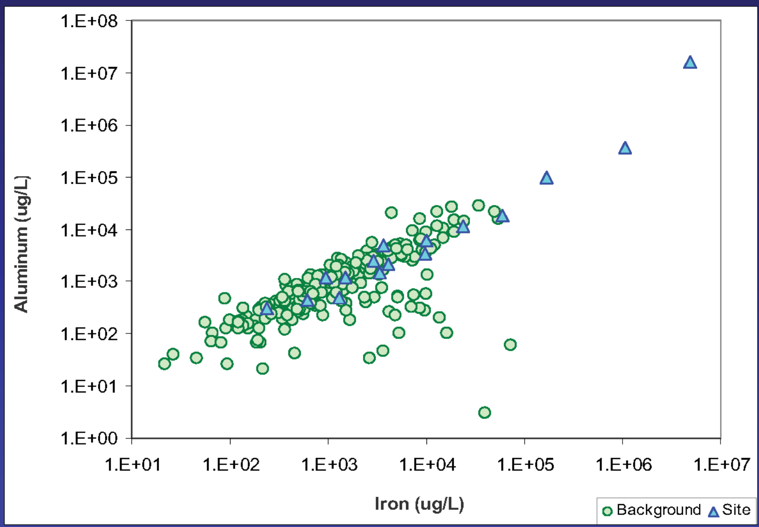
**Consider all available data!**

16

# Groundwater Example 1

17

## Aluminum vs. Iron in Unfiltered Groundwater, Alabama Site




*n* = 16, *m* = 300

**pH:** 4.9 to 8.3

mean = 6.6

**DO:** 1.1 to 6.9 mg/L

mean = 5.2 mg/L

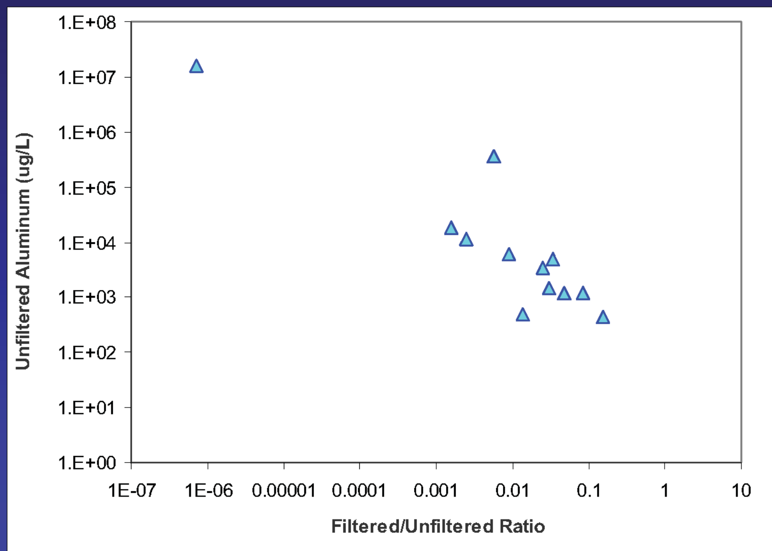
**ORP:** +148 to +272 mV

mean = +212 mV

(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007)

18

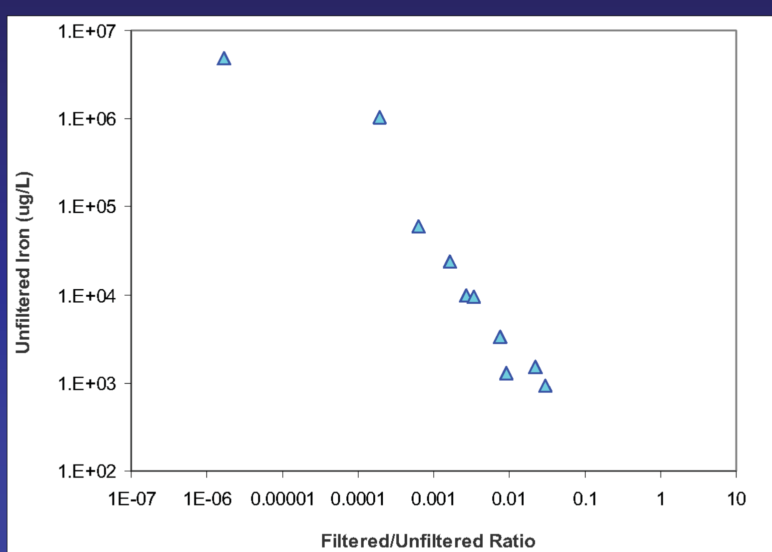
# Unfiltered Aluminum vs. Filtered/Unfiltered Ratios in Groundwater, Alabama Site




(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007)

19

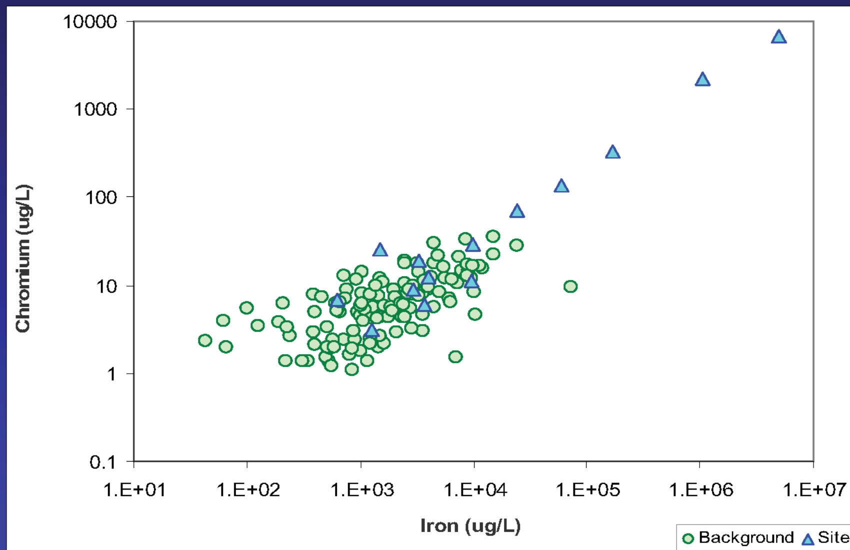
# Unfiltered Iron vs. Filtered/Unfiltered Ratios in Groundwater, Alabama Site




(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007)

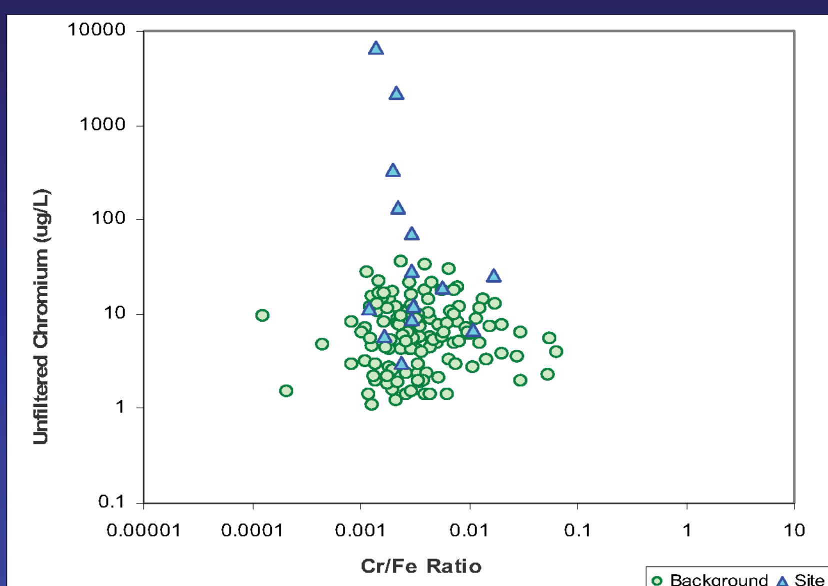
20

# Chromium vs. Iron in Unfiltered Groundwater, Alabama Site



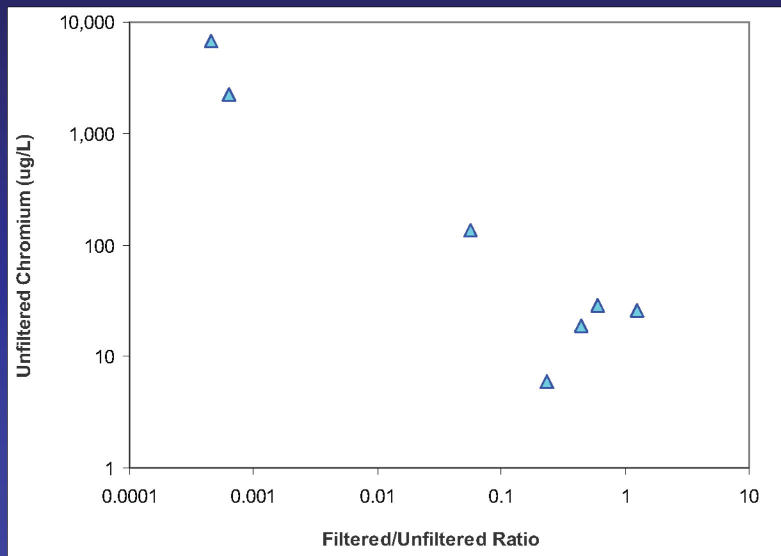

(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007) 21

# Chromium vs. Cr/Fe Ratios in Unfiltered Groundwater, Alabama Site




(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007) 22

# Unfiltered Chromium vs. Filtered/Unfiltered Ratios in Groundwater, Alabama Site




(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007)

23

# Reductive Dissolution Process

- Releases of organic contaminants (fuel, solvents, landfill leachate) can stimulate microbial activity, resulting in local reducing conditions.
- Local reducing conditions drive the dissolution of Fe oxides and Mn oxides, thereby mobilizing trace elements that were adsorbed on the oxide surfaces.
- Reducing conditions can also be natural (wetlands, swamps).

1-24

# Effects of Reducing Conditions on Metal Mobilities

| | |
|---|---|
| • $Fe^{3+} \rightarrow Fe^{2+}$ | Drives dissolution of iron oxides |
| • $Mn^{4+} \rightarrow Mn^{2+}$ | Drives dissolution of manganese oxides |
| • V, Ni, Cr, etc. | Mobilized by dissolution of oxides |
| • $As^{5+} \rightarrow As^{3+}$ | Limits adsorption of arsenic |
| • $Se^{6+} \rightarrow Se^{4+}$ | Limits adsorption of selenium |

1-25

# Evidence for Reductive Dissolution

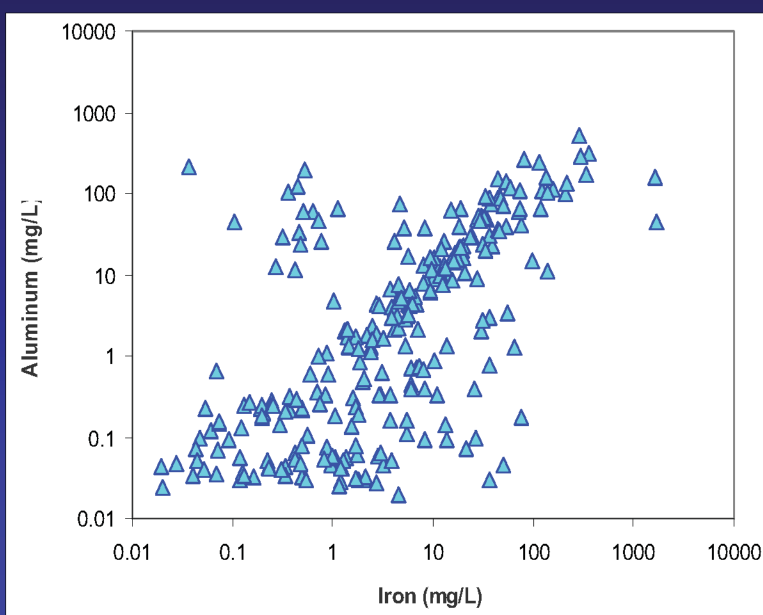
- Identified by correlations of metal concentrations with indicators of local redox depression:
  - Low ORP and DO (least reliable indicator)
  - Elevated dissolved Fe and Mn (filtered/unfiltered ratios ~1)
  - Elevated Fe/Al ratios
  - Lower sulfate and nitrate
  - Detectable sulfide and ammonia
  - Detectable hydrogen, methane, ethene, ethane
  - Anaerobic Cl-solvent degradation products
    - *cis*-1,2-DCE
    - Vinyl chloride
    - Chloroform
    - Trichloromethane, Dichloromethane, Chloromethane

1-26

# Groundwater Example 2

27

## Aluminum vs. Iron in Unfiltered Groundwater, Georgia Facility (background study)




*n* = 352

pH: 4.3 to 8.4

mean = 5.9

DO: 1.3 to 12.6 mg/L

mean = 8.4 mg/L

No filtered splits

(Thorbjornsen & Myers, *Environmental Forensics*, 8:25-35, 2007)

28

# Groundwater Example 3

29

## Background Investigation, New Mexico Facility

- Former central NM military base.
- 70 background groundwater samples obtained for background study.
  - Upper Granular Unit (40)
  - Intermediate Unit (24)
  - Deep Unit (6)

30

# Field Parameters, NM Facility

**Background Field Readings**

pH: 6.5 to 7.7

mean = 7.1

DO: 0.16 to 9.2 mg/L

mean = 4.8 mg/L

ORP: -83 to +347 mV

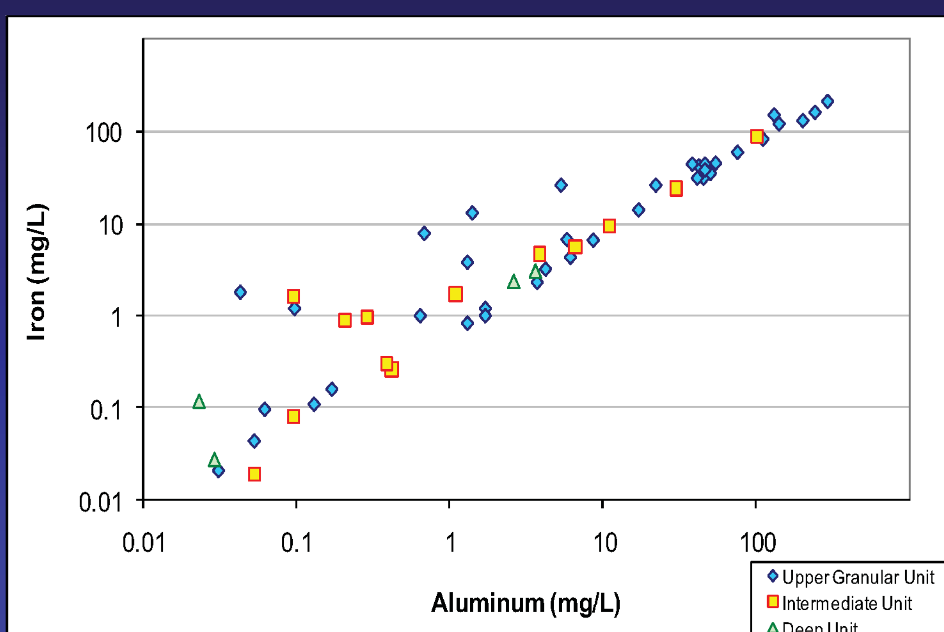
mean = +85 mV

Turbidity: 1 to 999 NTU

mean = 169 NTU

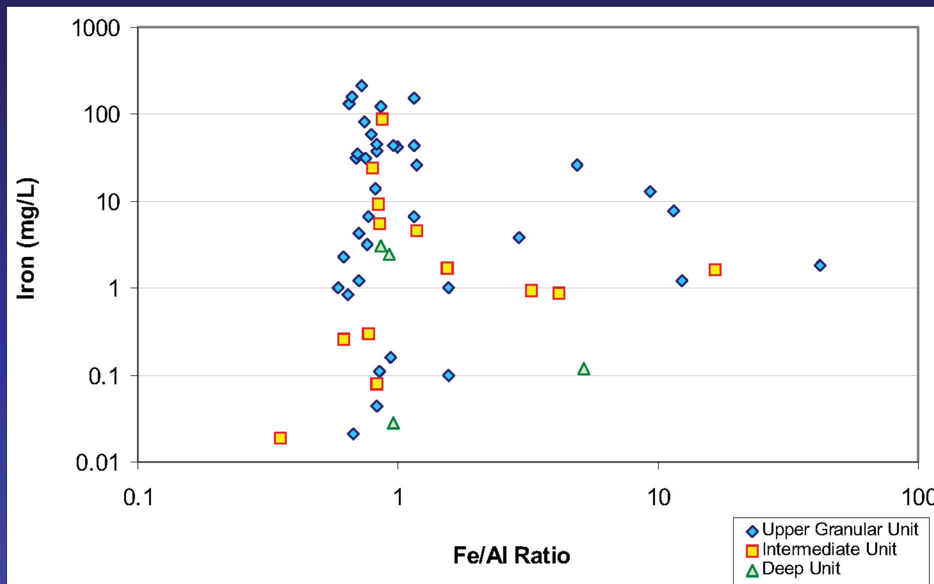
31

# Iron vs. Aluminum, NM Facility



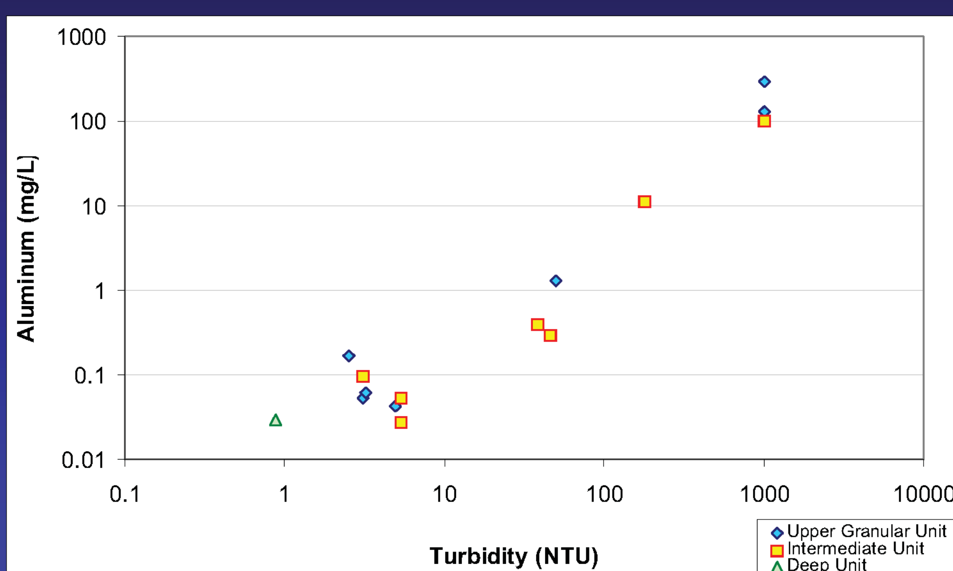

1-32

# Iron vs. Fe/Al Ratios, NM Facility



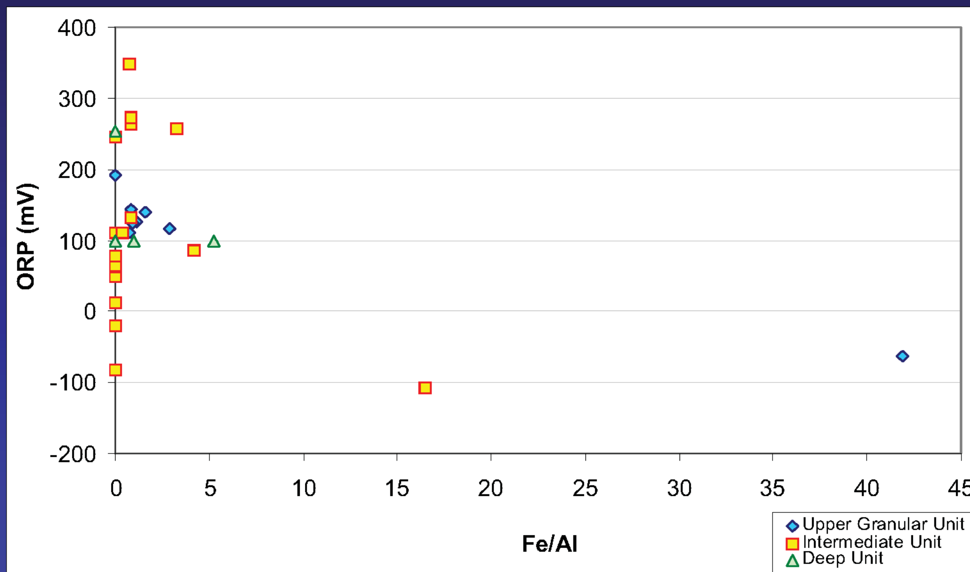

1-33

# Aluminum vs. Turbidity, NM Facility



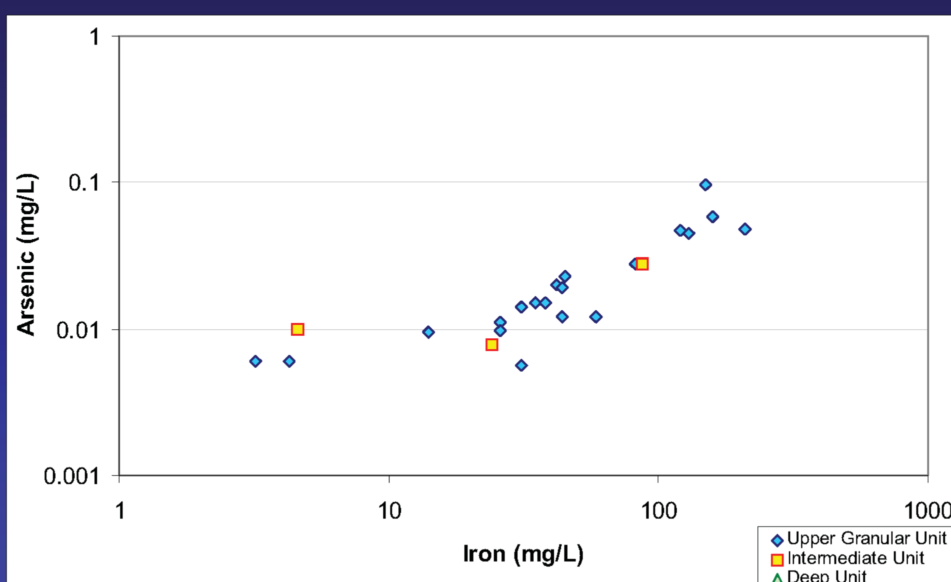

1-34

# ORP vs. Fe/Al Ratios, NM Facility



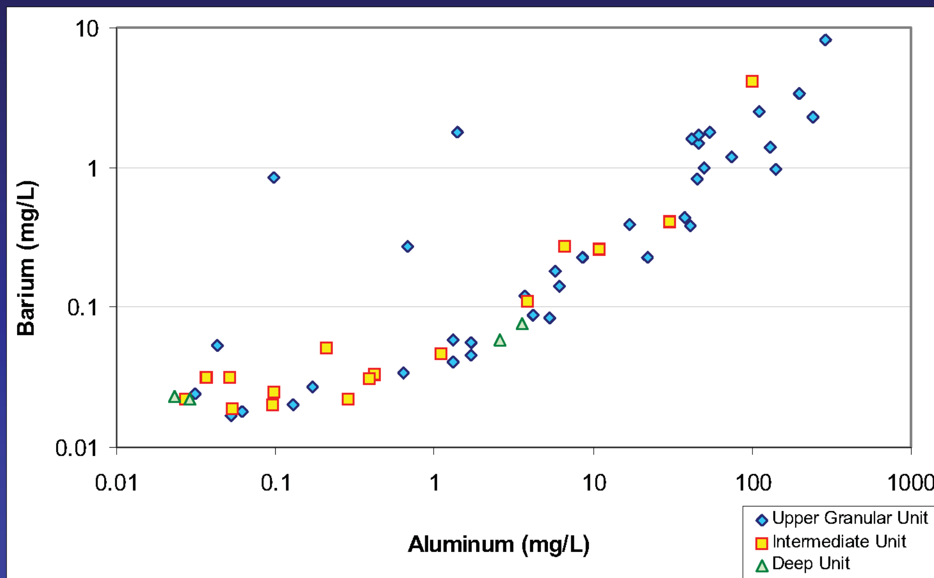

1-35

# Arsenic vs. Iron, NM Facility



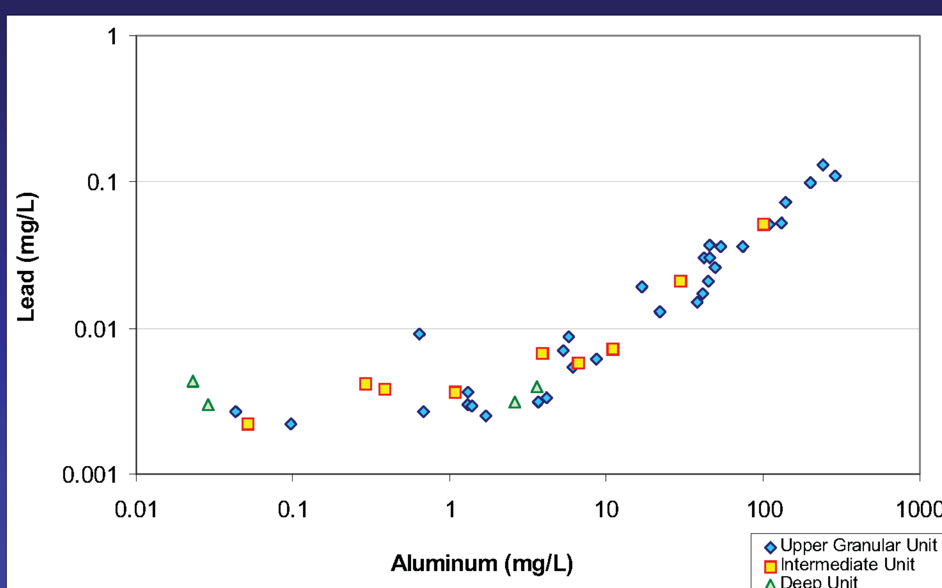

36

# Barium vs. Aluminum, NM Facility




1-37

# Lead vs. Aluminum, NM Facility



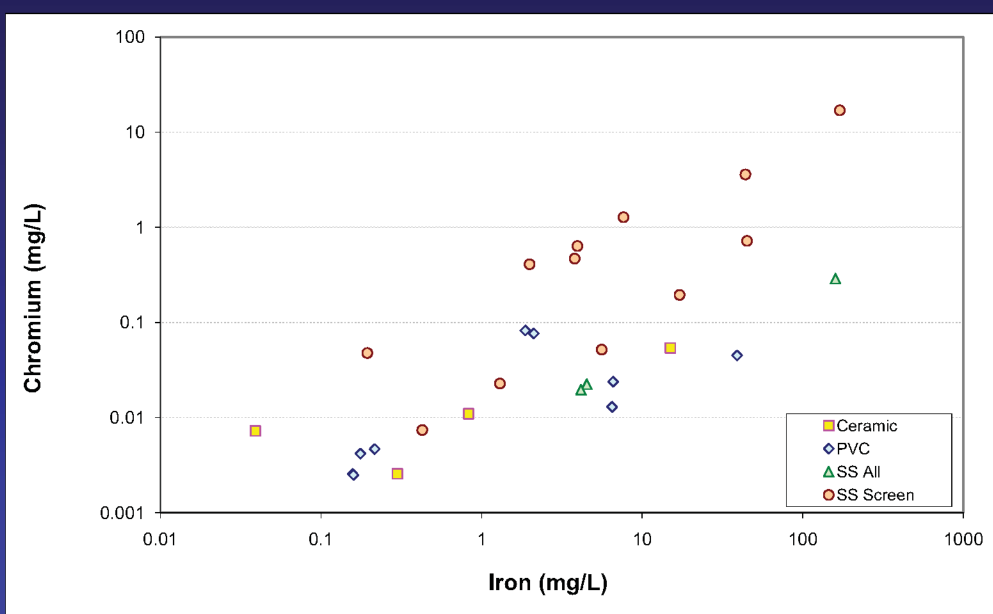

1-38

# New Mexico Facility

- Well construction materials:
  - PVC screen and riser
  - SS screen and PVC riser
  - SS screen and riser
  - PVC riser with Barcad sampler (ceramic)

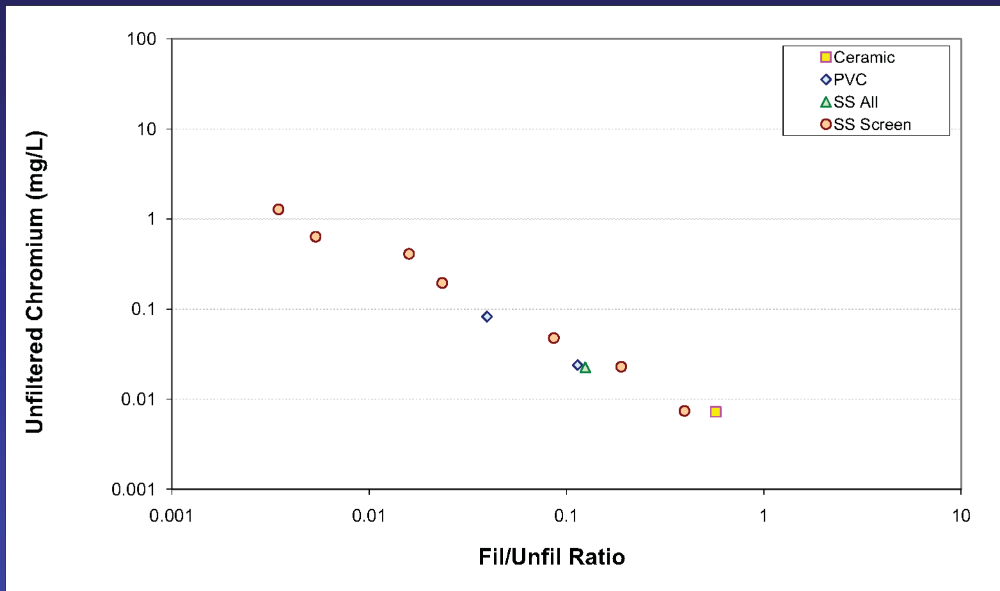
39

# Chromium vs. Iron, NM Facility



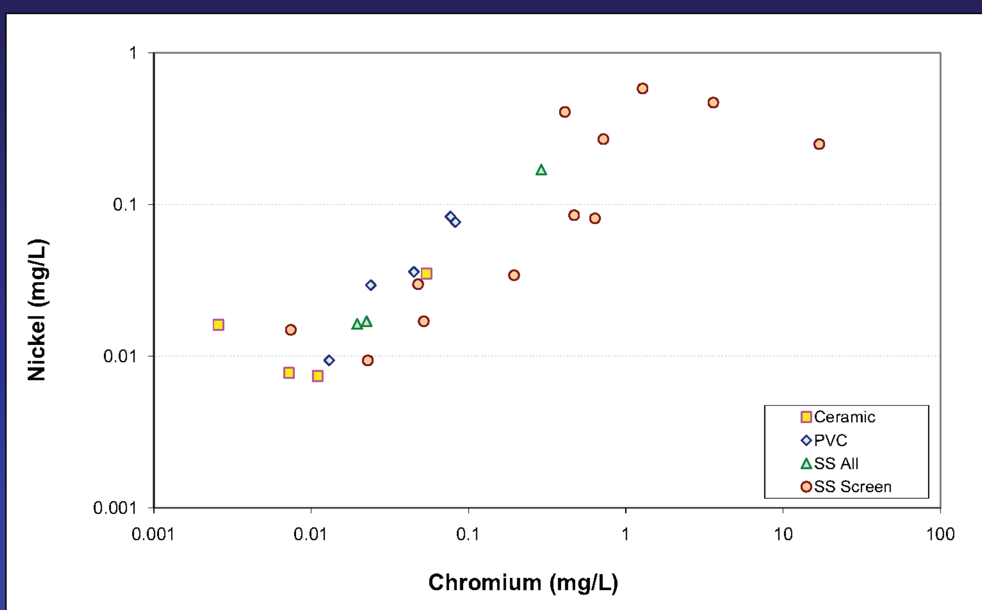

40

# Unfiltered Chromium vs. Filtered/Unfiltered Ratios, NM Facility




41

# Nickel vs. Chromium, NM Facility




42

## Evidence for a Stainless-Steel Source for Elevated Chromium and Nickel

- Cr correlated with Fe in unfiltered splits
- Cr present as particulates (Fil/Unfil <1)
- Ni correlated with Al in unfiltered splits
- Ni correlated with Cr in unfiltered splits

43

# Applications of Geochemical Evaluations

1-44

## Applications of Geochemical Evaluations

- Site-to-background comparisons
  - determine presence/absence or nature/extent of contamination
  - support risk assessments (refine lists of chemicals of concern)
- Work plans
  - evaluate existing data to refine analytical needs, determine where to place new wells

45

## Applications of Geochemical Evaluations

- Compliance monitoring
  - distinguish between naturally high background vs. contamination
- Remedial actions
  - confirm that remedial action is required
  - evaluate compatibility with metals (oxic vs. reducing remedies for organics)

46

## Applications of Geochemical Evaluations

- Long-term monitoring optimization
  - remove naturally occurring metals and unimpacted wells from LTM program (performed at Wright Patterson AFB)

47

## Applications of Geochemical Evaluations

- Background studies
  - evaluate statistical outliers
  - exclude contaminated samples from BG data set
  - ensure representativeness of BG data
  - compare subgroups (aquifers, surface water bodies, watersheds, etc.)

48

## Applications of Geochemical Evaluations

- Identification of processes controlling element concentrations
  - Geochemical evaluation permits mechanistic explanations, which a statistical approach cannot provide (turbidity effects, naturally reducing zones, etc.)

49

## Ravenna Groundwater Evaluation

- 234 wells sampled in October, 2009.
- 23 elements analyzed in filtered and unfiltered splits.
- Seven field parameters measured.
- Validated data received last week.
- Geochemical evaluation underway.

50

# References


- Thorbjornsen, K. and Myers, J., 2008, “Geochemical Evaluation of Metals in Groundwater at Long-Term Monitoring Sites and Active Remediation Sites,” *Remediation*, Vol. 18, Issue 2, pp. 99-114.
- Thorbjornsen, K. and Myers, J., 2007, “Identifying Metals Contamination in Groundwater Using Geochemical Correlation Evaluation,” *Environmental Forensics*, Vol. 8, Nos. 1-2, pp. 25-35.
- Thorbjornsen, K. and J. Myers, 2007, “Identification of Metals Contamination in Firing-Range Soil Using Geochemical Correlation Evaluation,” *Soil & Sediment Contamination*, Vol. 16, No. 4.
- Myers, J. and K. Thorbjornsen, 2004, “Identifying Metals Contamination in Soil: A Geochemical Approach,” *Soil & Sediment Contamination: an International Journal*. Amherst Scientific Publishers, Vol. 13, no 1, January/February 2004, pp. 1-16.

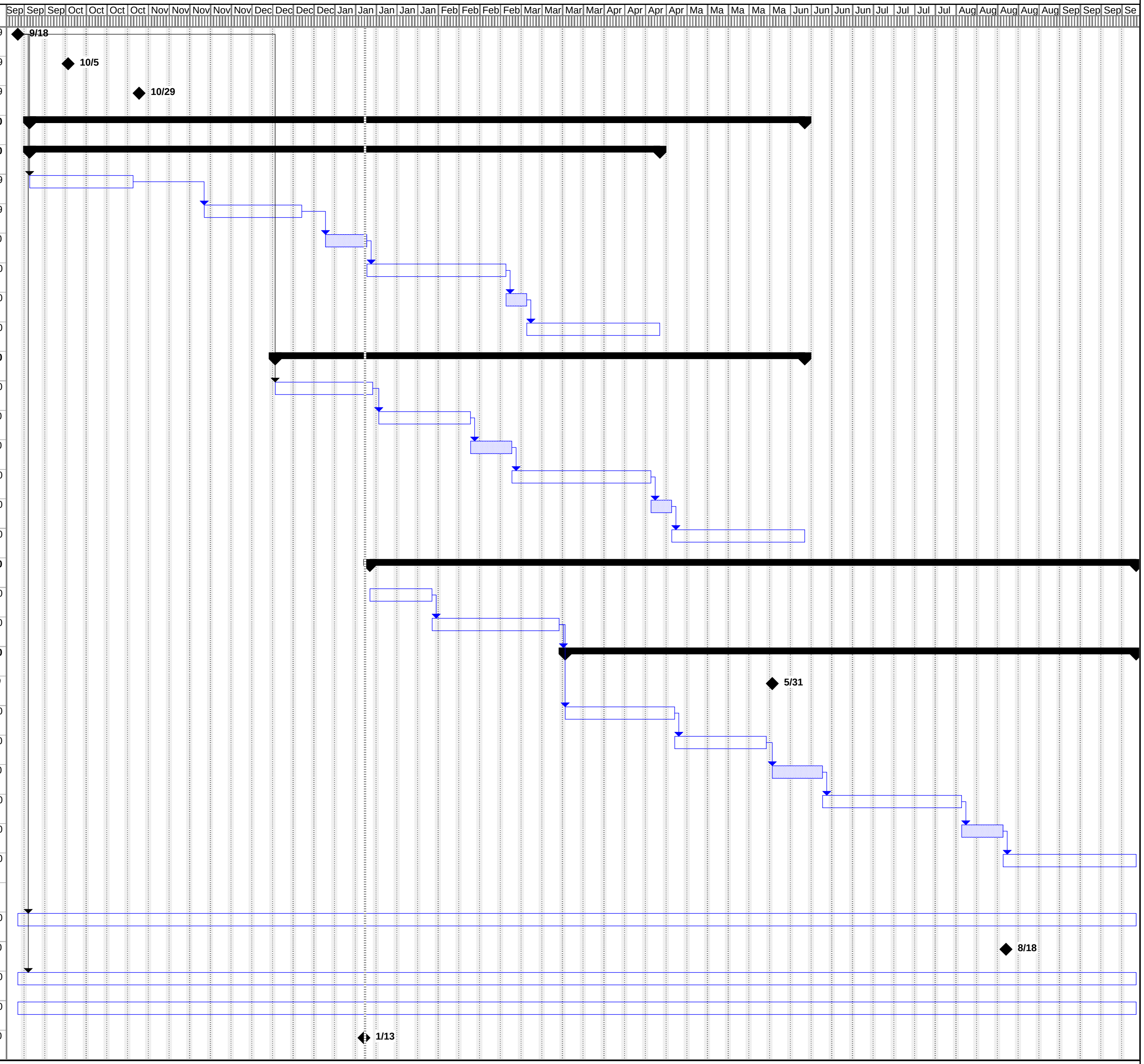
# *APPENDIX B*
# *PROJECT SCHEDULE*

Shaw Environmental & Infrastructure, Inc.
Contract No. W912QR-08-D-0013

PROPOSED WORK SCHEDULE FOR
GEOCHEMICAL EVALUATION OF METALS IN GROUNDWATER
Ravenna Army Ammunition Plant

Version: 0
Date : 4 January 2010

| ID | | Task Name | Duration | Start | Finish |
|---|---|---|---|---|---|
| 1 | | Award | 0 days | Fri 9/18/09 | Fri 9/18/09 |
| 2 | | Project Manager Assigned | 0 days | Mon 10/5/09 | Mon 10/5/09 |
| 3 | | Kick Off Call | 0 days | Thu 10/29/09 | Thu 10/29/09 |
| 4 | | **Plan Prep** | **188 days** | **Tue 9/22/09** | **Thu 6/10/10** |
| 5 | | **Work Plan** | **153 days** | **Tue 9/22/09** | **Thu 4/22/10** |
| 6 | | Pre Draft WP Prep | 25 days | Tue 9/22/09 | Mon 10/26/09 |
| 7 | | Army Review | 23 days | Fri 11/20/09 | Tue 12/22/09 |
| 8 | | Draft WP Prep | 10 days | Thu 12/31/09 | Wed 1/13/10 |
| 9 | | Army/Regulator Reviev | 33 days | Thu 1/14/10 | Mon 3/1/10 |
| 10 | | Final WP Prep | 5 days | Tue 3/2/10 | Mon 3/8/10 |
| 11 | | Army/Regulator Reviev | 33 days | Tue 3/9/10 | Thu 4/22/10 |
| 12 | | **QCP Plan** | **129 days** | **Mon 12/14/09** | **Thu 6/10/10** |
| 13 | | Pre Draft QCP Prep | 25 days | Mon 12/14/09 | Fri 1/15/10 |
| 14 | | Army Review | 23 days | Mon 1/18/10 | Wed 2/17/10 |
| 15 | | Draft QCP Prep | 10 days | Thu 2/18/10 | Wed 3/3/10 |
| 16 | | Army/Regulator Reviev | 33 days | Thu 3/4/10 | Mon 4/19/10 |
| 17 | | Final QCP Prep | 5 days | Tue 4/20/10 | Mon 4/26/10 |
| 18 | | Army Review | 33 days | Tue 4/27/10 | Thu 6/10/10 |
| 19 | | **Evaluation Report Prep** | **185 days** | **Fri 1/15/10** | **Thu 9/30/10** |
| 20 | | Data Transfer from Army | 15 days | Fri 1/15/10 | Thu 2/4/10 |
| 21 | | Data Review/Format | 31 days | Fri 2/5/10 | Fri 3/19/10 |
| 22 | | **Prep Evaluation Report** | **139 days** | **Mon 3/22/10** | **Thu 9/30/10** |
| 23 | | *Contractual Pre Draft D* | *0 days* | *Mon 5/31/10* | *Mon 5/31/10* |
| 24 | | Pre Draft Report Prep | 27 days | Mon 3/22/10 | Tue 4/27/10 |
| 25 | | Army Review | 23 days | Wed 4/28/10 | Fri 5/28/10 |
| 26 | | Draft Report Prep | 13 days | Mon 5/31/10 | Wed 6/16/10 |
| 27 | | Army/Regulator Reviev | 33 days | Thu 6/17/10 | Mon 8/2/10 |
| 28 | | Final Report Prep | 10 days | Tue 8/3/10 | Mon 8/16/10 |
| 29 | | Army/Regulator Reviev | 33 days | Tue 8/17/10 | Thu 9/30/10 |
| 30 | | | | | |
| 31 | | Status Meetings (3 total) | 270 days | Fri 9/18/09 | Thu 9/30/10 |
| 32 | | RAB Meetings (1 total) | 0 days | Wed 8/18/10 | Wed 8/18/10 |
| 33 | | Bi-weekly Calls/Monthly Reporti | 270 days | Fri 9/18/09 | Thu 9/30/10 |
| 34 | | Records of Conversation | 270 days | Fri 9/18/09 | Thu 9/30/10 |
| 35 | | Kick off Meeting | 0 days | Wed 1/13/10 | Wed 1/13/10 |




Project Schedule base 011110 update
Date: 4 January 2010

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Task | | Progress | | Summary | | External Tasks | | Deadline | |
| Split | | Milestone | | Project Summary | | External Milestone | | | |

# APPENDIX C
# OHIO EPA APPROVAL LETTER

*Note: This is a placeholder page. Shaw will supply a signed authorization page to be inserted into the final hard copy document as soon as it becomes available. Replacement CDs that include the signed authorization page will also be supplied.*

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