

Project Final Report

**Arsenic Species (III,V) Distribution
In Wisconsin Groundwaters:
Field Measurements and Prediction Using
Multivariate Analysis of Geochemical Data**

(06-CTP-03, WR05R001)

By

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PROJECT SUMMARY

Title: Arsenic Species (III,V) Distribution In Wisconsin Groundwaters: Field Measurements And Prediction Using Multivariate Analysis Of Geochemical Data.

Project I.D.: 06-CTP-03, WR05R001

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Contract Period: July 01, 2005 through June 30, 2007.

Background/Need: The environmental fate, toxicity, and mitigation strategies of arsenic are dependent upon its complex chemical speciation. Thus critical information pertinent to identification of arsenic release mechanisms can be obtained through studies of arsenic speciation (especially oxidation state). Only trace quantities of organic arsenic species are found in WI groundwaters, thus the study focused on the more toxic and dominant inorganic forms of arsenic (arsenate and arsenite). Arsenate (As V) is the oxidized form of arsenic and is anionic at relevant groundwater pH ranges. Arsenite (AsIII) is the reduced form of arsenic and is uncharged under typical groundwater pH ranges. Arsenate, because of its charge, has a stronger capacity to sorb to aquifer surfaces and is therefore less mobile in groundwater systems than the reduced (arsenite form).

Objectives: The four principal goals of this study were to:

1. Perform a meta-analysis of existing groundwater data for co-variation of geochemical analytes and test their association with total and speciated arsenic concentrations using multivariate statistical methods.
2. Determine the concentrations of arsenic and primary redox-active species [Fe(II/III), nitrate/ammonia, sulfate/sulfide, oxygen, DOC] in Wisconsin groundwaters.
3. Quantify the occurrence and distribution of arsenic species (III and V) in Wisconsin groundwaters.
4. Examine relationships between arsenic oxidation state speciation and aquifer geochemistry and test the hypothesis that arsenic speciation can be predicted from aquifer geochemistry.

Methods: The study included a meta-analysis of existing groundwater data, a detailed field study of 57 wells in Wisconsin, and multivariate statistical analyses. The field study focused on measuring arsenic speciation (III and V) and important

geochemical parameters in 57 sites in Wisconsin. A 4x4 matrix of sites was constructed with Ca and Fe as the primary variables, and sulfate and total As levels secondary variables. This construct facilitated ANOVA statistical testing. Arsenic species separation was performed on-site using As(V)-specific solid-phase extraction columns. This approach avoided the speciation changes that occur as a result of redox transformations of common drivers during storage. Arsenic (along with a large suite of other elements) was determined using high-resolution ICP-MS, which with an As reporting limit of $0.02 \mu\text{g L}^{-1}$, ensured that the study matrix was complete and accurate.

Results and Discussion: Analysis of >5300 well records compiled from nine states showed that the data sets have very limited information on arsenic speciation, redox sensitive species, and are compromised by poor detection limits. Thus global models of arsenic speciation based upon these existing data were of only limited value. Meta-analyses identified several potentially predictive, commonly measured, geochemical analytes (calcium, iron, sulfate, and sodium) and field study was structured around these variables. Regression models demonstrated that a large fraction of the variance in the measured fraction of total arsenic present as As(III) could be explained by redox (Eh) levels. In multiple regression models, only a few other geochemical factors (pH, Ca, sulfate) enhanced predictive power over that of redox alone, and their contribution was comparatively minor. Redox, however, was a relatively poor predictor of total arsenic levels. The field data generated in this study clearly confirmed theoretical Eh-pH arsenic speciation relationships, a finding that few other studies have documented.

Conclusions/Implications/Recommendations: Our primary conclusion from this effort is that a large proportion of the variance in the measured fraction of total arsenic present as As(III) can be explained by redox (Eh) levels. The practical implication of this finding is that one may be able to use the relatively un-demanding redox measurement as an acceptable surrogate for arsenic oxidation state speciation. This work also provides a tool to use extant or basic geochemical data, where arsenic concentrations are not available, or are suspect, to estimate the proportion of the most toxic form of arsenic

Related Publications and Presentations:

1. Kerr S.C., M.M. Shafer, J. Overdier, and D.E. Armstrong. **2008.** Hydrologic and biogeochemical controls on trace element export from Northern Wisconsin wetlands. Accepted for publication in *Biogeochemistry* (01/19/2008).
2. Shafer M.M., J. Overdier, and D.E. Armstrong. Controls on arsenic oxidation state speciation in Wisconsin groundwaters. Manuscript in-preparation for submission to *Aquatic Geochemistry*.

Key Words: Arsenic, Groundwater, Speciation, Redox, Geochemistry

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INTRODUCTION

There are widespread occurrences of elevated arsenic (As) levels in ground and drinking waters throughout Wisconsin (Burkell and Stoll 1995, WDNR, 2000, Thornburg and Sahai 2004). Ingestion of inorganic As has been shown to cause skin, bladder and lung cancers (NRC, 1999). The Wisconsin drinking water standard for As is based on the EPA's maximum contaminant level and was $50 \mu\text{gL}^{-1}$ in 1980 (US EPA 1980), but was recently decreased to $10 \mu\text{gL}^{-1}$ (World Health Organization guideline, WHO 1993). As of 2003, 17% of 3300 wells sampled in Outagamie and Winnebago counties had As levels between $10 \mu\text{gL}^{-1}$ and $50 \mu\text{gL}^{-1}$ and 3% of the As concentrations in these wells exceeded $50 \mu\text{gL}^{-1}$ (WDNR, 2003). Therefore, a critical need exists to develop tools which will improve our ability to identify aquifers with potential for elevated As levels.

Arsenic is a metalloid whose environmental fate, toxicity and mitigation strategies vary according to its complex chemical speciation. Arsenic in groundwater systems exists primarily as either oxidized (arsenate, AsV) or reduced (arsenite, AsIII) oxyanions (refer to Appendix B for additional details on As speciation and chemistry). Isolated occurrences of methylated forms have been noted, particularly in organic-influenced aquifers, but are generally insignificant in regional groundwater supplies. Arsenate ($\text{pK}_{\text{a}1} = 2.19$) is negatively charged at pH levels in common groundwater (6-9), where AsIII ($\text{pK}_{\text{a}1} = 9.20$) is uncharged. Arsenate sorbs more strongly to common minerals and aquifer matrices and is therefore less mobile than uncharged AsIII (Smedley and Kinniburgh 2002). Due to its electroneutrality, AsIII is more difficult to remediate from drinking water, which is why a pre-oxidation step is typically required. Arsenite is generally more toxic to humans than AsV, and is retained in tissues to a greater extent than arsenate (NRC 1999). The toxicity of AsIII is driven by the binding to sulfur groups in important proteins. Arsenate is a biological analogue for phosphate and can therefore disrupt the production of ATP. Since mobility, toxicity and mitigation varies with the speciation of As, it is important to identify As release mechanisms in a species-specific (III or V) manner.

Two principal mechanisms have been identified for release of As from aquifers, both relevant to Wisconsin groundwaters. Arsenic contained in the sulfide bearing cement horizon is released when the iron sulfide minerals are oxidized.



In the regions where the static water level is close to the cement horizon, oxidative dissolution of the As rich pyrite/marcasite minerals is the likely driving force for AsV mobilization (i.e. the oxidation hypothesis). Therefore if this is the driving factor affecting AsV mobilization, the iron and sulfate would be closely correlated with higher AsV/AsIII concentration ratios.

Reductive dissolution has also been identified as a possible dominant factor in As mobilization in aquifers in Bangladesh (Ahmed et al. 2004), Illinois (Holm, 2003) and southeastern Wisconsin (Gotkowitz et al. 2003). This occurs when the Fe in the iron oxy-hydroxides is reduced thereby releasing sorbed As (i.e. the reduction hypothesis). The reductive dissolution process can be represented by the following mechanism:



This mechanism results in the release of both sorbed As(V) and As(III), with the preferential release of As(III), and is accompanied by microbial reduction of As(V) to arsenite. A correlation of total As and HCO_3^- was observed by Nickson et al. 2000, which is suggestive of the reductive hypothesis. This association, however, could be established with much greater certainty if As(III) concentrations were compared rather than just total arsenic.

The concentration of the As species released from the mechanisms described above can be modified or even reversed by surrounding geochemical factors. For example, at groundwater pH ranges, most soluble Fe species are positively charged and will strongly bind anions such as As(V). Ions and chemical constituents other than those described above (HCO_3^- , Fe^{2+} and SO_4^{2-}) may be involved in both the redox chemistry and mobilization of arsenic. Factors such as groundwater age and residence time, kinetic constraints of mineral dissolution and anthropogenic influence will influence arsenic release. Arsenic in groundwater was found to increase over time in Glacial Drift aquifers in Illinois, therefore there may be an association of mobilized As with groundwater residence time as measured by oxygen isotope ratios. The reductive dissolution of metal oxyhydroxides and the oxidation of sulfide minerals could also occur for manganese based minerals.

Some ions may be directly involved in As release; namely PO_4^{3-} , HCO_3^- , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and SO_4^{2-} , while other ions (e.g. NH_4^+) are good indicators of redox potential (Eh) of the groundwater system (Table 1). In fact, early predications held that As(III)/As(V) ratios would follow redox profiles in groundwater systems, though demonstrating this in actual environmental settings has been difficult due to the complexities of the groundwater systems (Smith et al. 2003) and challenging analytical issues. It is also important to note that As concentrations in groundwater cannot simply be predicted by presence in the solid phase (Warner, 2001).

Table 1. Electrochemical Series

Redox half reaction	Std. Electrode Potential (V)
$\text{N}_2\text{O} + 2\text{H}^+ + 2\text{e}^- = \text{N}_2 + \text{H}_2\text{O}$	1.77
$\text{O}_{2(\text{g})} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	1.23
$\text{Fe}(\text{OH})_3 + 3\text{H}^+ + \text{e}^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	0.95
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.771
$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- = \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	0.58
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- = \text{NO}_2^- + 2\text{OH}^-$	0.01
$\text{N}_2 + 2\text{H}_2\text{O} + 6\text{H}^+ + 6\text{e}^- = 2\text{NH}_4\text{OH}$	0.092
$\text{S}(\text{s}) + 2\text{e}^- = \text{S}^{2-}$	-0.47
$\text{SO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- = \text{S}_2\text{O}_3^{2-} + 6\text{OH}^-$	-0.57
$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- = \text{SO}_3^{2-} + 2\text{OH}^-$	-0.93

A multivariate approach is warranted to elucidate driving mechanisms in As(V)/As(III) mobilization in groundwater, and speciation will assist in the distinction between the various mechanistic possibilities (Smith et al. 2003; Meglen, RR 1992), improving upon earlier bivariate analyses (Holm et al. 2004, IDWR 2004).

The **four principal goals** of this study were therefore to:

1. Perform a meta-analysis of existing groundwater data for co-variation of geochemical analytes and test their association with total and speciated arsenic concentrations using multivariate statistical methods.
2. Determine the concentrations of arsenic and primary redox-active species [Fe(II/III), nitrate/ammonia, sulfate/sulfide, oxygen, DOC] in Wisconsin groundwaters.
3. Quantify the occurrence and distribution of arsenic species (III and V) in Wisconsin groundwaters.
4. Examine relationships between arsenic oxidation state speciation and aquifer geochemistry and test the hypothesis that arsenic speciation can be predicted from aquifer geochemistry.

PROCEDURES and METHODS

The study included a meta-analysis of existing groundwater data, a detailed field study of 60 wells in Wisconsin, and multivariate statistical analyses.

A. Meta-analysis: Data from the following sources were assembled for the meta-analysis:

1. Oakland County Michigan. 37 samples. [Ground-Water Quality Atlas of Oakland County, MI. Water-Resources Investigation Report 00-4120]
2. Mahomet Aquifer Illinois; Champaign and Tazwell counties. 144 samples. [Illinois Department of Natural Resources, WMRC Report RR-107, May 2004].
3. Idaho – Washington County. 75 samples. [Ground water Quality Technical Report No. 6. Idaho Division of Environmental Quality, September 1995].
4. Minnesota Pollution Control Authority. 954 samples.
5. New Jersey. 170 samples. [Ambient Ground Water Quality in the Newark Basin, New Jersey. By M.S. Serfes, Digital compilation by G.C. Herman and M.S. Serfes, N.J. Geol. Survey Digital Geodata Series DGS96-3].
6. Ohio. 72 samples. [WDR-OH-AR-02.2. 2003 USGS Water Data Report OH-3-2].
7. Ohio. 21 samples. [Miami, OH].
8. New England Coastal Basin. 804 samples. [USGS Water Resources Investigations Report 99-4162]. 1999.
9. Wisconsin. 2648 samples. [Department of Natural Resources, Municipal and Private Wells].
10. Ontario, Canada. 430 samples.

In addition to the total arsenic data (speciated in a just a few studies), we have incorporated the following supporting geochemical data from each sample into the database (Note: the degree of comprehensiveness of the geochemical data varies greatly among the databases assembled – some e.g. only have total arsenic): 1. Well depth; 2. Temperature; 3. pH; 4. Specific Conductance; 5. Dissolved Oxygen; 6. Dissolved Solids 7. Hardness/Alkalinity; 8. Carbonate/Bicarbonate; 9. Sulfate; 10. Phosphate; 11. Chloride; 12. Bromide; 13. Fluoride; 14. Calcium; 15. Magnesium; 16. Potassium; 17. Silica; 18. Nitrogen Species (ammonia, nitrate, nitrite); 19. Dissolved Organic Carbon; 20. Trace metals.

B. Field Studies: The field study focused on measuring arsenic speciation (III and V) and a large suite of geochemical parameters in 57 of the previously statistically analyzed sites (all in Wisconsin). Low volume purging and pumping techniques were used for the collection of samples (Creasey and Flegel 1999, Shafer et al. 1991). In-line filtration was performed with pre-cleaned, high capacity, all polypropylene 0.45µm-rated filter capsules.

Arsenic species separation was performed on-site using As(V)-specific solid-phase extraction columns (refer to Appendix B). This approach avoided the speciation changes that occur as a result of redox transformations of common drivers during storage (even when “preservatives” such as HCl/EDTA are added). Arsenic (along with a large suite of other elements) was determined using high-resolution ICP-MS, which with a reporting limit of 0.02 µg L⁻¹, ensured that the study matrix was complete and accurate. Traditional ICP-MS techniques for arsenic are compromised by severe ArCl and other mass overlaps at m/z 75 (As). The high resolution capability of this ICP-MS eliminates (mass-resolves) interferences at mass 75.

The critical redox sensitive species measured included:

1. Iron Oxidation State (II and III)
 - a. Ferrous (II). On-site ferrozine complexation
 - b. Total (Ferrous + Ferric). HR-ICP-MS
2. Nitrogen species
 - a. Nitrate+Nitrite. Lachat discrete analyzer
 - b. Ammonia. Lachat discrete analyzer
3. Sulfur Species
 - a. Sulfate. Ion chromatography
 - b. Sulfide. Ion selective electrode
4. Dissolved Oxygen and Redox by multiparameter sonde

Other Supporting Analytes measured included:

5. Chloride and Phosphate by Ion Chromatography
6. Elemental Analysis by High Resolution ICP-MS (52 elements; refer to App. B)
7. Dissolved Organic Carbon (DOC) by high temperature combustion
8. Oxygen isotopes (¹⁸O/¹⁶O) by Isotope Ratio Mass Spectrometry
9. Temperature, pH, Specific Conductance, by multiparameter sonde

A 4x4 matrix of sites was constructed with using nearly universally available well concentrations of calcium and iron as the primary stratification variables, and sulfate and total arsenic levels as secondary variables (gradients within each cell). This construct facilitated ANOVA statistical testing.

Table 2. Sampling Site Matrix.

	1	2	3	4
	5	6	7	8
	9	10	11	12
	13	14	15	16
(Iron-ppb) Site ID (SpCond-µS)	Major Ion Level 1 Calcium < 20 ppm SpCond < 200 µS	Major Ion Level 2 Calcium 20 - 53 ppm SpCond 200 - 530 µS	Major Ion Level 3 Calcium 54 - 72.5 ppm SpCond 540 - 725 µS	Major Ion Level 4 Calcium > 72.5 ppm SpCond > 725 µS
Iron Level 1 < 25 ppb	(0.8) T5 20.4 (48) (0.6) T5 20.2 (43) (2.3) T5 10.3 (55)	(26) Twin Valley (342) (4.4) Devil's Lake Quartzite (319) (3.7) Devil's Lake East (229) (7.2) Devil's Lake Ice Age (232)	(1.9) Kegonsa Family Camp (710) (6.0) Kegonsa Beach (710) (12) KMspr FH Peter Farm (639) (11) Beloit (611) (1.7) Mackenzie Wildlife (574) (2.1) Mackenzie Picnic (605)	(0.8) Mendota #1 MHH (814) (5.1) Lomira (828) (3.2) UW Arlington Farm (730) (7.4) Mendota #2 MHH (729)
Iron Level 2 25 - 185 ppb	(27) T5 10.1 (57) (30) M 36.96 (123) (27) M 36.5 (111) (53) T2 10.7 (155)	(32) Hickory Ridge (328) (55) Plamann Pavilion (516) (159) Plamann Shelter (529)	(143) KMspr FH Bld #2 (636) (52) PSL/SRC (543)	(86) EAA 3674 (928)
Iron Level 3 185 - 1400 ppb	(547) T5 30.5 (58) (229) T2 90.4 (91) (1015) M 25.3 (86) (1110) M 35.5 (84)	(478) Buboltz Nat. Ctr. (528) (326) Navarion Nat. Ctr. (299) (581) Rest Area #2 (526) (852) Reek School (467) (1137) Fendryk House (509)	(1077) Picket GELC (606) (558) KMSP Mauthe Bathhouse (561) (841) KMSP Long Lake (683) (1399) Rest Area #3 (581) (1378) Okauchee Lake #1 (695)	(426) EAA 50 (770) (1129) KMspr FH Bld #1 (733)
Iron Level 4 > 1150 ppb	(1997) T5 60.4 (117) (4142) T2 10.3 (106) (3663) T5 95.4 (126)	(5273) Kegonsa Boat Landing (498) (1625) Ledge House (438) (2470) KMSP Horse Camp (492) (2827) ENEE (506)	(2550) EAA TV055 (565) (2626) KMSP Mauthe 500s (573) (5459) Ledge Camp area (680) (1484) Okauchee Lake #2 (668) (1647) Rest Area #1 (579)	(7184) Neenah (1437) (3296) Picket CC (807)

RESULTS and DISCUSSION

A. Meta-analysis: The first 6+ months of this two-year project were dedicated to mining extant databases that we obtained from the Wisconsin Department of Natural Resources and other groundwater geochemistry databases from around the country [refer to list above]. The geology represents several aquifers across the Midwest, with a range of deposit types as well (Precambrian, Cambrian, Ordovician, Cretaceous, Devonian, and mixed Quaternary). Basic geochemical and arsenic data from these systems/studies was assembled into a large Access database. This effort likely represents the largest of its type to date. These data were analyzed by multivariate statistical methods including factor analysis. Analysis of the >5300 well records compiled from nine states showed that the data sets have very limited information on arsenic speciation, redox sensitive species, and are compromised by poor detection limits. Even after segregating the larger database into sub-sets of wells with similar data completeness, it still proved quite difficult to generate stable and robust factor models. Further complicating this statistical analysis was the need, because of extant data quality/quantity issues, to run multiple models to cover the desired range of site geochemistries. Thus global models of arsenic speciation based upon these existing data were of only limited value. Meta-analyses, however, identified several potentially predictive, commonly measured, geochemical analytes (calcium, iron, sulfate, and sodium) and the field study was structured around these variables. The large geochemical databases that we

assembled from the meta-analyses of extant data and our detailed field studies will be made available for use by researchers and regulatory agencies.

B. Field studies: 57 wells from within Wisconsin were chosen [as described above] for detailed chemical characterization. These sites were very carefully sampled and analyzed for the suite of analytes listed in the methods section above [and in Appendix B]. This new large and complete data set was analyzed using multivariate statistical methods to assess the predictive power of geochemical variables for major As species.

The sampling/analytical program generated data for the following arsenic species:

- (a) Total Arsenic: (Dissolved + Particulate; III + V)
- (b) Particulate Arsenic: ($> 0.4 \mu\text{m}$; III + V)
- (c) Dissolved Arsenic: ($< 0.4 \mu\text{m}$) (i) dissolved **Arsenic III** (ii) dissolved **Arsenic V**

The well sampling program was very successful in capturing the desired concentration range of each geochemical variable, and thereby validating the primary and secondary matrix sampling constructs (refer to Appendix B). For example: calcium over the range of 5 to >200 mg/L; iron over the range of 0.001 to >20 mg/L (Figure 2); sulfate over the range of below detection to >250 mg/L; pH over the range of 5.5 to 8.5; dissolved oxygen over the range of below detection to nearly saturated; sulfide over the range of below detection to >100 ppb; and total arsenic from 0.02 to over 85 ppb (Figure 1).

Figure 1. Concentration Ranking of Measured Total Arsenic and As(III).

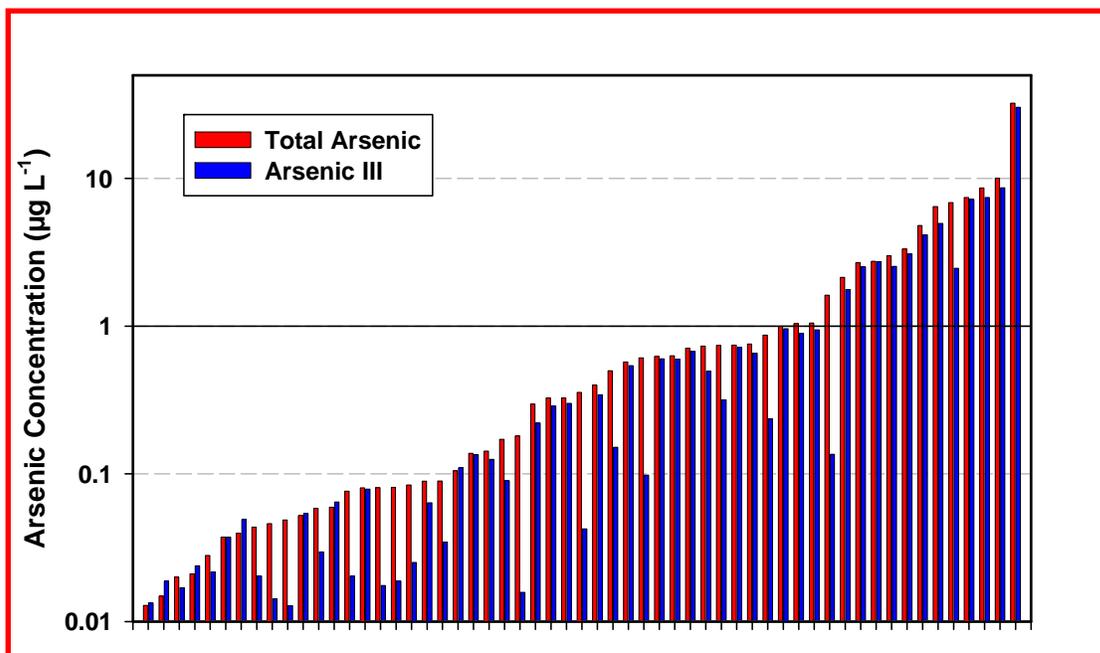
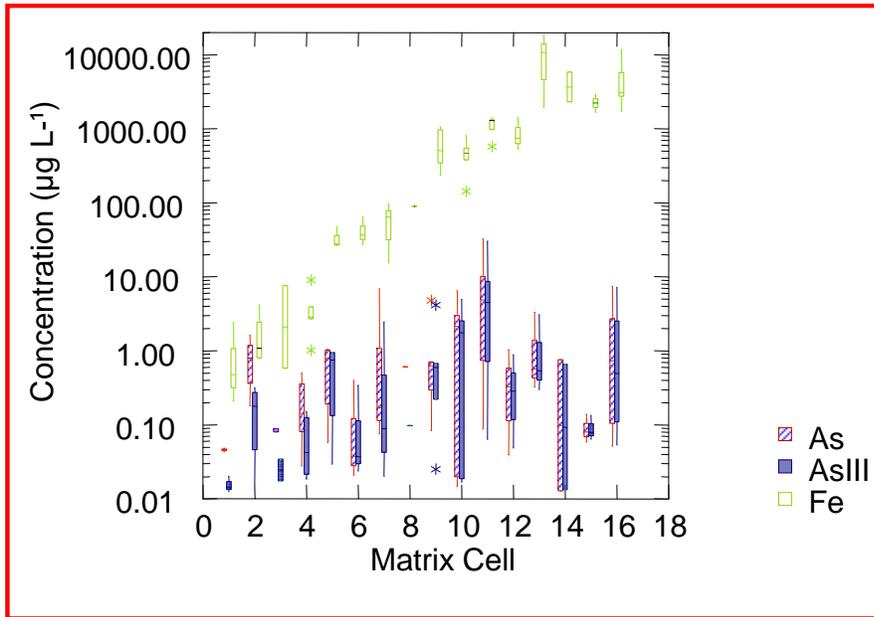


Figure 2. Arsenic, Arsenic(III) and Fe(II) Concentration Distributions.



The study matrix effectively represented the range in ferrous (Fe(II)) concentrations in moving from matrix cell 1 to cell 16 (**Figure 2**). Total arsenic and arsenic III concentrations were well correlated with Fe(II) through the first three iron quartiles (**Figure 2**). Average total arsenic and arsenic III levels were not significantly different among the Ca quartiles.

Figure 3. Arsenic Speciation [% As(III)] versus Redox Potential.

The fraction of total arsenic present as As(III) is highly correlated with redox (Eh) ($r = 0.69$), (**Figure 3**). The correlation with redox is even stronger ($r = 0.89$) when one restricts the analysis to 14 samples collected along a single groundwater flow-path (Appendix B; **Figure B-1**).

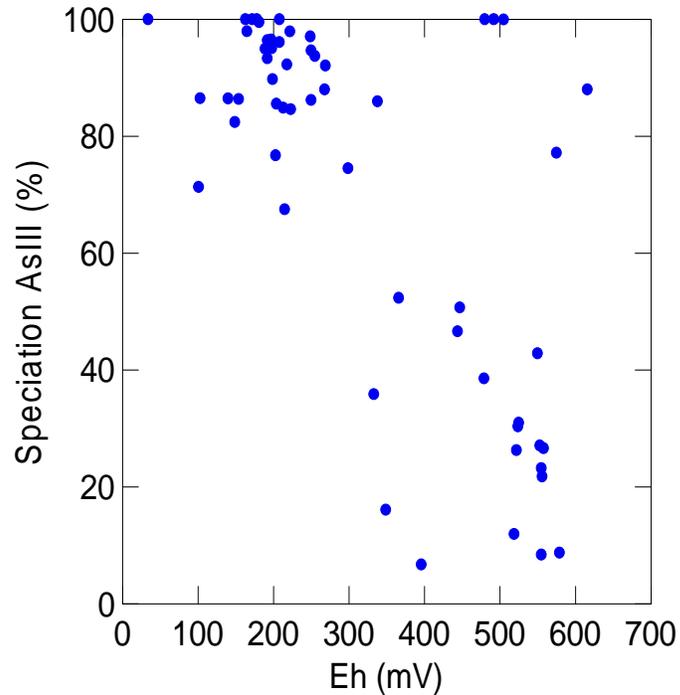


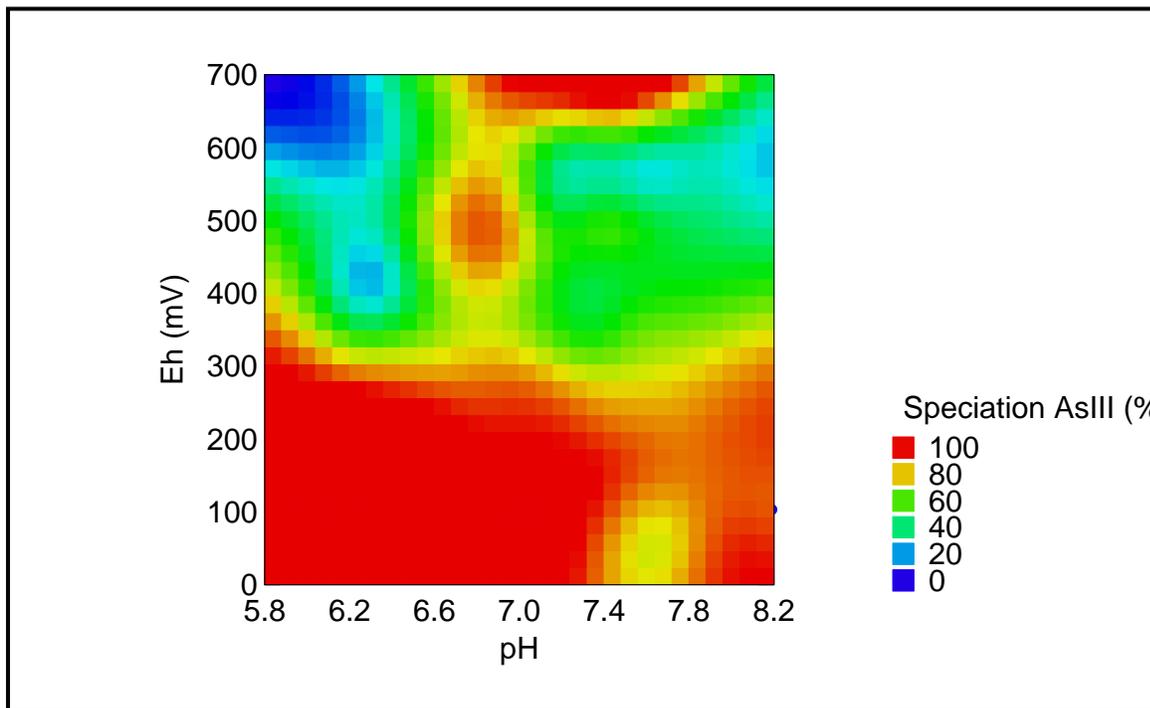
Table 3. Selected Multiple-Linear Regression Model [%As(III)] Outcomes

	Eh	Fell	Ca	SO ₄	Na	R =	Adjusted R ²
% AsIII	x					0.692	0.469
% AsIII		x				0.494	0.231
% AsIII			x			0.110	0.011
% AsIII				x		0.070	0.003
% AsIII					x	0.080	0.005
% AsIII	x	x				0.710	0.486
% AsIII		x		x		0.542	0.268
% AsIII	x	x		x		0.716	0.485
% AsIII	x	x	x	x		0.722	0.484
% AsIII	x			x		0.692	0.460
% AsIII				x		0.066	0.003
% AsIII	x	x	x		x	0.717	0.476
% AsIII	x		x		x	0.708	0.473
% AsIII	x				x	0.699	0.470
% AsIII	x		x			0.696	0.465
% AsIII		x	x	x	x	0.554	0.254

Regression models demonstrated that a large fraction of the variance in the measured fraction of total arsenic present as **As(III)** could be explained by redox (Eh) levels (**Table 3**). In multiple regression models, only a few other geochemical factors (pH, Ca, sulfate) enhanced predictive power over that of redox alone, and their

contribution was comparatively minor. Redox, however, was a relatively poor predictor of **total** arsenic levels. The field data generated in this study (**Figure 4**) clearly confirmed theoretical Eh-pH arsenic speciation relationships (Appendix B), a finding that few other studies have documented.

Figure 4. Eh-pH Surface Plot of Well Arsenic Data.



CONCLUSIONS and RECOMMENDATIONS

Our primary conclusion from this effort is that a large proportion of the variance in the measured fraction of total arsenic present as As(III) can be explained by redox (Eh) levels. This clearly confirmed theoretical Eh-pH arsenic speciation relationships, a finding that few other studies have documented. The practical implication of this finding is that one should be able to use the relatively undemanding redox measurement as an acceptable surrogate for the fraction of total arsenic present as As(III), i.e. arsenic speciation. Redox, however, was a relatively poor predictor of total arsenic levels. In multiple regression models, only a few other geochemical factors (pH, Ca, sulfate) enhanced predictive power over that of redox alone, and their contribution was comparatively minor. This work significantly improves on past studies (McArthur et al. 2001, Ahmed et al. 2004) due to the addition of arsenic chemical speciation measurements as well as improved statistical methods (Holm, 2003, IDWR, 2004).

Our study data and findings have broader implications for: (1) identifying release mechanisms from aquifer matrices, (2) geochemical associations, (3) mitigation strategies, (4) toxicity – health based decision/monitoring, and (5) tools for prediction of speciation.

A. The release mechanism for arsenic in ground water is a critical factor for understanding and predicting levels of arsenic species in ground/drinking water. Therefore this effort should be of interest to environmental chemists and environmental health scientists. These results will be useful to regulators for health-based decision making and prioritization of monitoring efforts. This work may also provide a tool to use extant geochemical data, where arsenic concentrations are not available, or are suspect, to estimate the proportion of the most toxic form.

B. Our well sampling program incorporated a set of private (homeowner) water supplies. These interactions are increasing awareness among the public of issues surrounding groundwater arsenic and providing visibility to research programs at the UW-Madison.

C. In developing/providing a very comprehensive geochemical database/analysis (cations and anions) of each of the study systems we are documenting the full suite and range of groundwater geochemistries that arsenic removal/treatment strategies will encounter. This information should ultimately help regulators and technology providers select/develop more robust treatment systems.

D. We are reporting concentrations for nearly 40 elements in the groundwaters, many of which are rarely if ever measured. In providing data for these elements, many of which are classed as potentially toxic, we are establishing critical "baseline" data that follow-up studies can benchmark.

Work remaining to be completed includes incorporating oxygen isotope data (to assess groundwater age – speciation relationships) into the models and performing additional statistical factor analyses.

The large geochemical databases that we assembled from the meta-analyses of extant data and our detailed field studies will be made available for use by researchers and regulatory agencies.

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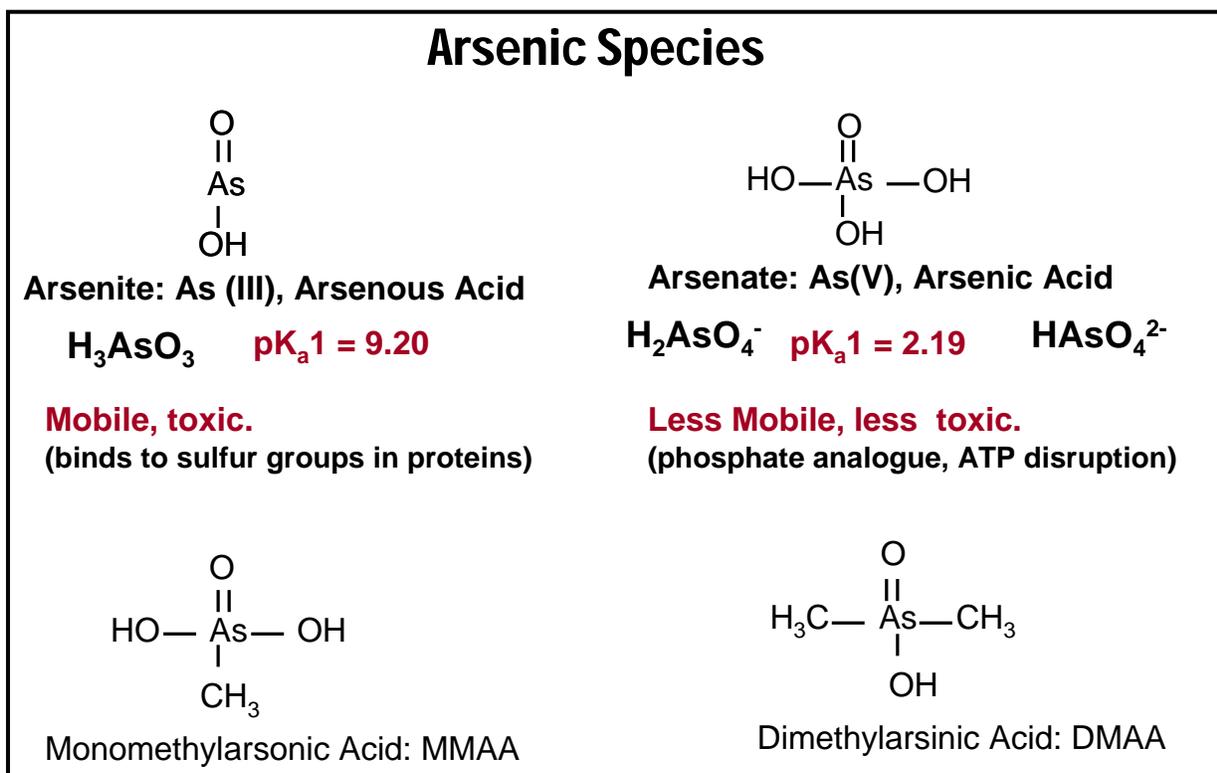
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APPENDIX A: Publications, Reports, and Presentations

1. Kerr S.C., M.M. Shafer, J. Overdier, and D.E. Armstrong. **2008**. Hydrologic and biogeochemical controls on trace element export from Northern Wisconsin wetlands. Accepted for publication in *Biogeochemistry* (01/19/2008).
2. Shafer M.M., J. Overdier, and D.E. Armstrong. Controls on arsenic oxidation state speciation in Wisconsin groundwaters. Manuscript in-preparation for submission to *Aquatic Geochemistry*.
3. Shafer M.M. Arsenic (III/V) Distribution in Wisconsin Groundwaters. Presentation before the Wisconsin Groundwater Coordinating Council (March 3, 2008)

APPENDIX B: Supplemental Information

B1. Arsenic Speciation & Geochemistry



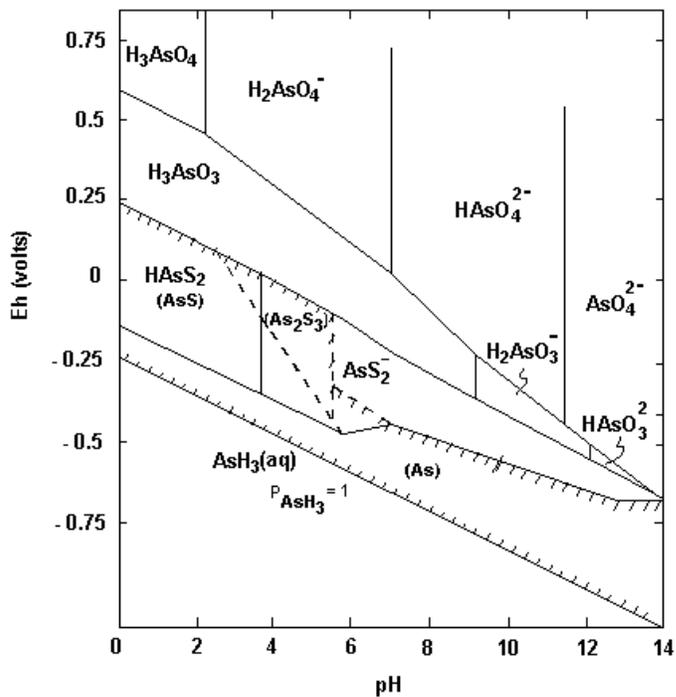


Fig. 2. The Eh-pH diagram for As at 25 °C and one atmosphere with total arsenic 10.5 mol/litre and total sulfur 10.3 mol/litre. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than 10.53 mol/litre (From: Ferguson & Gavis, 1972).

Electrochemical potential of some environmentally important redox pairs	
Chemical pair	E'_0 (mV)
O_2/H_2O	+818
SeO_4^{2-}/SeO_3^{2-}	+440
NO_3^-/NO_2^-	+430
Fe^{3+}/Fe^{2+}	+100
$HAsO_4^{2-}/H_3AsO_3$	+60
SO_4^{2-}/HS^-	-220
CO_2/CH_4	-244
S_0/HS^-	-270

Compiled from Bard et al. [71], Thauer et al. [72] and Macy [73].
FEMS Microbiology Ecology 48 (2004) pp.15-27

B2. Methods Detail

a. On-Site Separation of Arsenic Species

Arsenic Speciation Oxidation State: On-Site Separation

- In-line filtration to remove particulate species.
- In-line cartridge packed with As(V)-selective adsorbant (2.5 grams of aluminosilicate).
- 50 mL of groundwater sample collected after passage of 10 mL of rinse. = **As(III)**.
- Elute cartridge with dilute HCl. = **As(V)**.
- Or: **Filtered sample – As(III) = As(V)**.
- Quantitative in pH range from 4 to 9.
- Flow rate of 10-20 mL per minute.
- Rapid, minimizes speciation changes.
- Meng et al. 2001. Environ. Sci. Technol. 35:3476-3481.

b. Ferrous ion measurements (Fe^{2+})

Ferrous ion was measured using a modified version of the ferrozine complexation method, originally presented in Stookey 1970. In this method, ferrozine is added in the field to a sample collected into an Ar-purged bottle. The ferrozine binds the Fe^{2+} from solution and forms a magenta colored complex which is measured @ 562nm on a low noise, dual beam spectrophotometer.

c. Nitrogen Species Measurements (NH₄⁺, NO₃-NO₂)

Modified versions of EPA Methods 350.1 and 353.2 were used to simultaneously measure NH₃-N and NO₃⁻+NO₂⁻-N (Wisconsin State Lab of Hygiene (WSLH) ESS INO Method 220.3 rev 6). Sub-samples are preserved in the field with sulfuric acid. Quantitation limits are 0.048 mg NH₃-N/L and 0.061 mg NO₃+NO₂-N/L. Total nitrogen is determined by high temperature combustion followed by chemiluminescence detection of NO.

d. Sulfate/Sulfide measurements

Total sulfur was determined by HR-ICP-MS, with a quantification limit of 10 µg L⁻¹. Sulfide was determined with an ion-selective electrode. Sub-samples for sulfide are collected directly into SAOB buffer and S²⁻ is determined to a level of 2 µg L⁻¹. Sulfate is quantified using Ion Chromatography.

e. Elemental Analysis

Total Fe, Mn and a large suite of other elements (see table below) were measured using HR-ICP-MS.

Element Group	N	Elements Examined
Alkali Metals	5	Li, Na, K, Rb, Cs
Alkaline Earths	5	Be, Mg, Ca, Sr, Ba
Transition Metal Groups 3,4	5	Sc, Y, Ti, Zr, Hf
Transition Metal Groups 5, 6	4	V, Cr, Mo, W
Transition Metal Groups 7, 8, 9, 10	4	Mn, Fe, Co, Ni
Platinum Group	3	Rh, Pd, Pt
Transition Metal Groups 11, 12	5	Cu, Ag, Zn, Cd, Hg
Lanthanides	9	La, Ce, Nd, Sm, Eu, Tb, Dy, Er, Yb
Actinides	2	Th, U
Semi-Metals	5	Al, Sn, Sb, Tl, Pb
Non-Metals	5	Si, P, S, As, Se

f. Oxygen Isotope Ratios

Oxygen isotope (¹⁸O/¹⁶O) ratios are determined to estimate groundwater age. Established isotope ratio mass spectrometer techniques were employed.

g. Total Organic Carbon

Total organic carbon was measured using high temperature combustion (720°C) with NDIR detection (Shimadzu TOCV) with a detection limit of 20 ppb.

B3. Supplemental Figures

Figure B-1. Arsenic speciation [%As(III)] versus Eh along a groundwater flowpath in Vilas Co. WI (Big Muskie Lake to Allequash Creek flowpath).

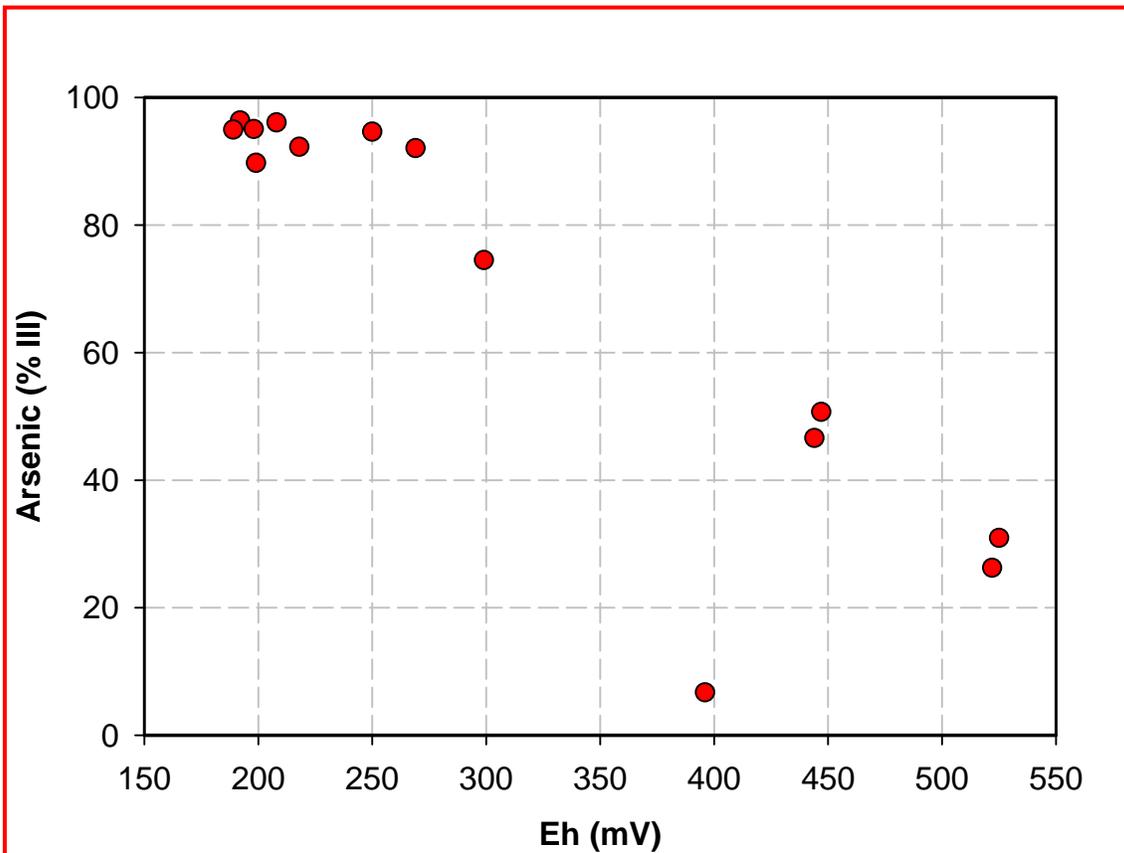


Figure B-2. Site Matrix: Quartile Distribution by Iron

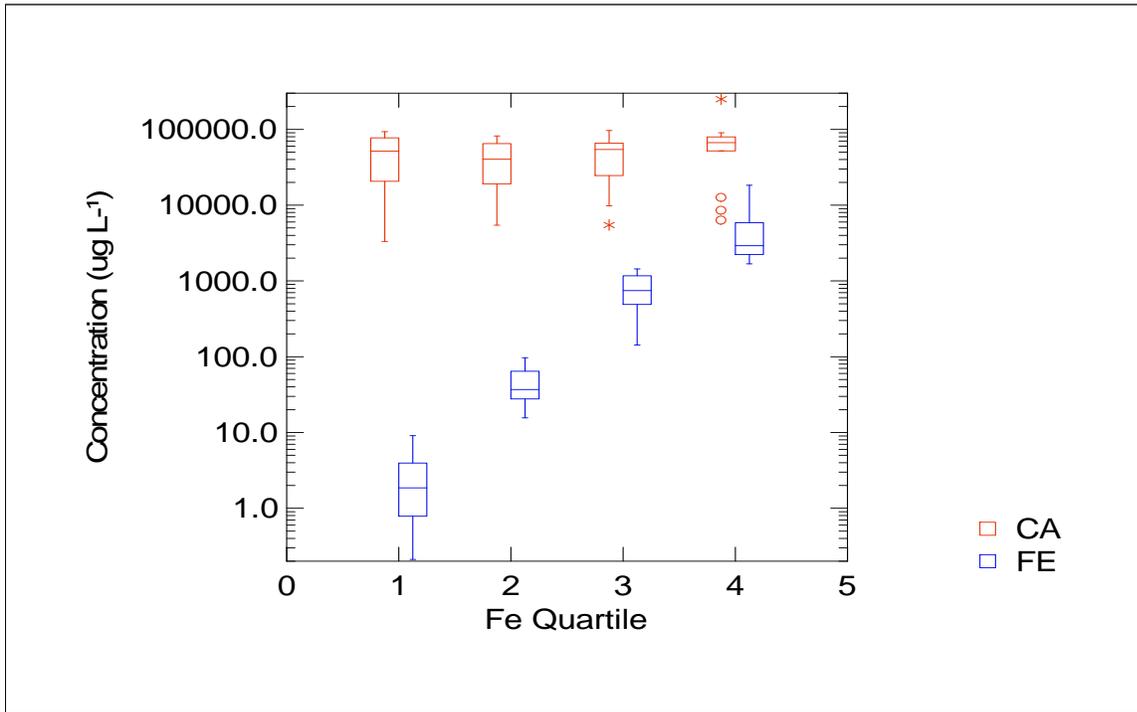


Figure B-3. Site Matrix: Quartile Distribution by Calcium

