Background Screening Methodology for Fort Wingate

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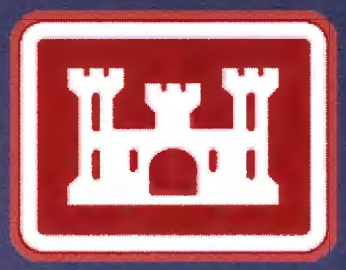

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Background Screening Methodology

- **Objective** – Evaluate existing data to identify and remove samples that are not representative of background concentrations. Use surviving data to characterize background.
- **Approach** – Rigorous, reproducible, multi-step screening process using statistical and geochemical evaluation methods.

Background Screening Methodology

Extraction of Background from Existing Data				
Facility Type	**Facility**	**State**	**EPA Region**	**Media**
Army	Ft. Gillem	GA	4	GW, SW, Soil, Sed
	Redstone Arsenal	AL	4	GW
Navy	Pearl Harbor Naval Complex	HI	9	SW, Sed
	Point Loma Naval Base	CA	9	GW
Air Force	Air Force Plant 6	GA	4	GW, SW, Soil, Sed
	Kirtland AFB	NM	6	GW, Soil
	Walker AFB	NM	6	GW
DOE	Sandia National Lab	NM	6	GW, Soil

Background Screening Methodology

- Completeness of analyses
- Organic contaminant screening
- Outlier testing
- High-nondetect testing
- Statistical evaluation via percentile plots
- Geochemical evaluation

Completeness of Analyses

- Reporting limits
- Laboratory qualifiers
- Field parameters (pH, DO, ORP, turbidity)
- Reference elements
  - Aluminum
  - Iron
  - Manganese
  - Calcium

Organic Contaminant Screening

- Samples with "significant" concentrations of VOC's or SVOC's will be considered suspect:
  - Significant = above RLs
  - Multiple organic detections
  - Samples with low estimated concentrations will be subject to geochemical evaluation

Outlier Testing

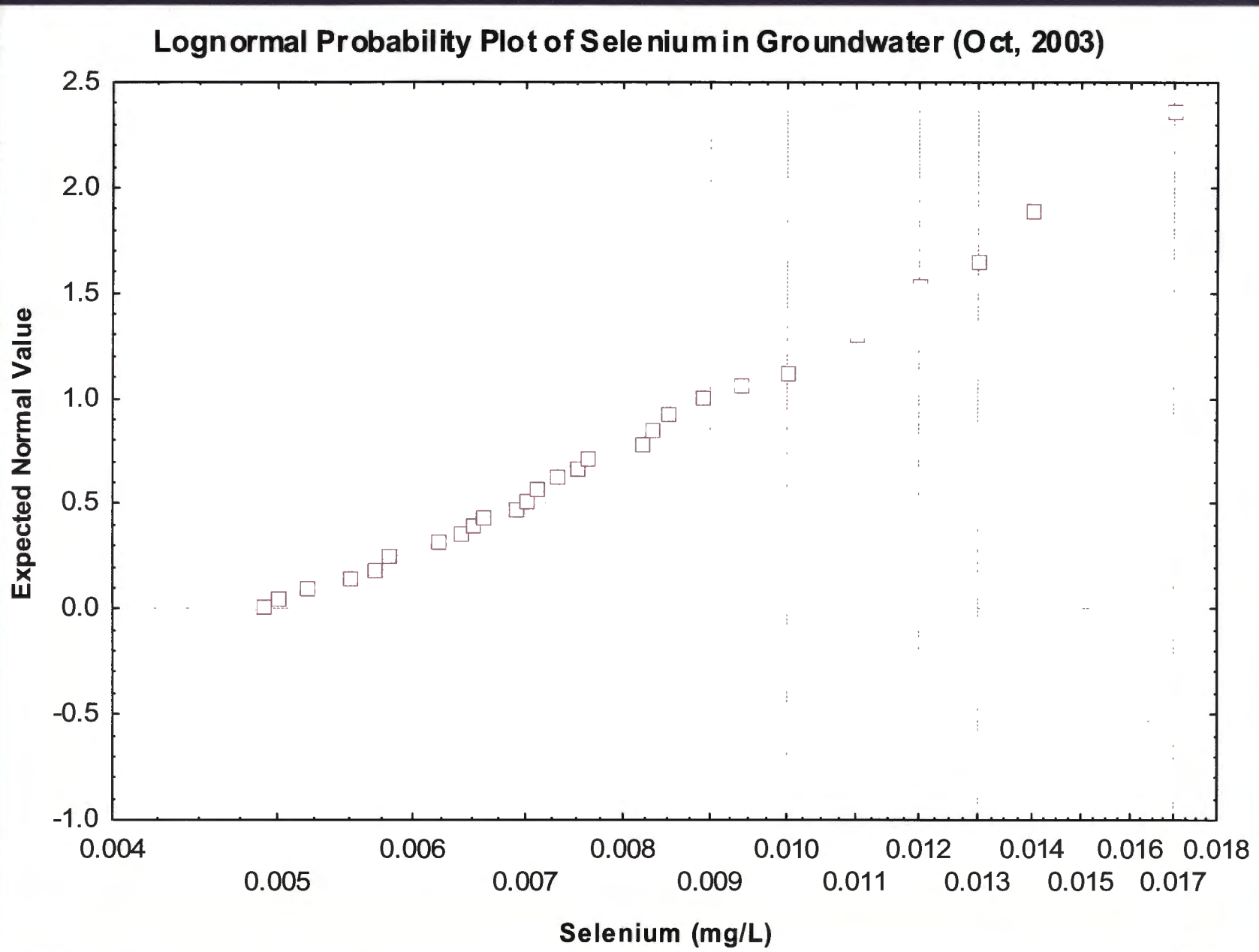
- The existing data for each element will be rank-ordered and the maximum value will be flagged if it is greater than 5 times the second-highest value (EPA, 1989).
- Identified outliers will be further examined in geochemical evaluation step to determine if there is a natural explanation for the elevated concentration.
- If outlier is a geochemical anomaly, then it will be deleted from the data set.

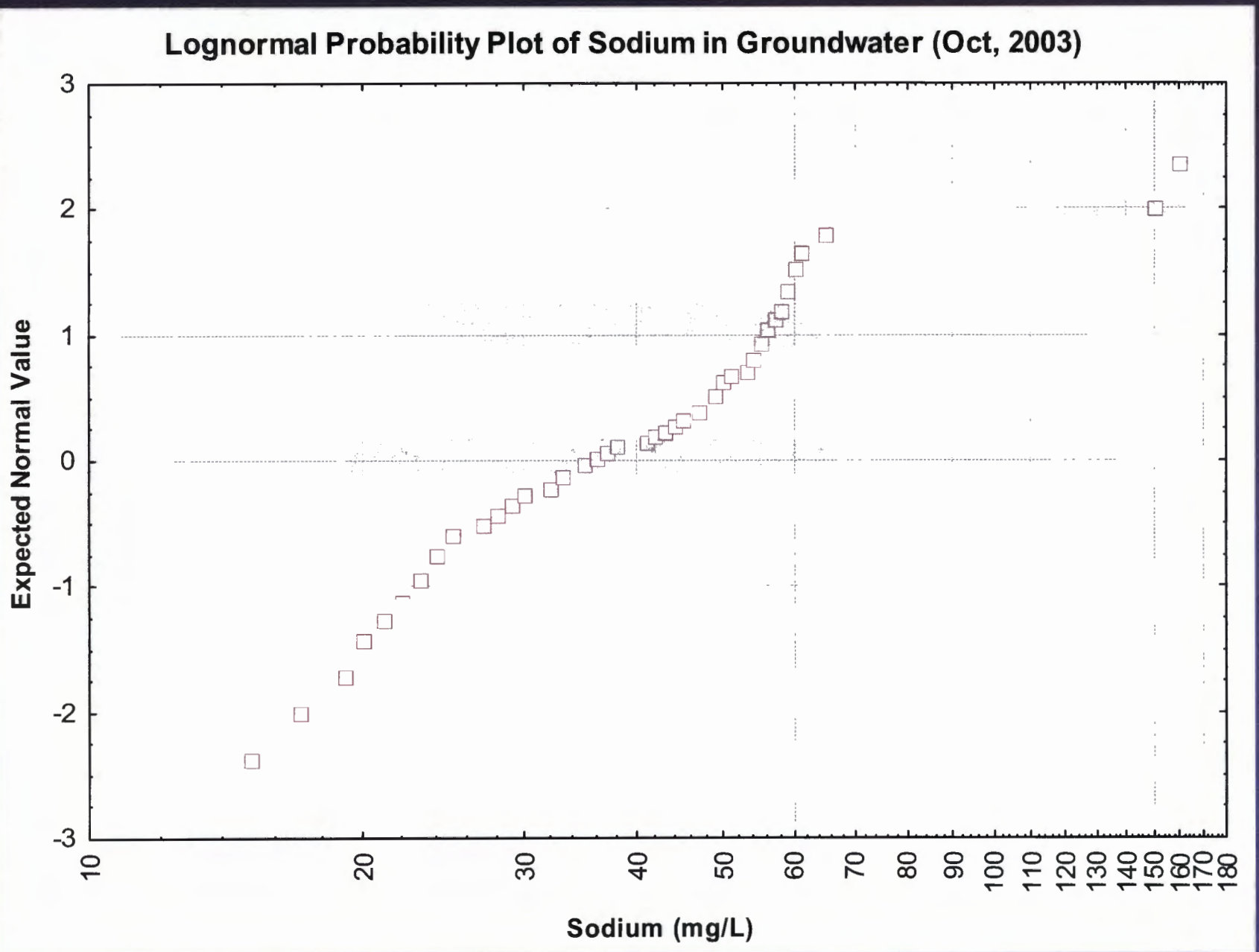
High-Nondetect Testing

- Nondetects whose replacement values (½ the RL) lie in the top ten percent of the distribution will be identified as "high nondetects" and will be eliminated from the data set. This step avoids high bias in the 95th upper tolerance limit background screening values.

Probability Plots

- Identifies statistical outliers
- Determines distributional shape (normal or lognormal)
- Identifies multi-modal distributions by break in slope


Lognormal Probability Plot of Selenium in Groundwater (Oct, 2003)
Expected Normal Value
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
0.004
0.005
0.006
0.007
0.008
0.009
0.010
0.011
0.012
0.013
0.014
0.015
0.016
0.017
0.018
Selenium (mg/L)


Lognormal Probability Plot of Sodium in Groundwater (Oct, 2003)
Expected Normal Value
3
2
1
0
-1
-2
-3
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Sodium (mg/L)

Geochemical Evaluation

- Used to distinguish between naturally high background concentrations versus contamination
  - Methods based on the known geochemical behavior of the elements
  - Compliments statistical evaluations
  - Determines if statistical outliers should be included or rejected
  - Can identify contamination, even if insignificant
  - Identifies processes controlling element concentrations

Geochemical Evaluation of Metals in Soil and Sediment

- **Oxyanionic elements – negatively charged speciation in solution**

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}
Molybdenum (VI)=	$HMoO_4^-$, MoO_4^{-2}
Uranium (VI) =	$UO_2(CO_3)_2^{-2}$

Geochemical Evaluation of Metals in Soil and Sediment

- **Cationic elements – positively charged speciation**

  Barium = Ba^{+2}

  Lead = Pb^{+2}

  Nickel = Ni^{+2}

  Zinc = Zn^{+2}

- **Mixed elements – multiple charges at equilibrium**

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

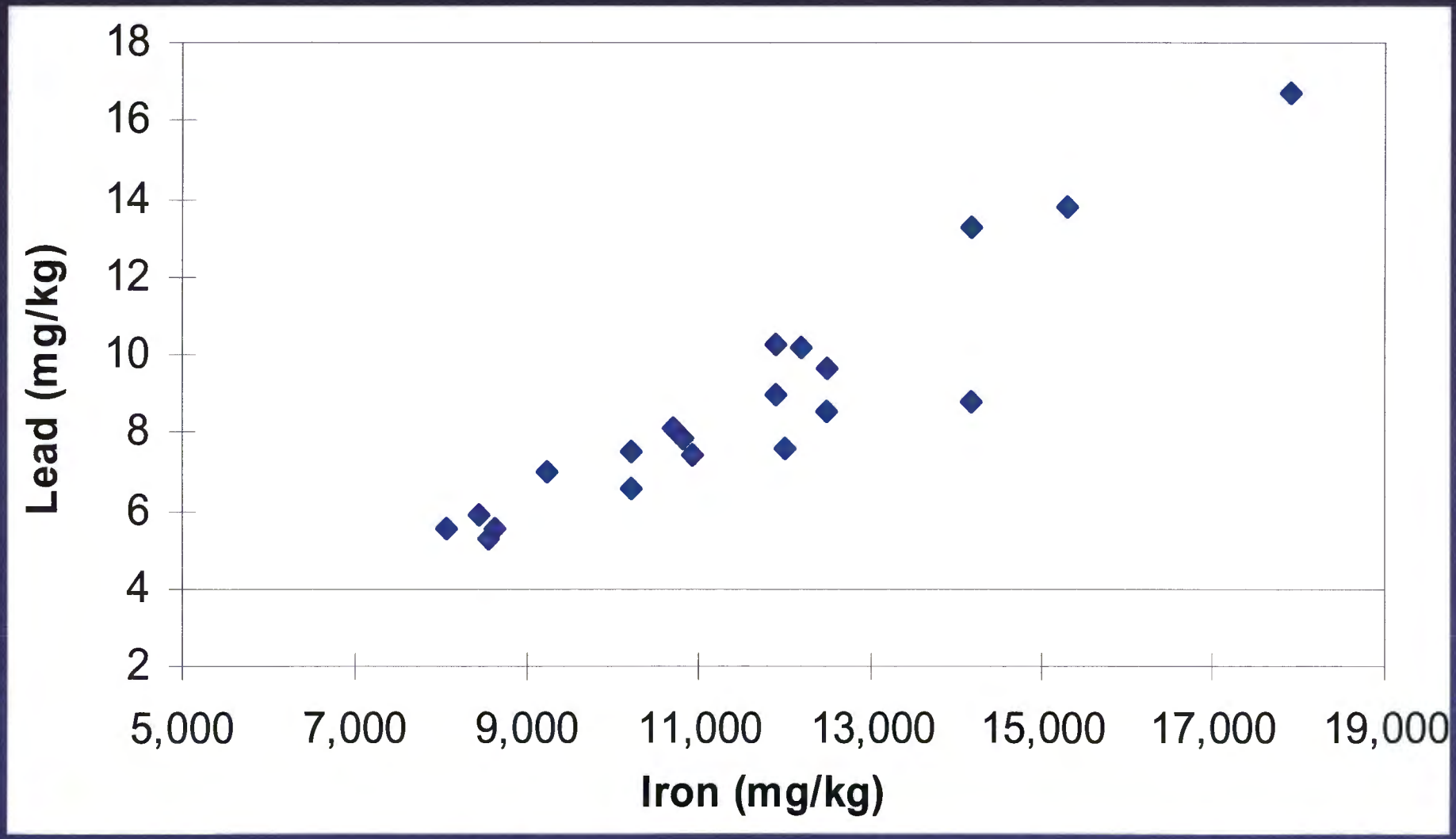
Surface Charges of Soil-Forming Minerals

- **Clays** = negative surface charge at neutral pH
  - Attracts Cu, Ni, Zn (small ionic radii)
- **Fe-oxides** = positive surface charge at neutral pH
  - Attracts As, Sb, Se, V, Mo, U
- Evaluate correlations with major elements
  - Use Fe for oxyanionic elements
  - Use Al (clays) and/or Mn for cationic elements
  - Trace elements will maintain near-constant ratios with Al, Fe, or Mn if naturally occurring

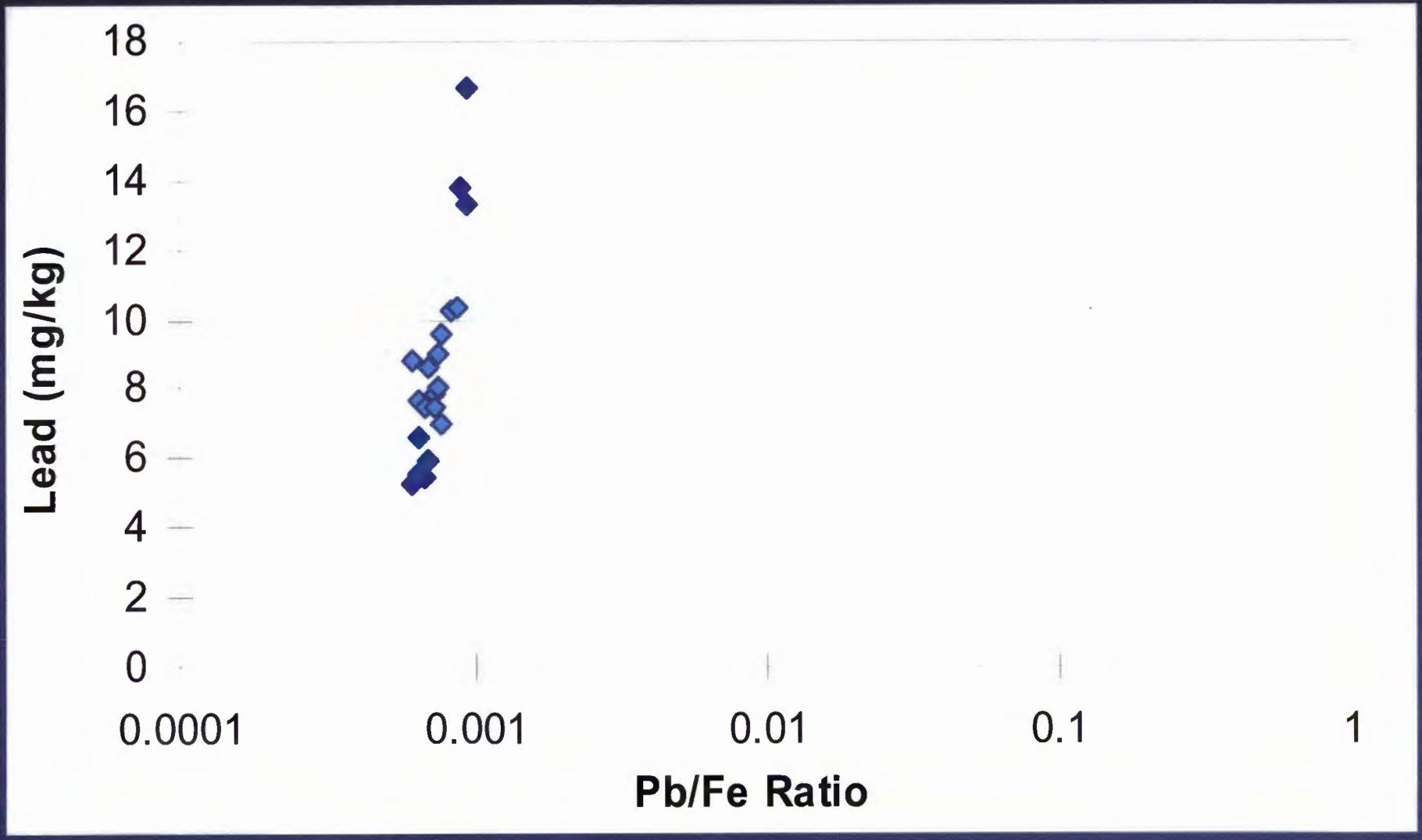
Deming Army Air Field, NM

- Twenty samples total
- Trench and soil borings
- Depths 0 to 15 ft.
- Analyzed for TAL metals

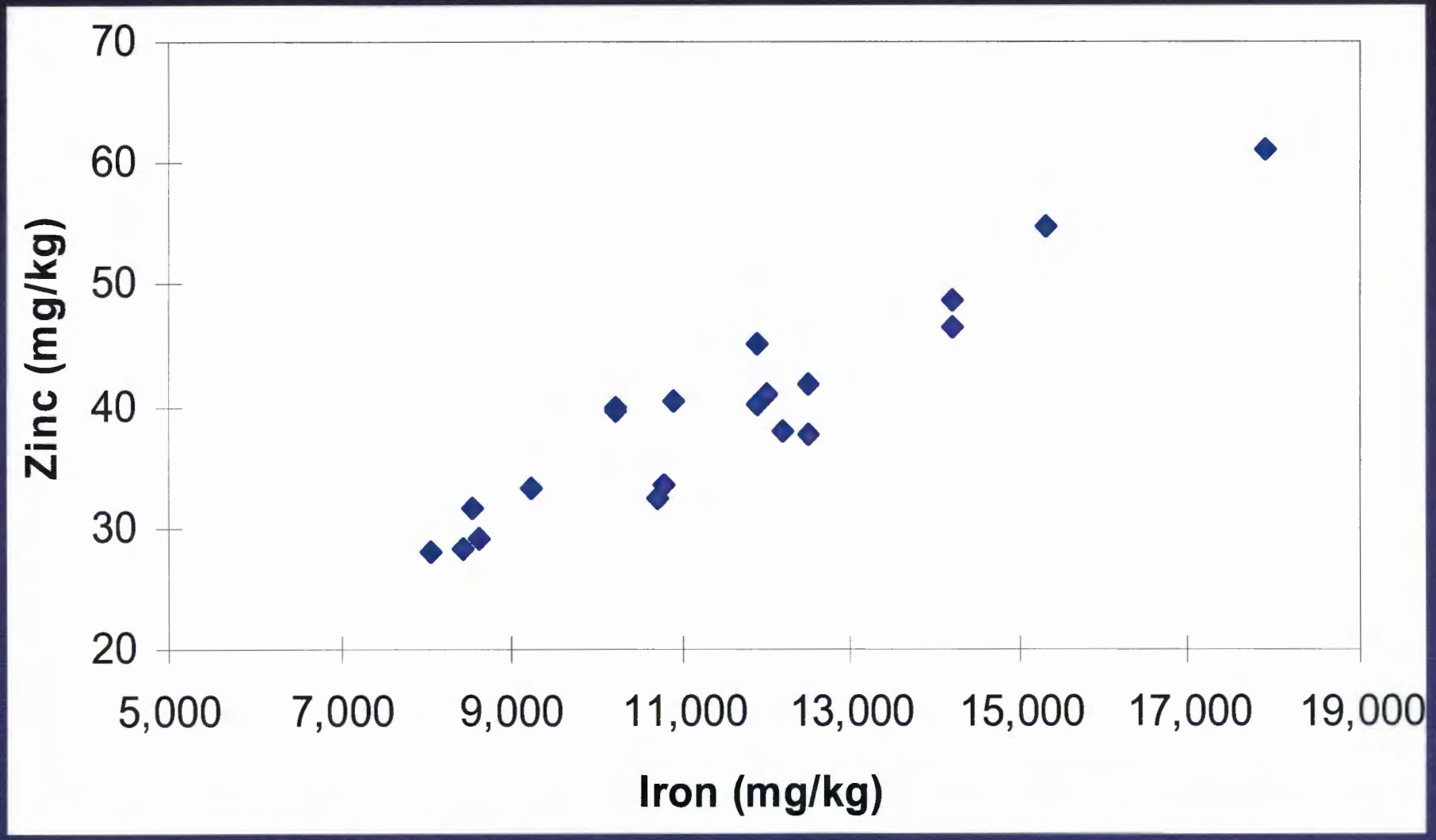
Deming Army Air Field, NM – Pb vs Fe



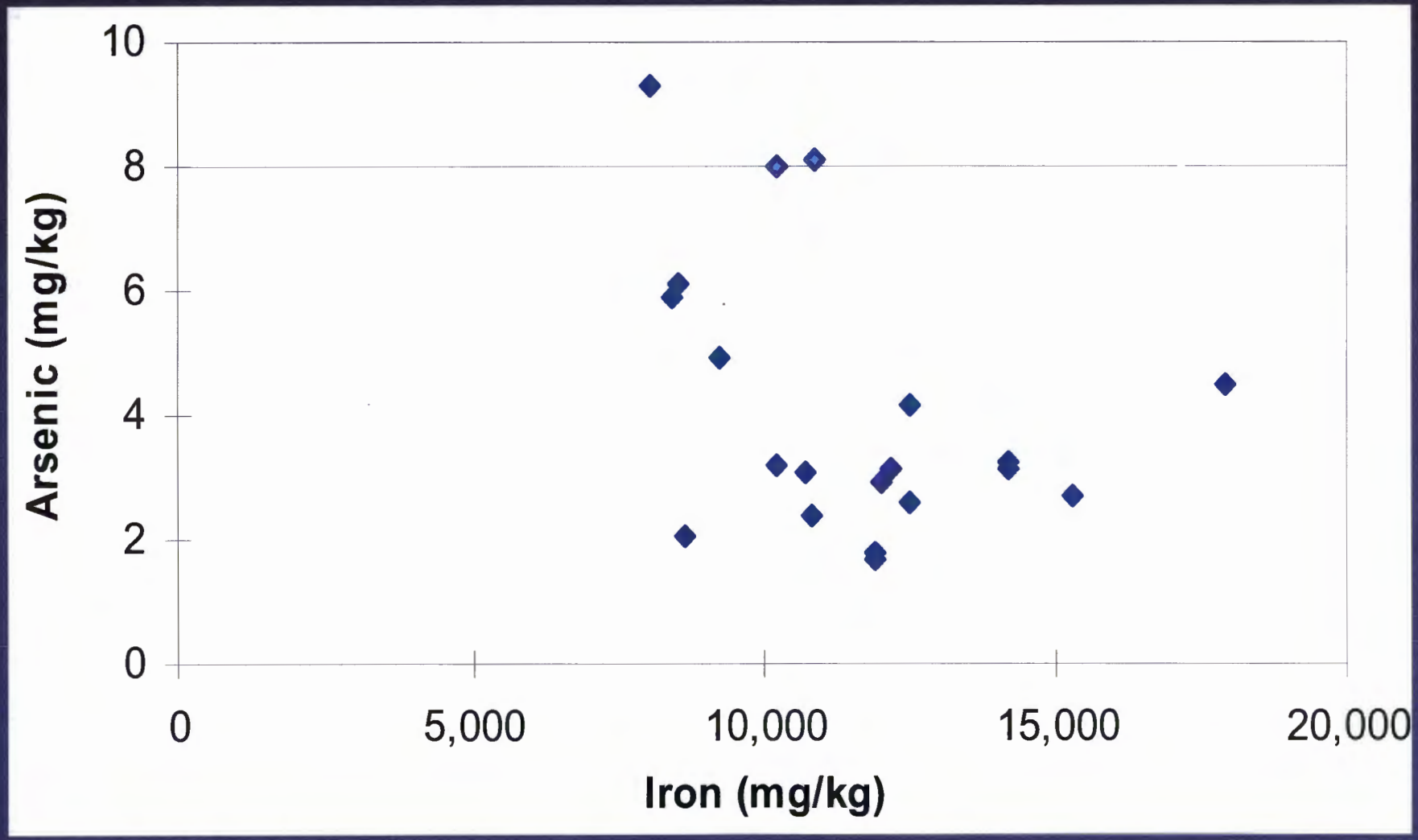
Deming Army Air Field, NM
Pb vs Pb/Fe Ratios



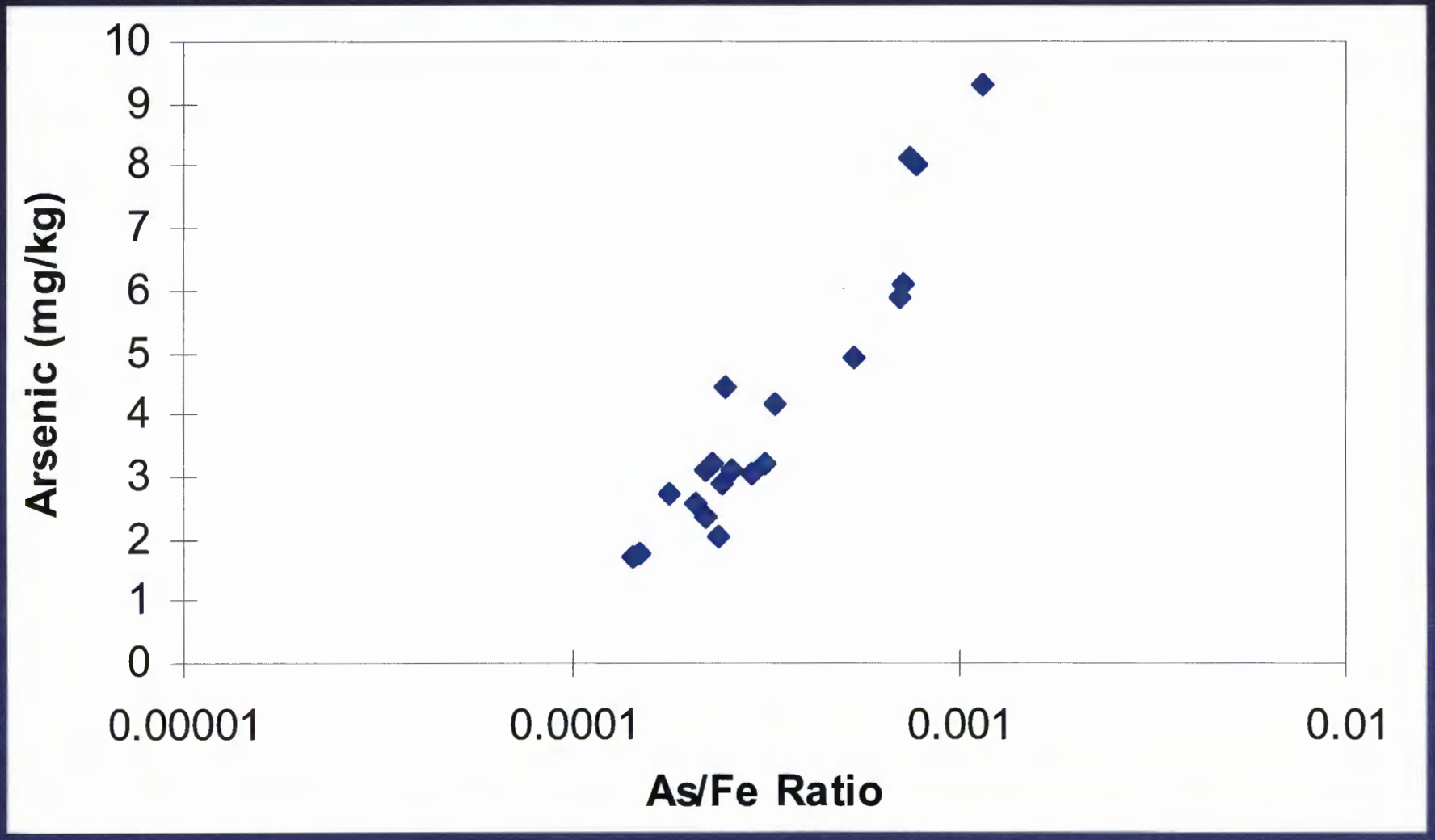
Deming Army Air Field, NM – Zn vs Fe



Deming Army Air Field, NM – As vs Fe



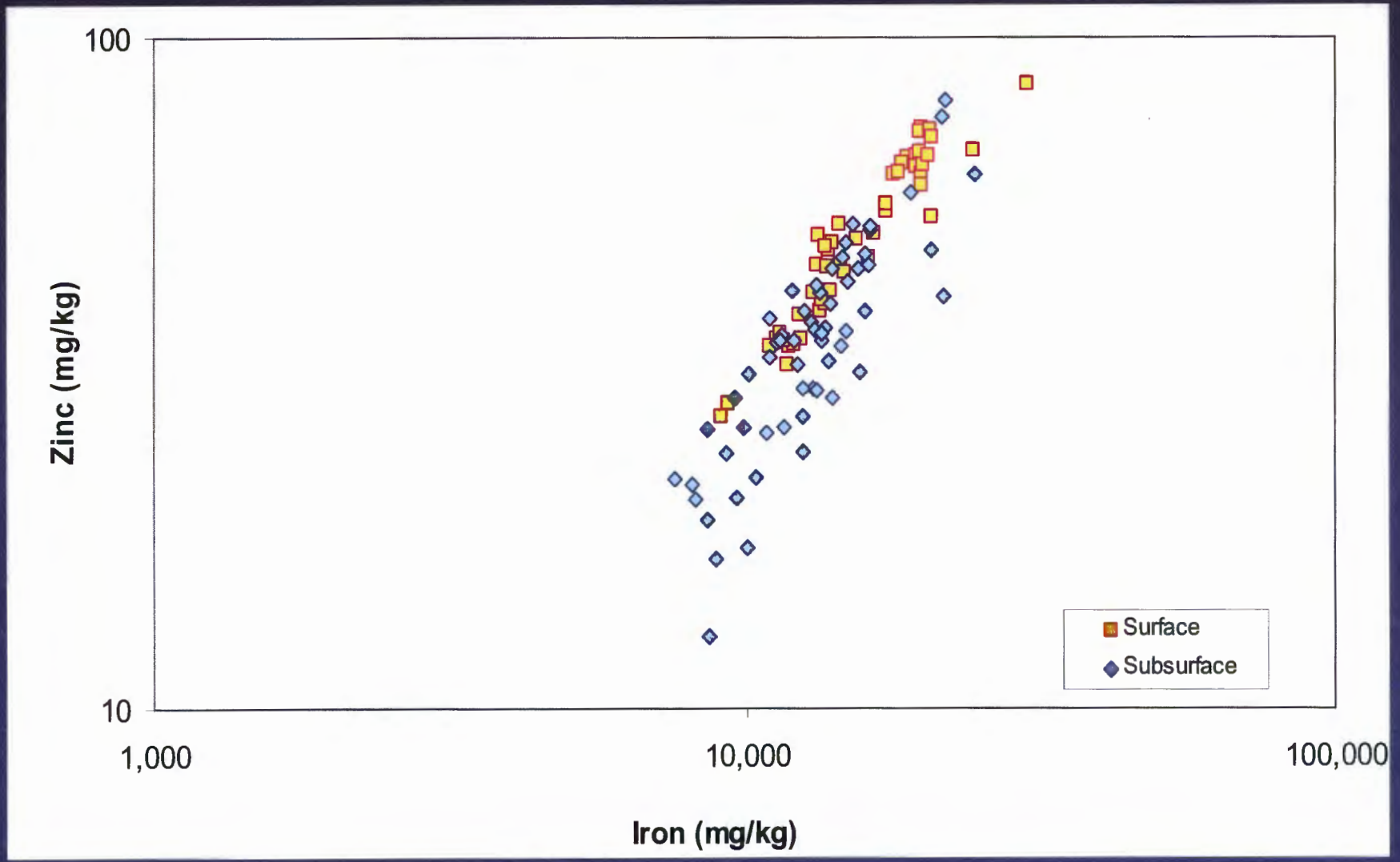
Deming Army Air Field, NM
As vs As/Fe Ratios



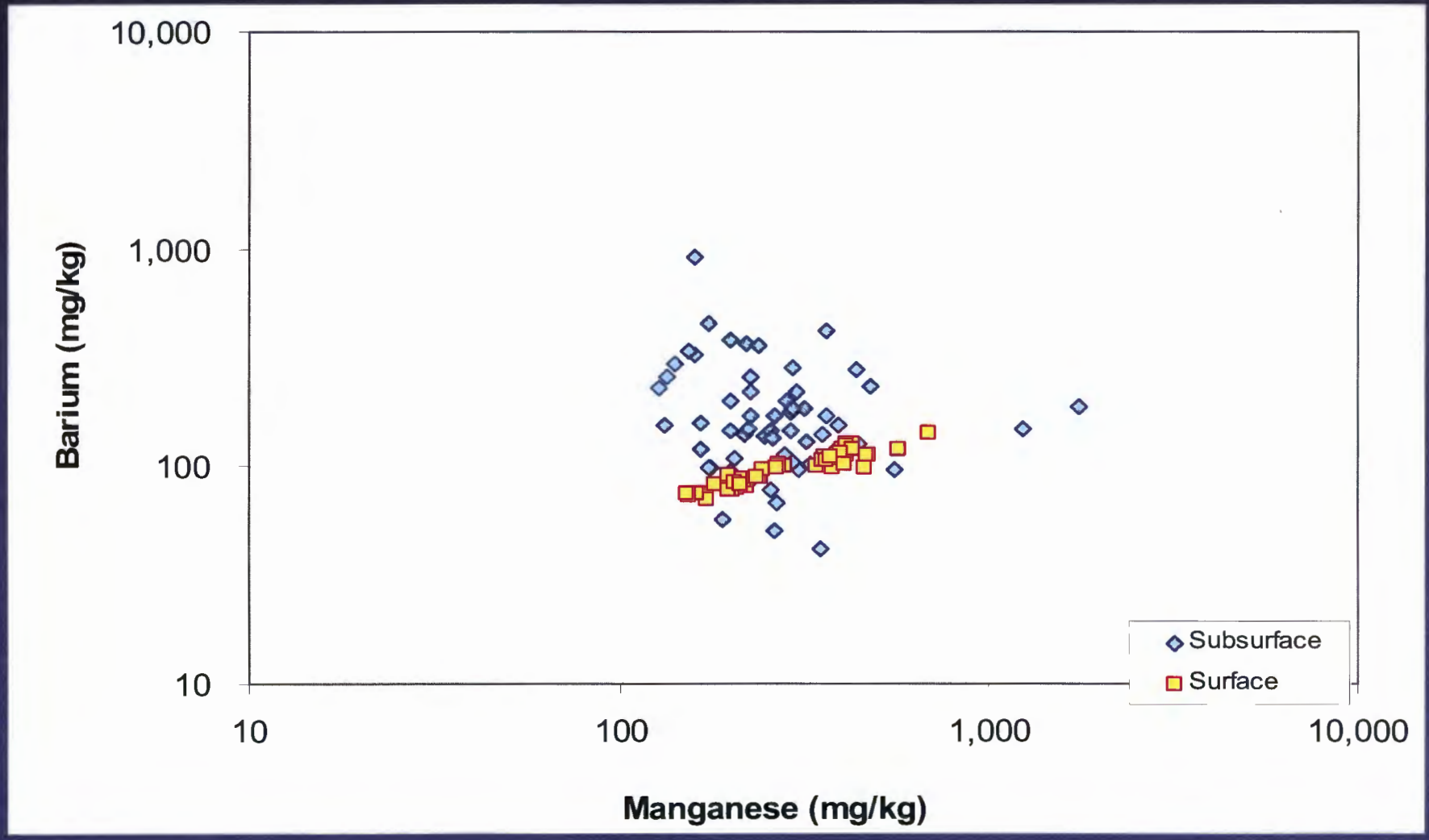
Former Walker AFB Background Soil Study

- 52 samples were obtained:
  - 15 surface samples
  - 37 subsurface samples from 5 to 50 feet bgs.

Former Walker AFB Background Soil Study

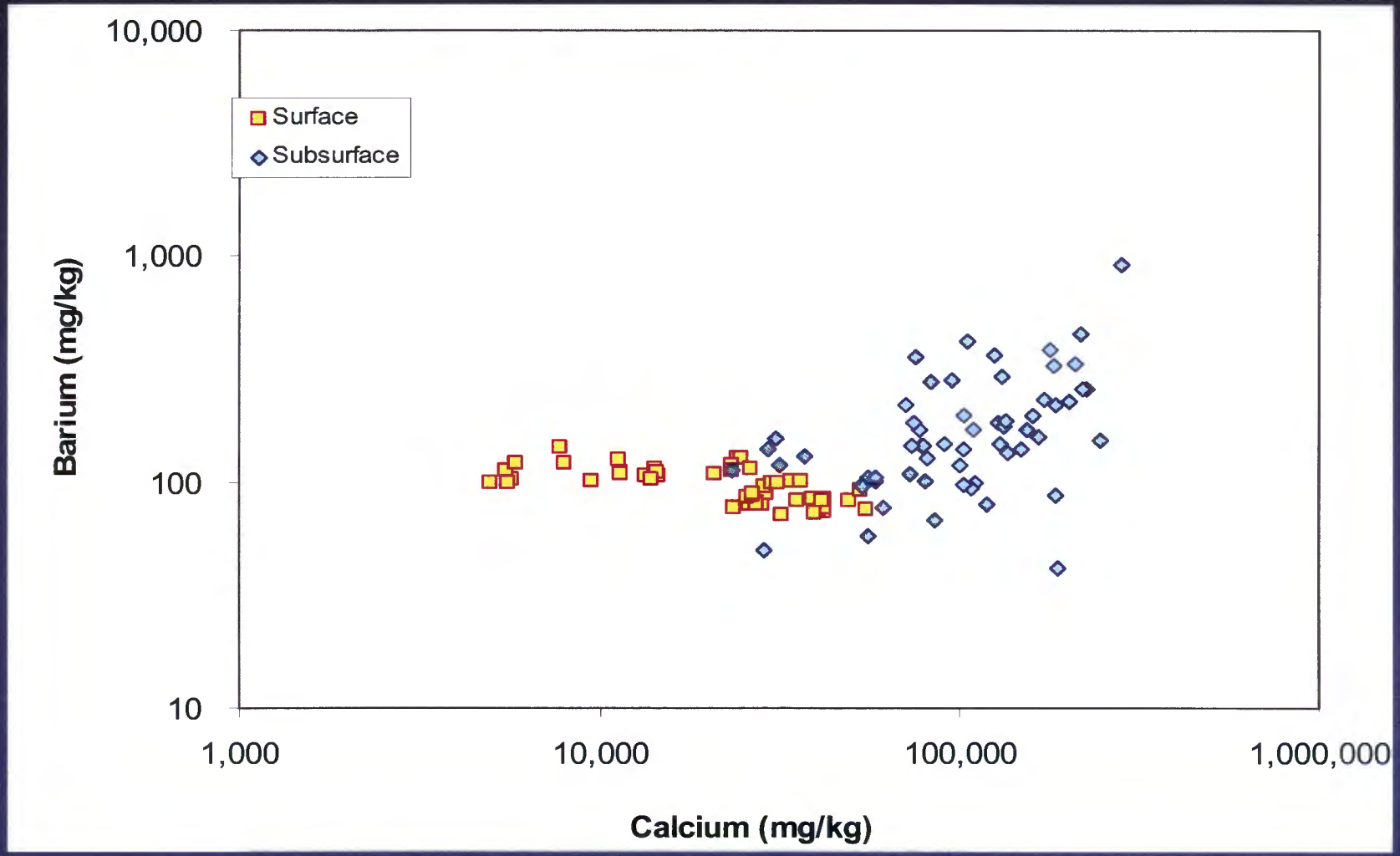


Former Walker AFB – Background Soil Study, Ba vs. Mn



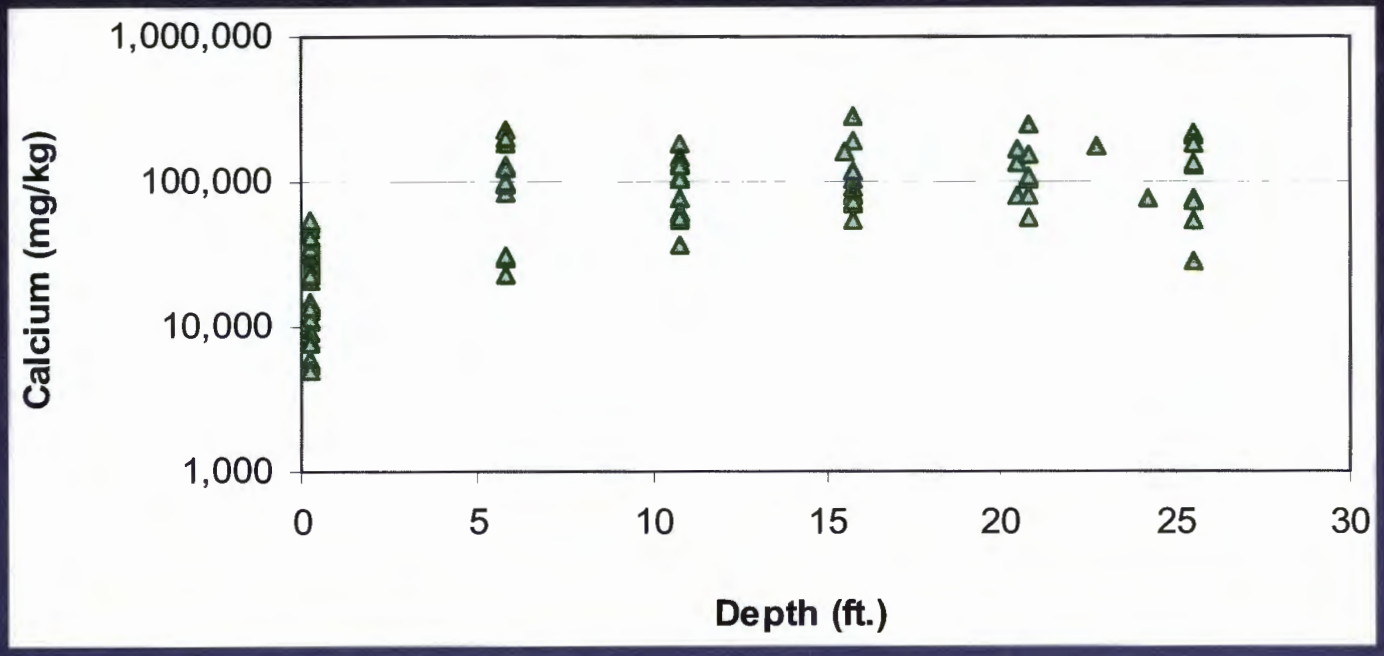
Ba correlated with Mn in surface samples but not subsurface

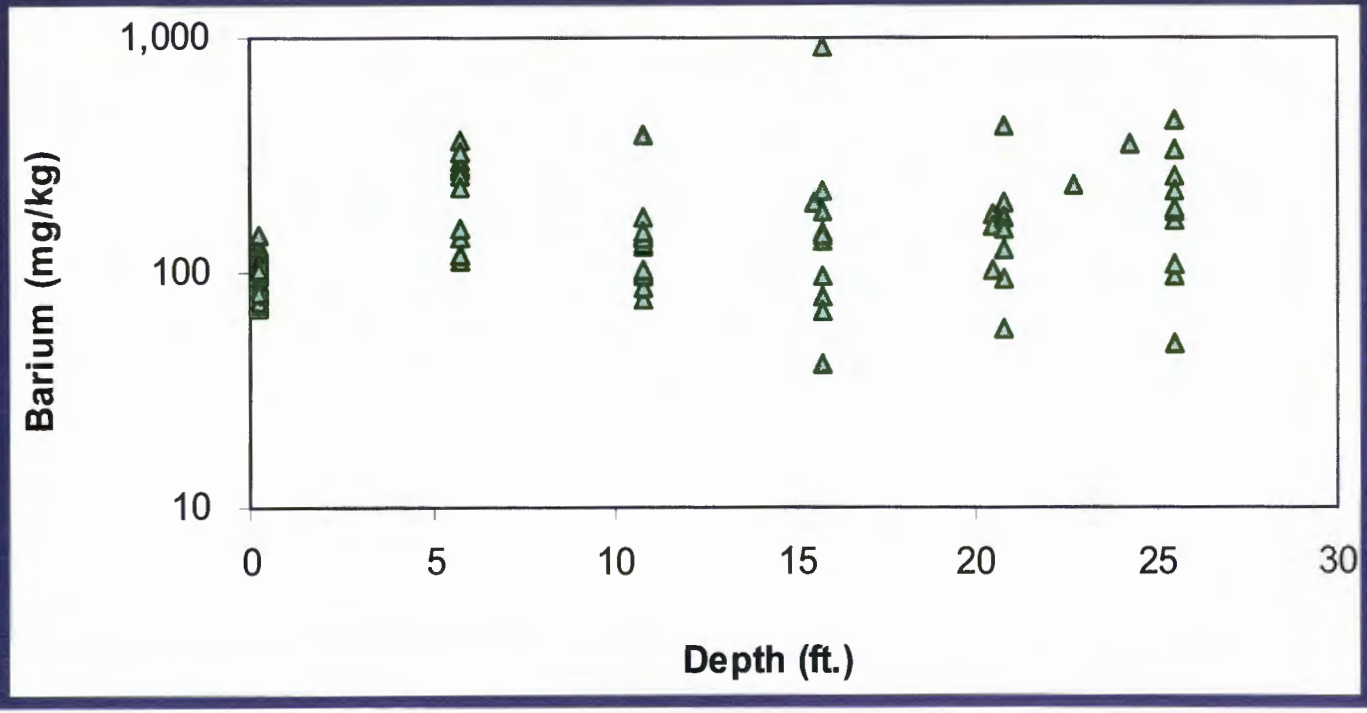
Former Walker AFB – Background Soil Study
Ba vs. Ca



Ba increases with Ca in most subsurface samples

Former Walker AFB – Background Soil Study Ca, Ba vs. Depth





Processes Considered in Geochemical Evaluation of Groundwater

- Suspended particulates
- Reductive dissolution
- pH effects
- Contamination

Effects of Suspended Particulates

- Suspended particulate diameters range = 100 to 0.001 micron. Some get through 0.45 micron filter.
- 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 >0.1 mg/L indicate suspended Al-bearing minerals (clays).
- In neutral pH, moderate to oxidizing redox conditions, Fe concentrations >0.1 mg/L indicate suspended iron oxides.
- Iron is soluble under reducing conditions.

Trace Metal Adsorption on Suspended Particulates

- **Clays** = negative surface charge at neutral pH
  - Attracts Cu, Ni, Zn (small ionic radii)
- **Fe-oxides** = positive surface charge at neutral pH
  - Attracts As, Sb, Se, V, Mo, U
- Evaluate correlations with major elements
  - Use Fe for oxyanionic elements
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  - Trace elements will maintain near-constant ratios with Al, Fe, or Mn if naturally occurring

Effects of Reductive Dissolution

- Releases of organic contaminants (fuel, solvents, landfill leachate) can establish local reducing environments via anaerobic microbial activity.
- These conditions drive the dissolution of iron oxides and manganese oxides, mobilizing trace elements that were adsorbed on the oxide surfaces.
- Reducing conditions can be natural (wetlands, swamps).

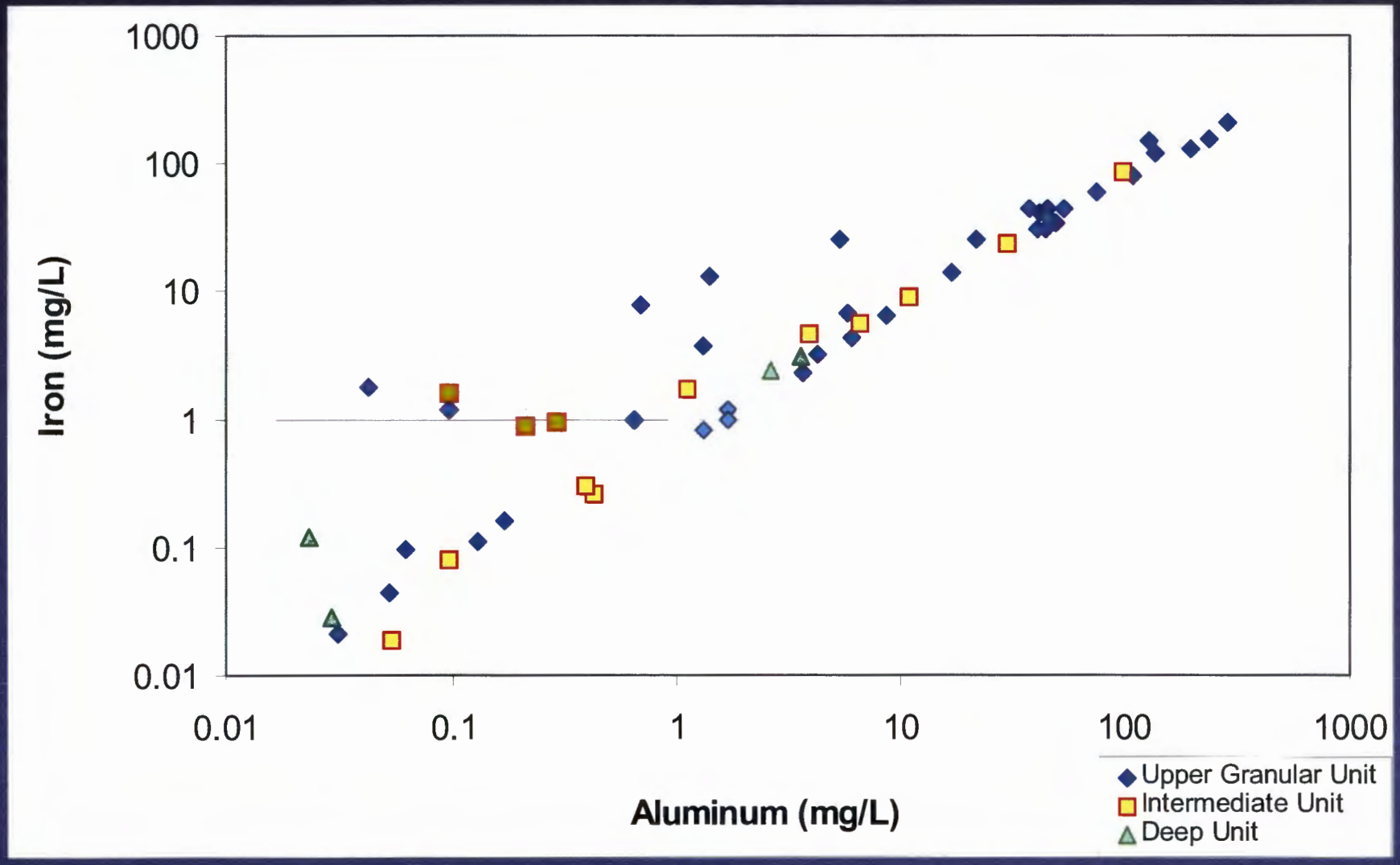
Identification of Reductive Dissolution

- Effects identified by correlations of metals with indicators of local redox depression:
  - Low ORP and DO
  - Elevated dissolved Fe and Mn (Filt/Unfilt ratios ~1.0)
  - Elevated unfiltered 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

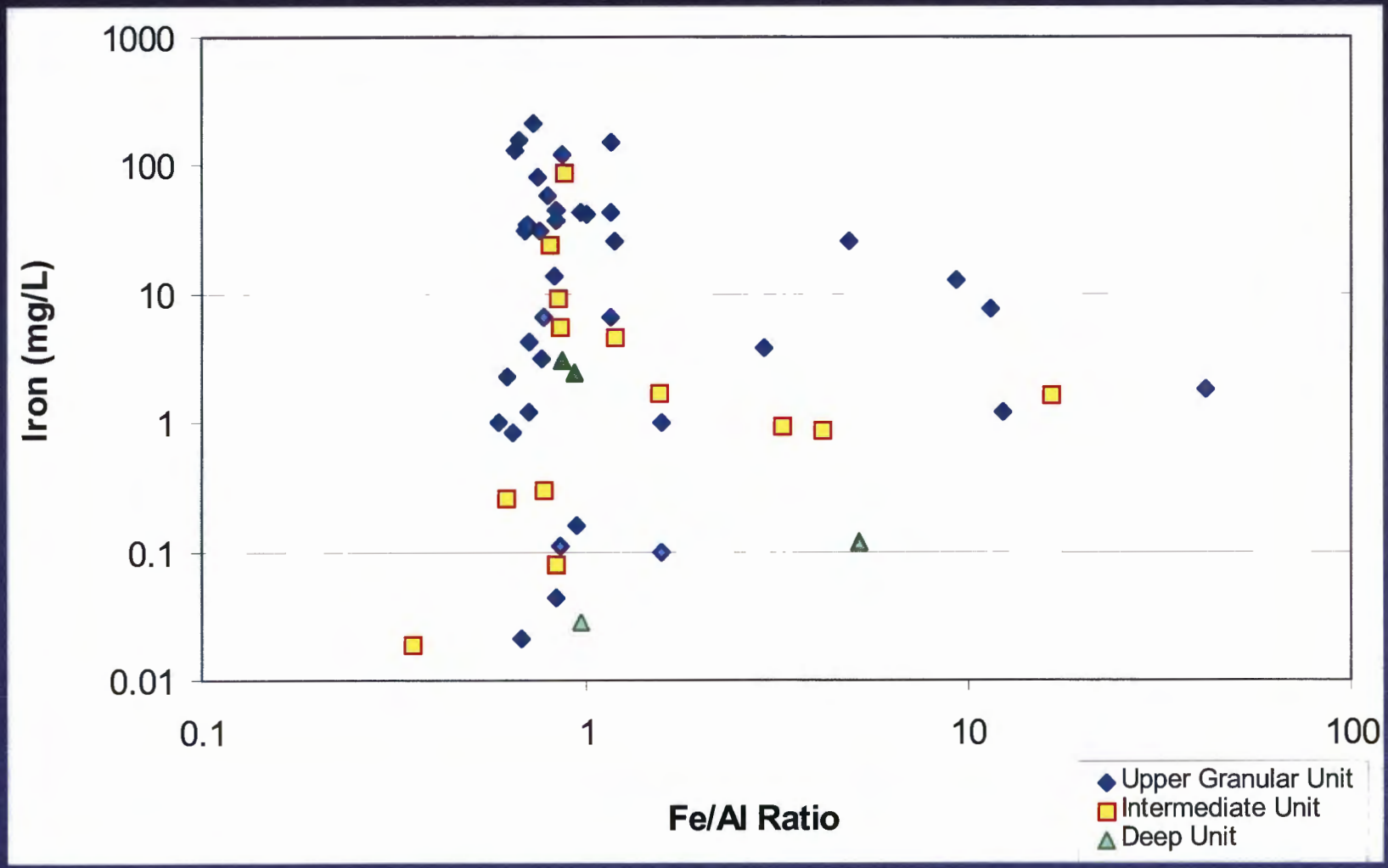
Geochemical Evaluation Examples from Walker AFB Groundwater

- Seventy samples obtained in October, 2003
  - Upper Granular Unit (40)
  - Intermediate Unit (24)
  - Deep Unit (6)
- Extracted background from data

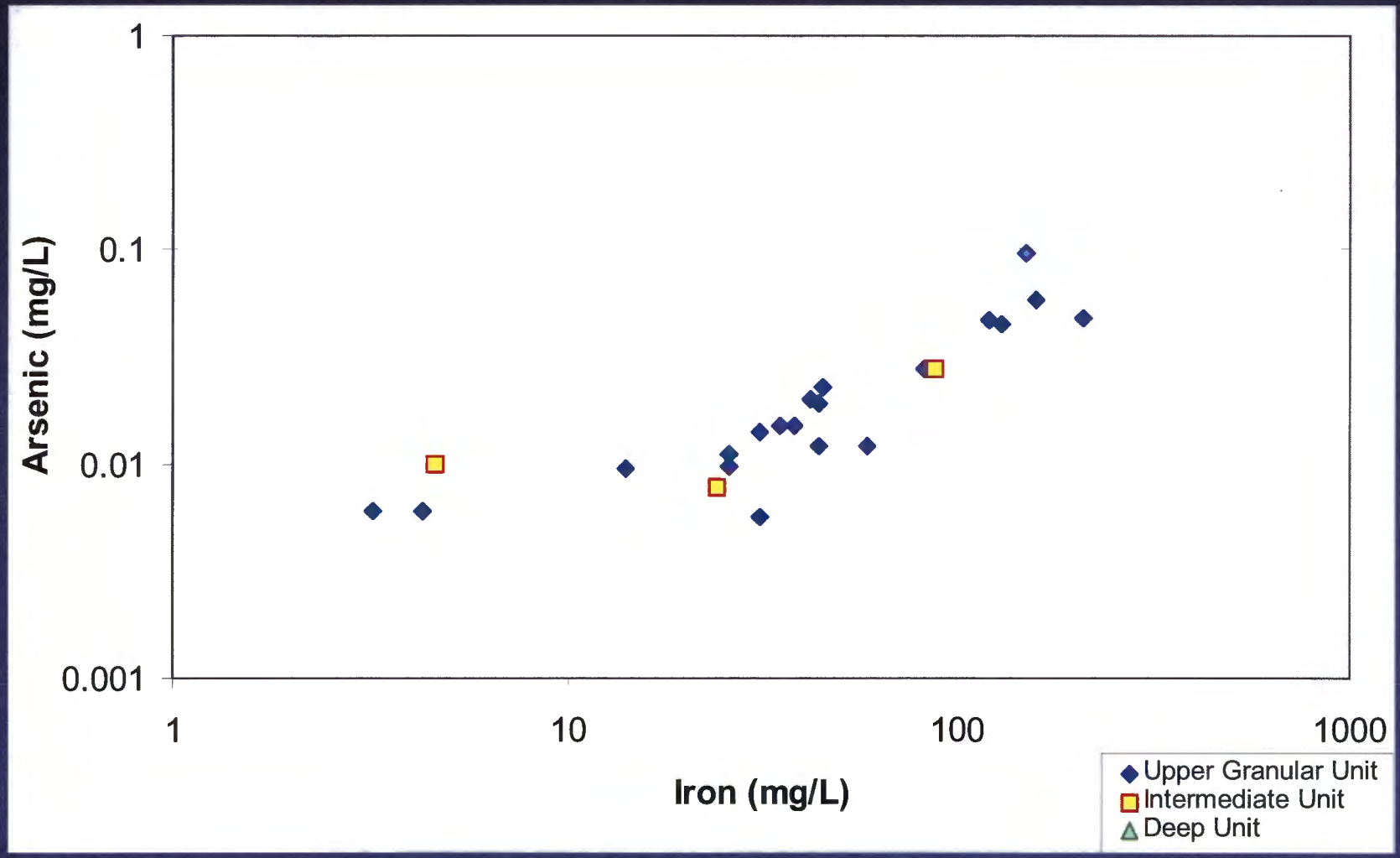
Iron vs. Aluminum



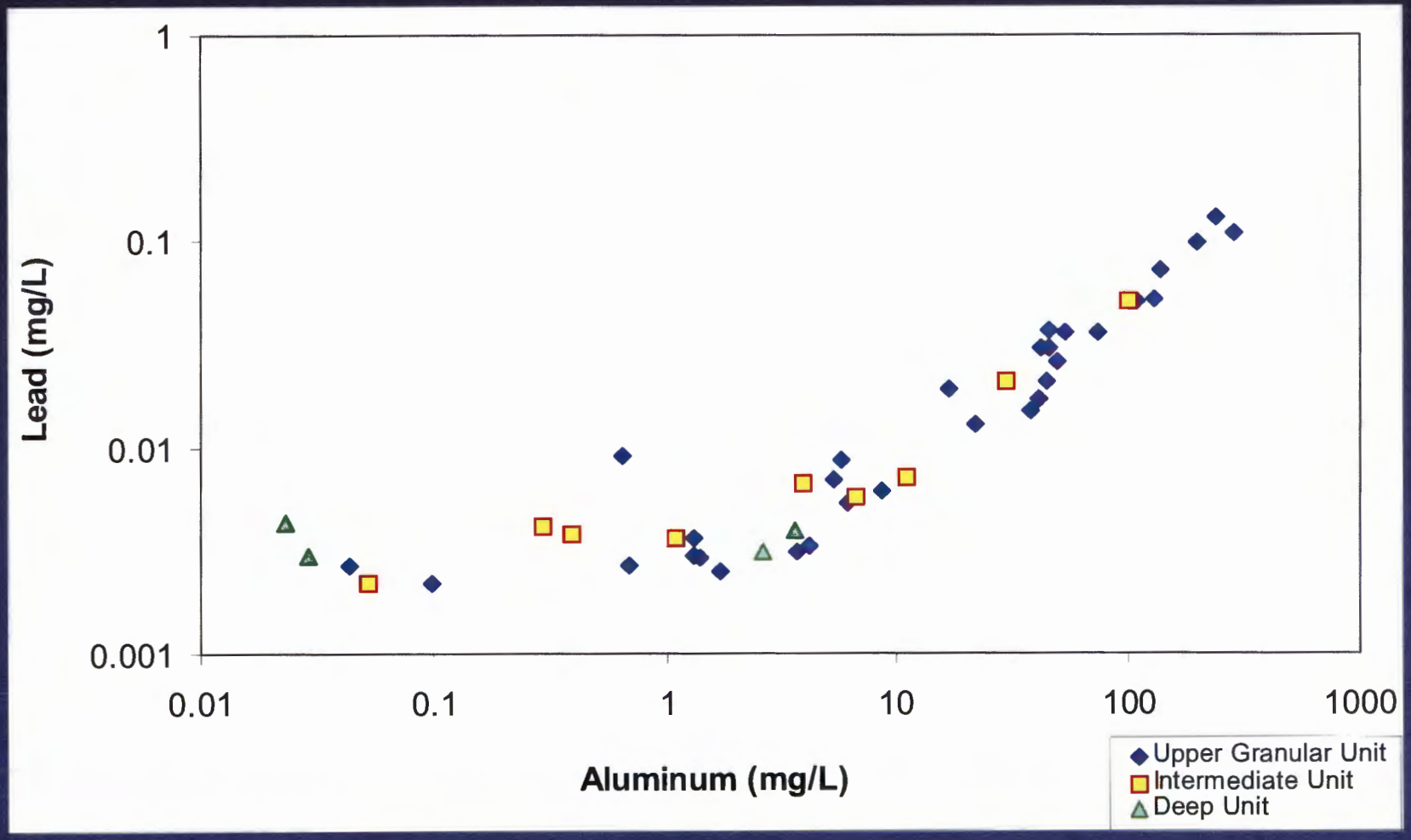
Iron vs. Fe/Al Ratios



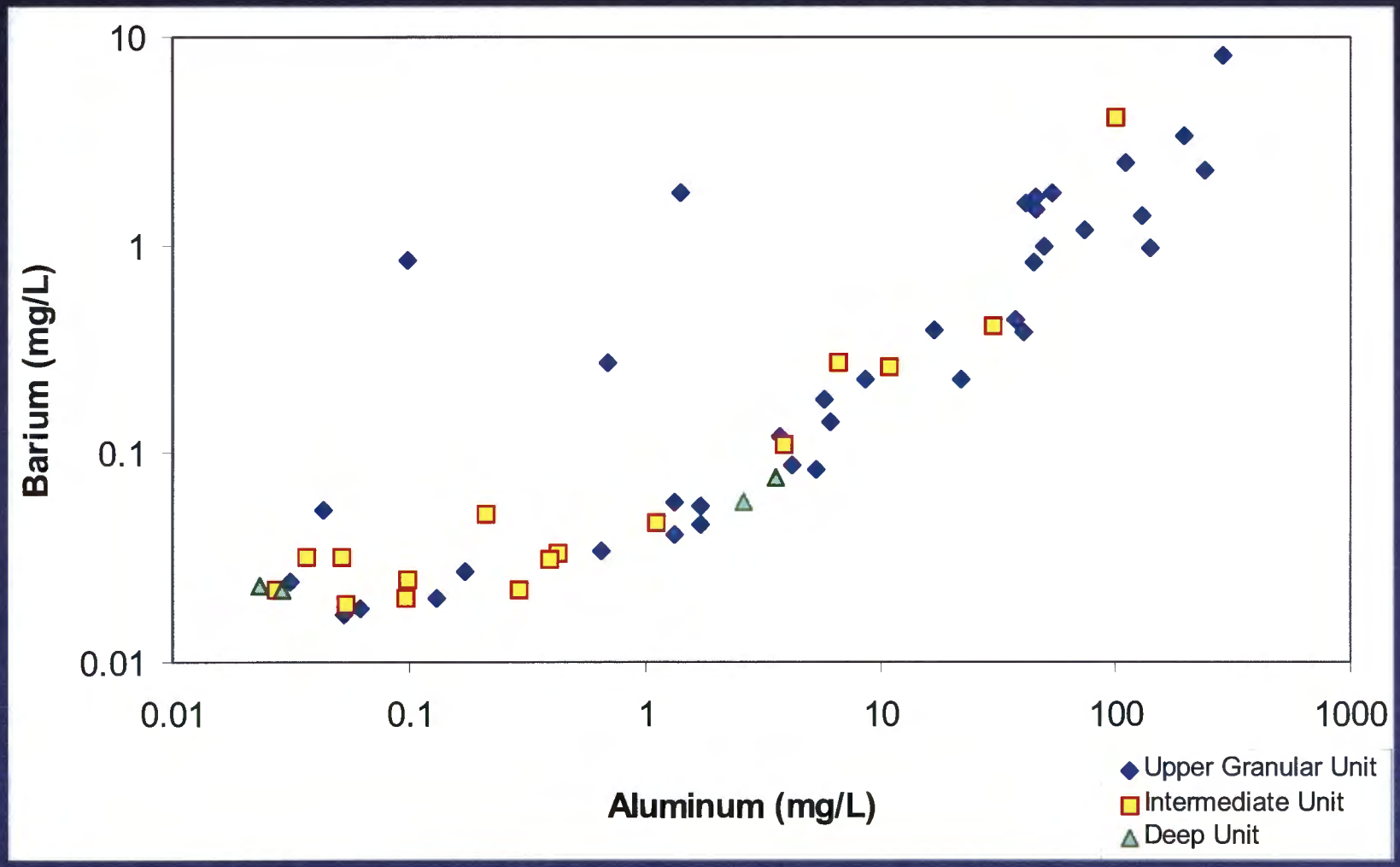
Arsenic vs. Iron



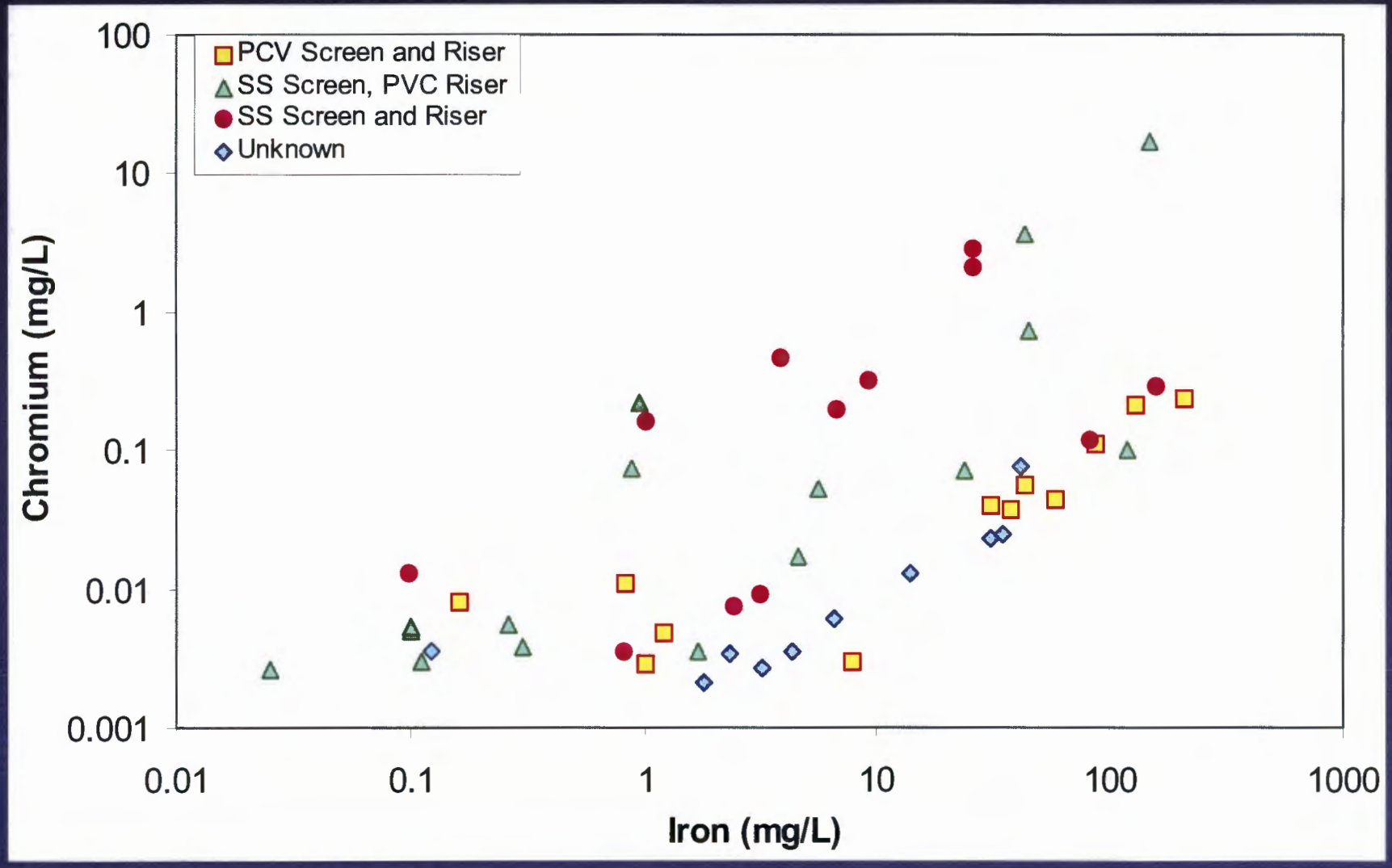
Lead vs. Aluminum



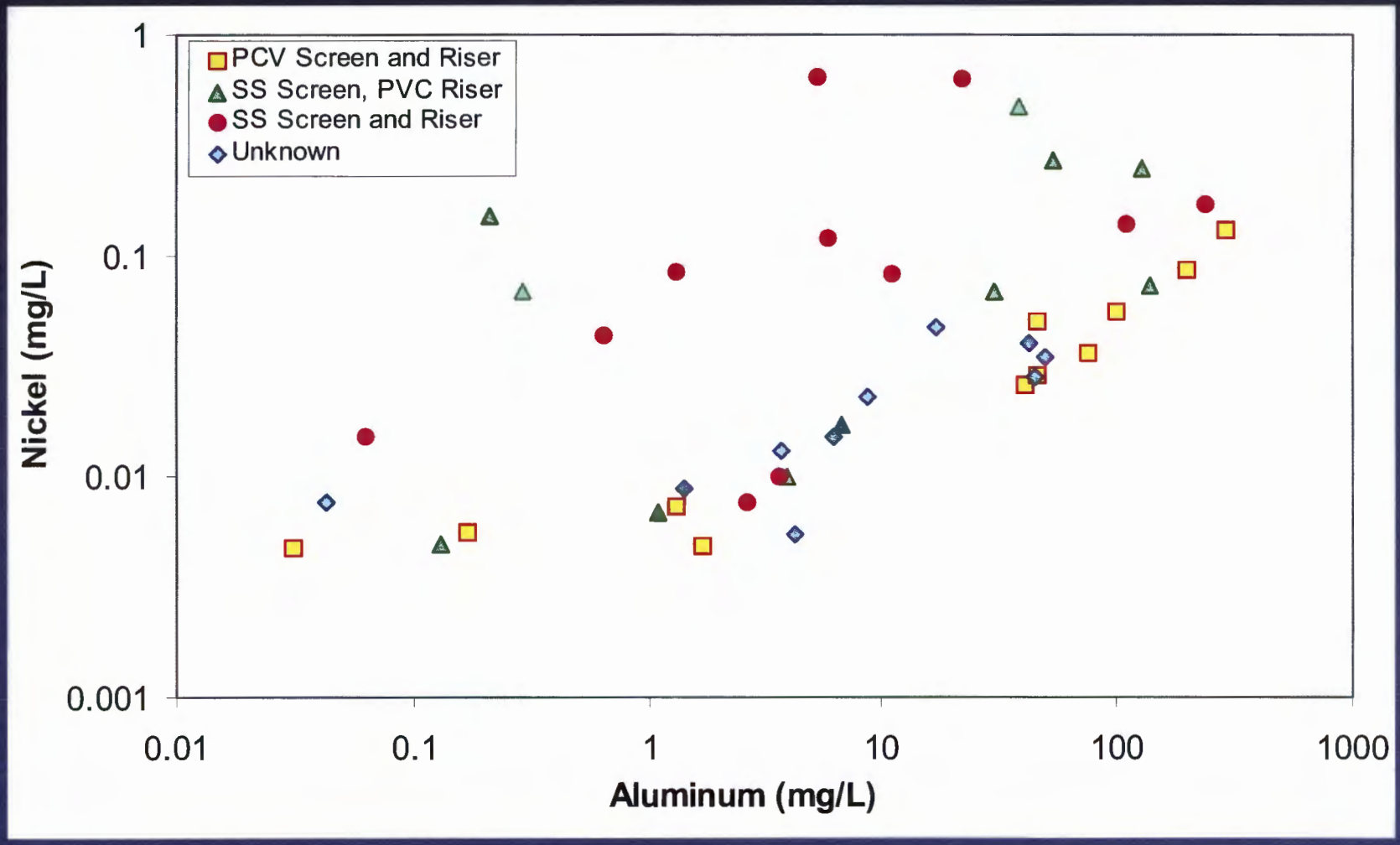
Barium vs. Aluminum



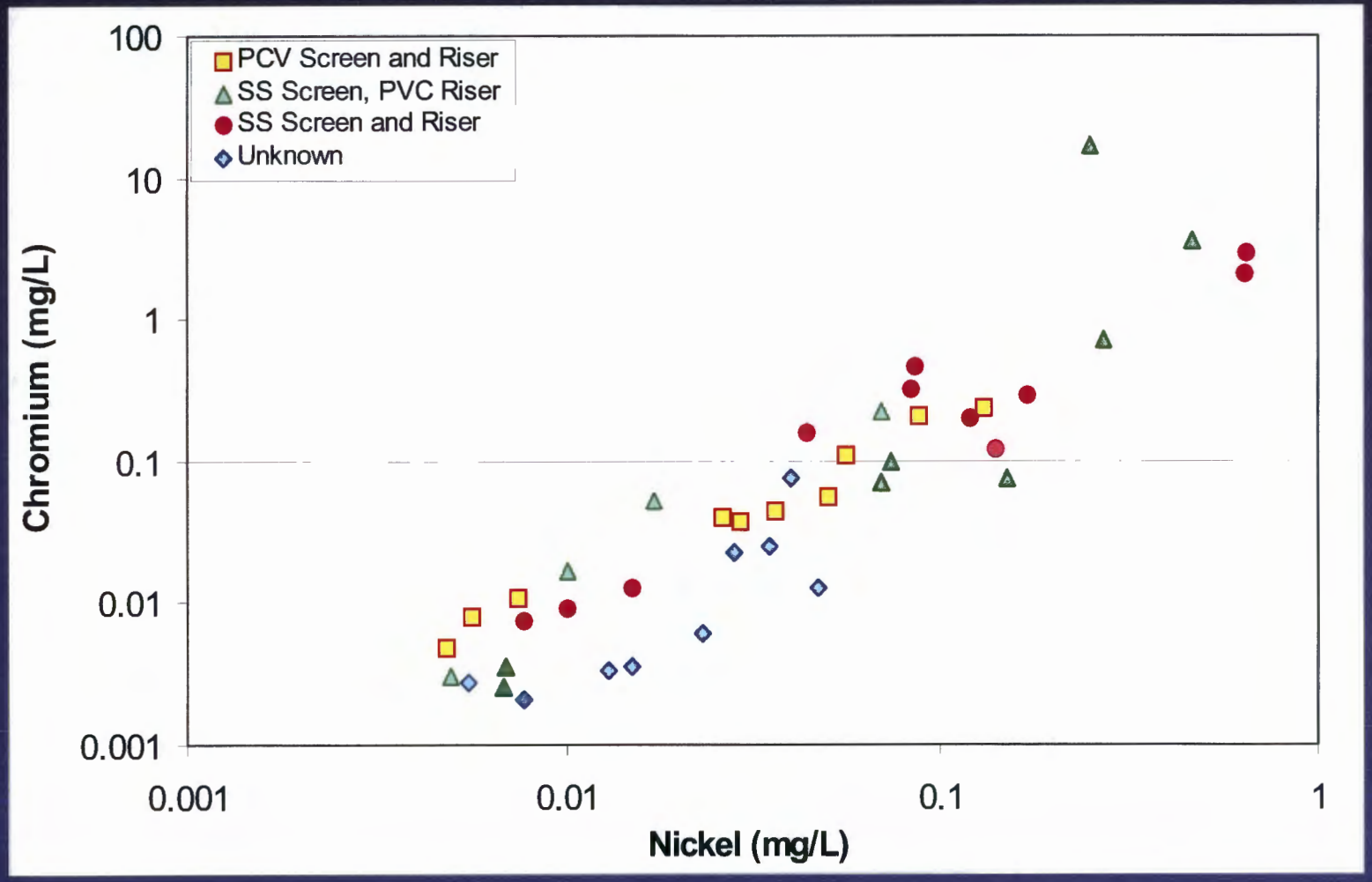
Chromium vs. Iron



Nickel vs. Aluminum



Chromium vs. Nickel



Background Screening Methodology Summary

- The proposed approach will be used to screen the existing analyses to yield a set of concentrations that represent background distributions for each element of interest in each media.
- The surviving data will be evaluated for adequacy with respect to number of samples and geographic coverage.
- The surviving data (and new data if needed) will be used to characterize the distributions of each element:
  - Min, mean, median, max, 95th UCL of mean, 95th UTL, standard deviation, etc.

Background Screening Methodology Summary (cont.)

- Background distributions can be used for:
  - Site-to-background comparisons
  - Identification of background concentrations that exceed regulatory criteria
  - Baseline risk assessments
  - Establishment of remediation goals
  - Providing insight into the site-specific processes controlling observed concentrations