Trace Element Contamination or High Background?
How to Tell Using Existing Soil Data

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Topics of Discussion

- Standard approach of statistical comparison to background
- Problems with standard approach
- Alternative approach
- Successful examples

Standard Approach

Statistical Comparisons to background

- **Bright Line** – Max BG, 2x mean, 3x median, mean+2σ, mean+3σ, 95th UTL, 95th UCL of mean, 95th percentile, 95th UCL of 95th percentile, etc.

- **Two-Sample Comparisons**
  - Parametric – t-test, F-test, ANOVA, etc.
  - Nonparametric – Mann-Whitney (WRS), Gehan's test, Quantile test, Nonpara ANOVA, Shift test, etc.

Standard Approach (continued)

- **Visual Comparisons**
  - Box and whisker plots
  - Probability plots
  - Histograms

Problems with Standard Approach

- Trace metals have large range (3 to 4 orders)
- Distributions are highly skewed (lognormal)
- Insufficient number of background samples
- Unequal sample sizes ($n_{Site} >> n_{BG}$)
- Assumes each element is independent

Problems with Standard Approach (continued)

- **Result:** Lots of apparent BG exceedences
- **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 analysis

Geochemical Evaluation of Metals in Soils

- **Trace elements are associated with specific minerals, yielding good correlations**
- **Oxyanionic elements – negatively charged speciation in oxic pore fluid**

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 Soils

- **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) = $Cr(OH)_2^{+}$, $Cr(OH)_3^{\circ}$, $Cr(OH)_4^{-}$

Surface Charges of Soil Minerals

- **Clays** = negative surface charge at neutral pH
  - Attracts Cu, Ni, Zn

- **Mn-oxides** = negative surface charge at neutral pH
  - Attracts Ba, Co, Pb

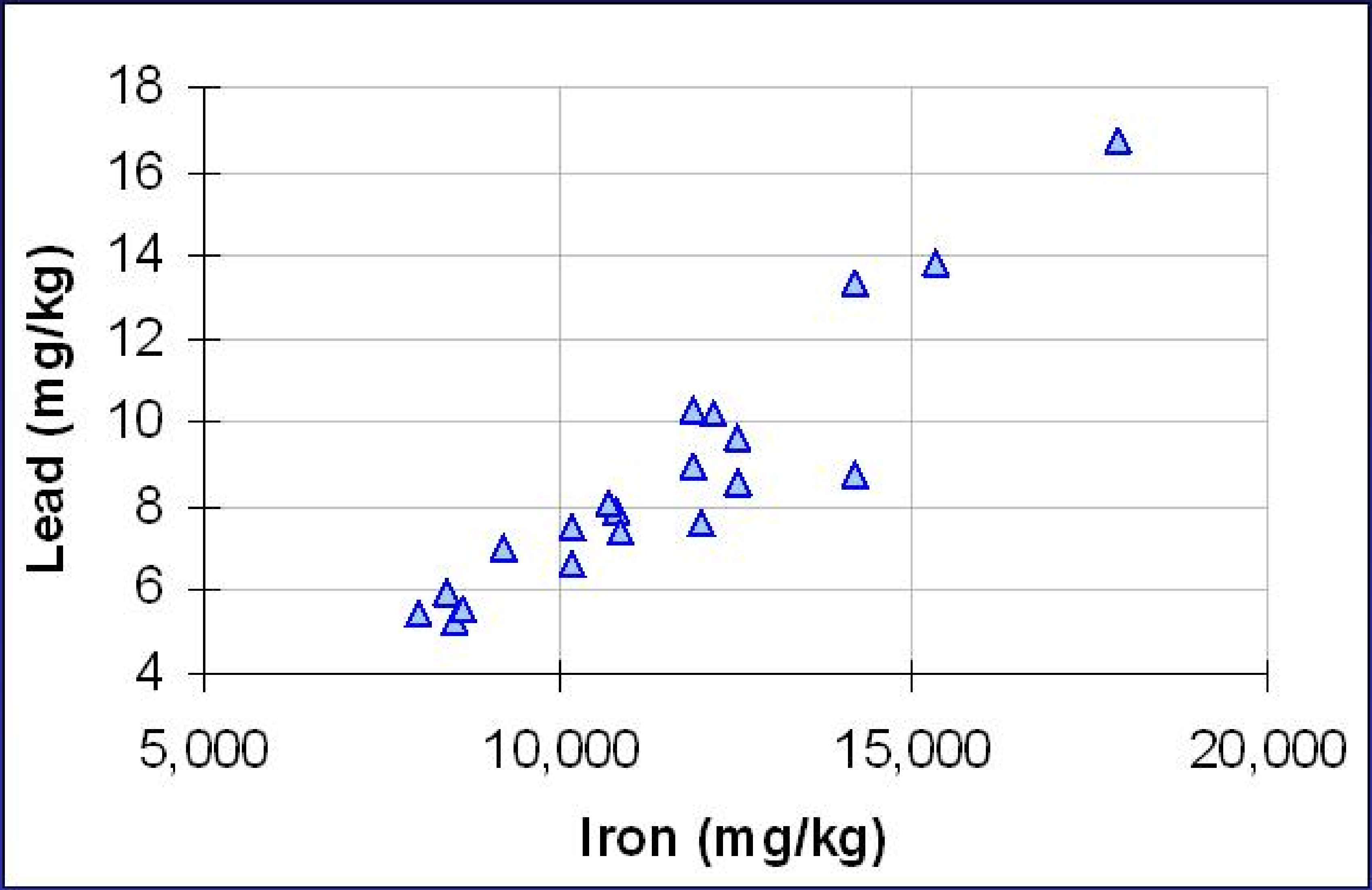
- **Fe-oxides** = positive surface charge at neutral pH
  - Attracts As, Sb, Se, V, Mo, U

- Evaluate correlations with major elements
  - Use Fe for oxyanionic elements
  - Use Al (clays) and/or Mn for cationic elements
  - Use Ca in limestone or arid terrains

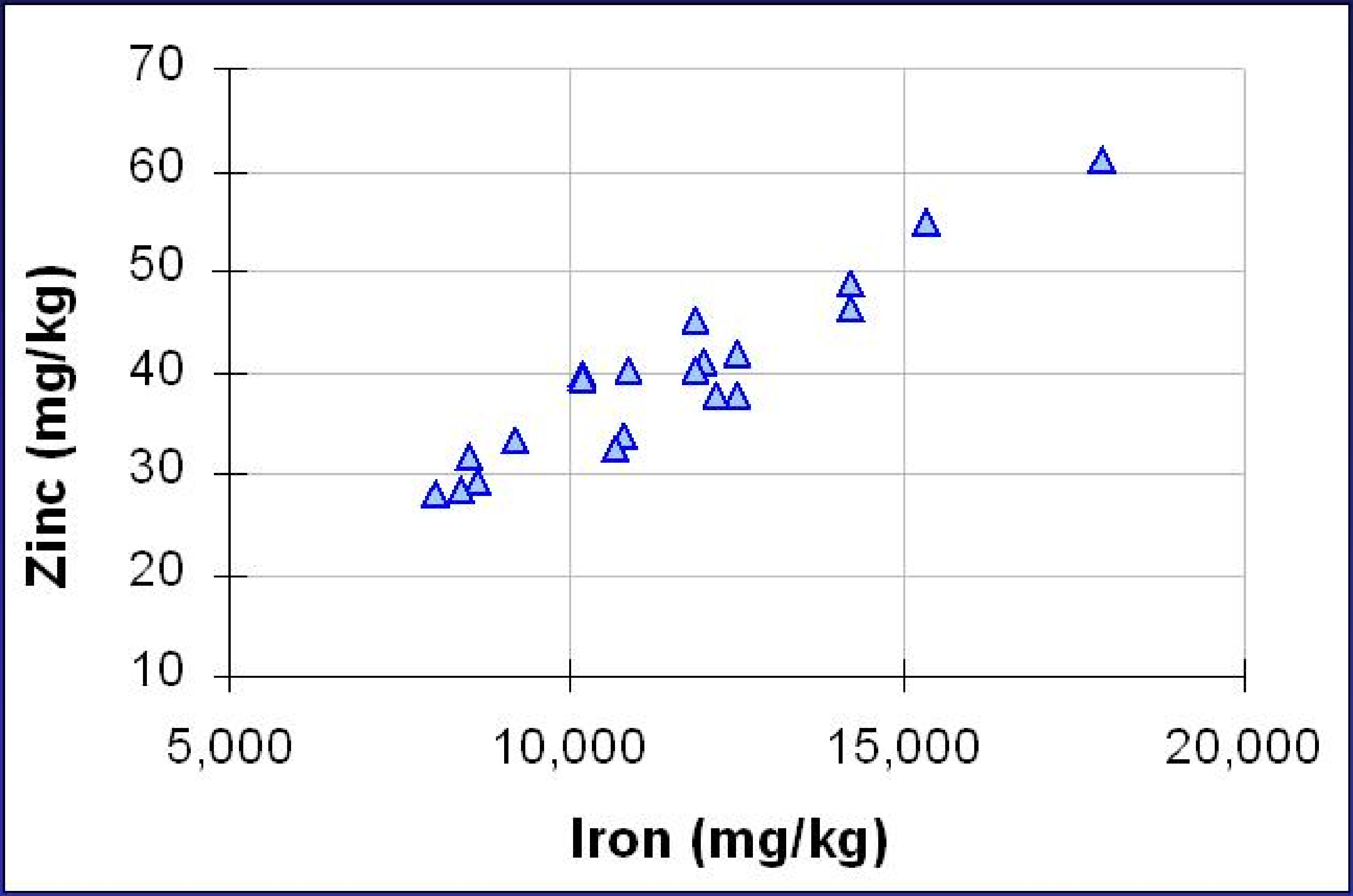
Deming Army Air Field, NM

- Twenty samples total
- Trench and soil borings
- Depths 0 to 15 ft.
- Analyzed for TAL metals
  - Lead vs Iron
  - Zinc vs Iron
  - Arsenic vs Iron

Deming Army Air Field, NM



Deming Army Air Field, NM



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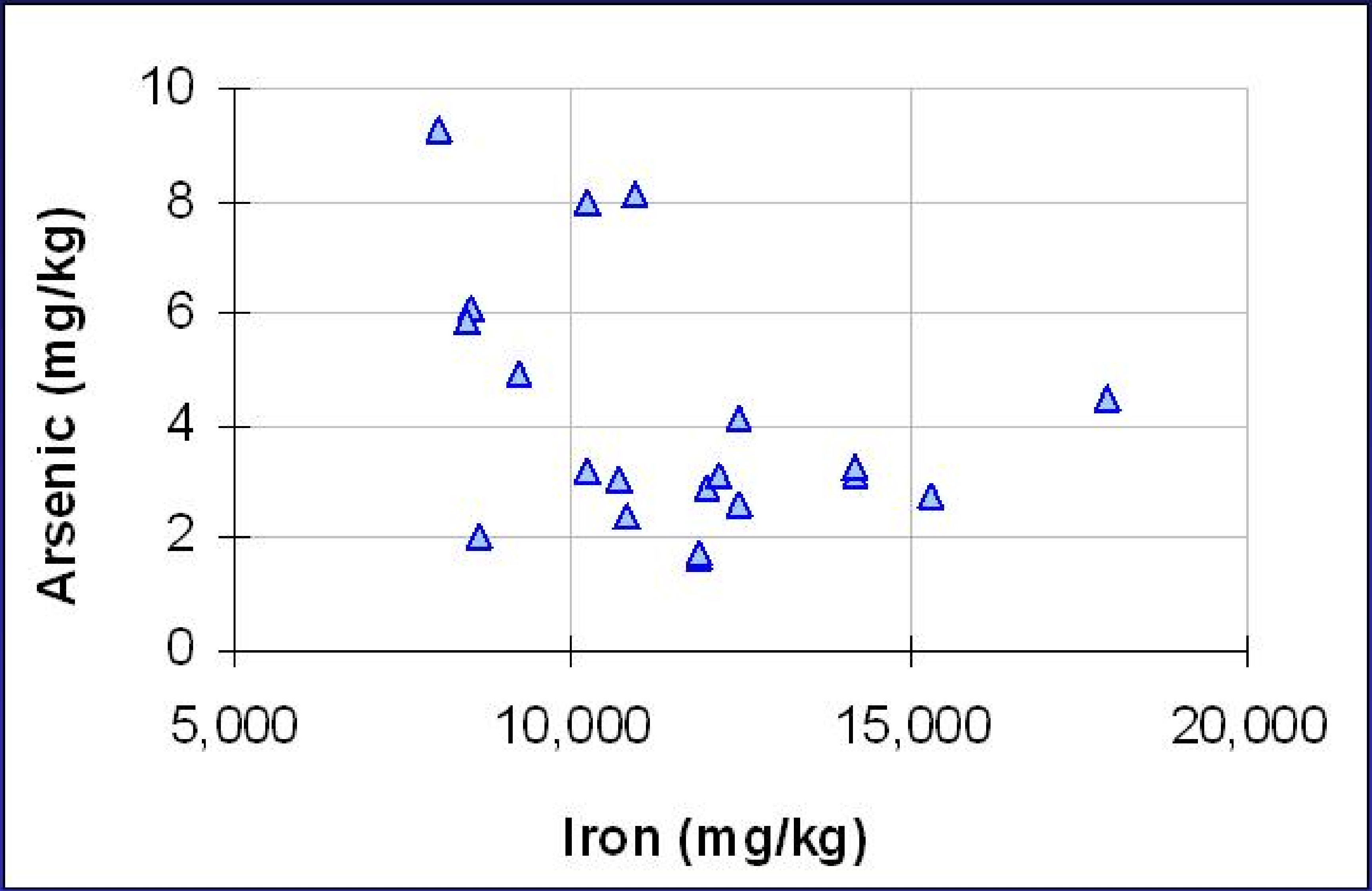
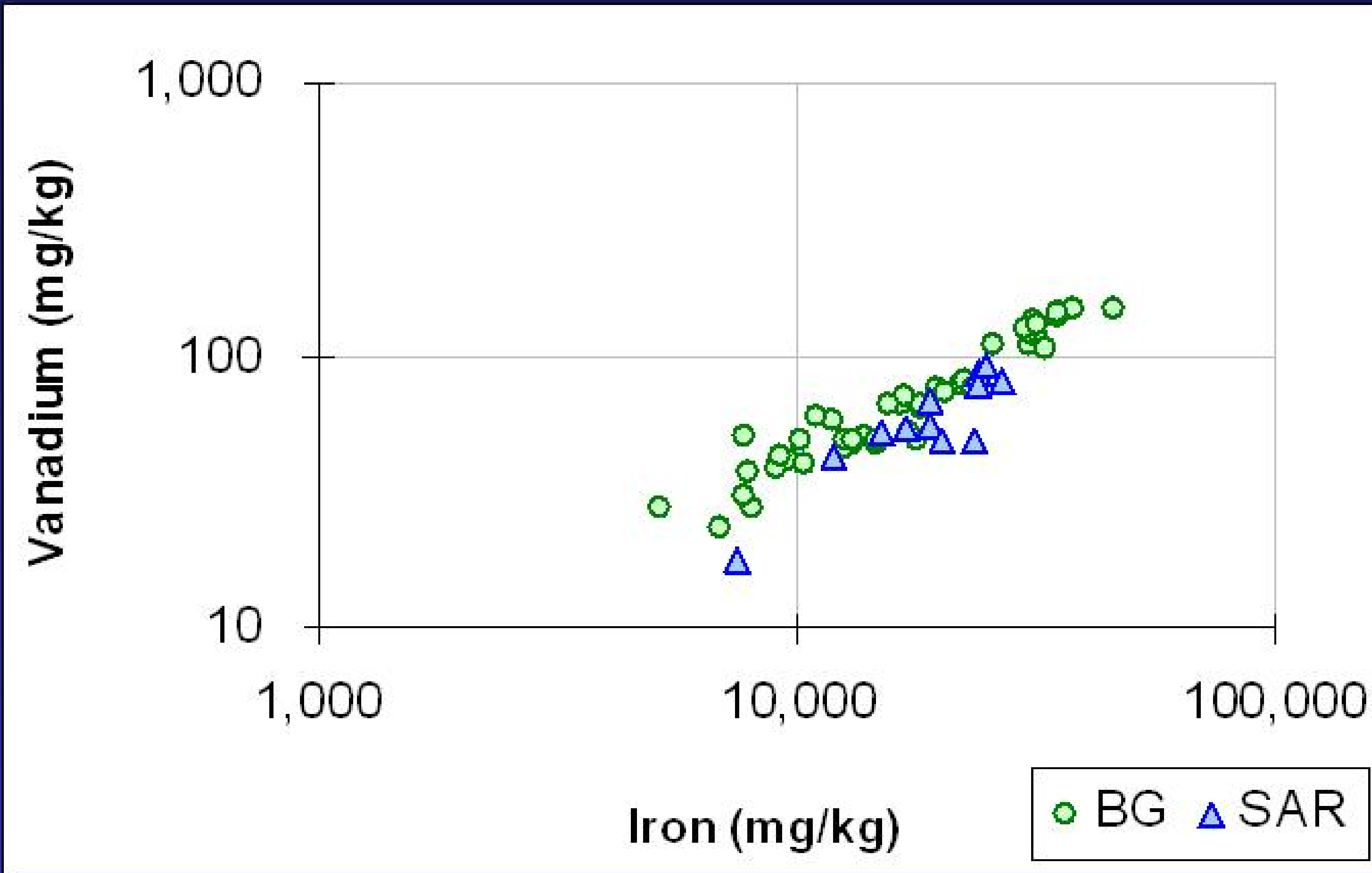


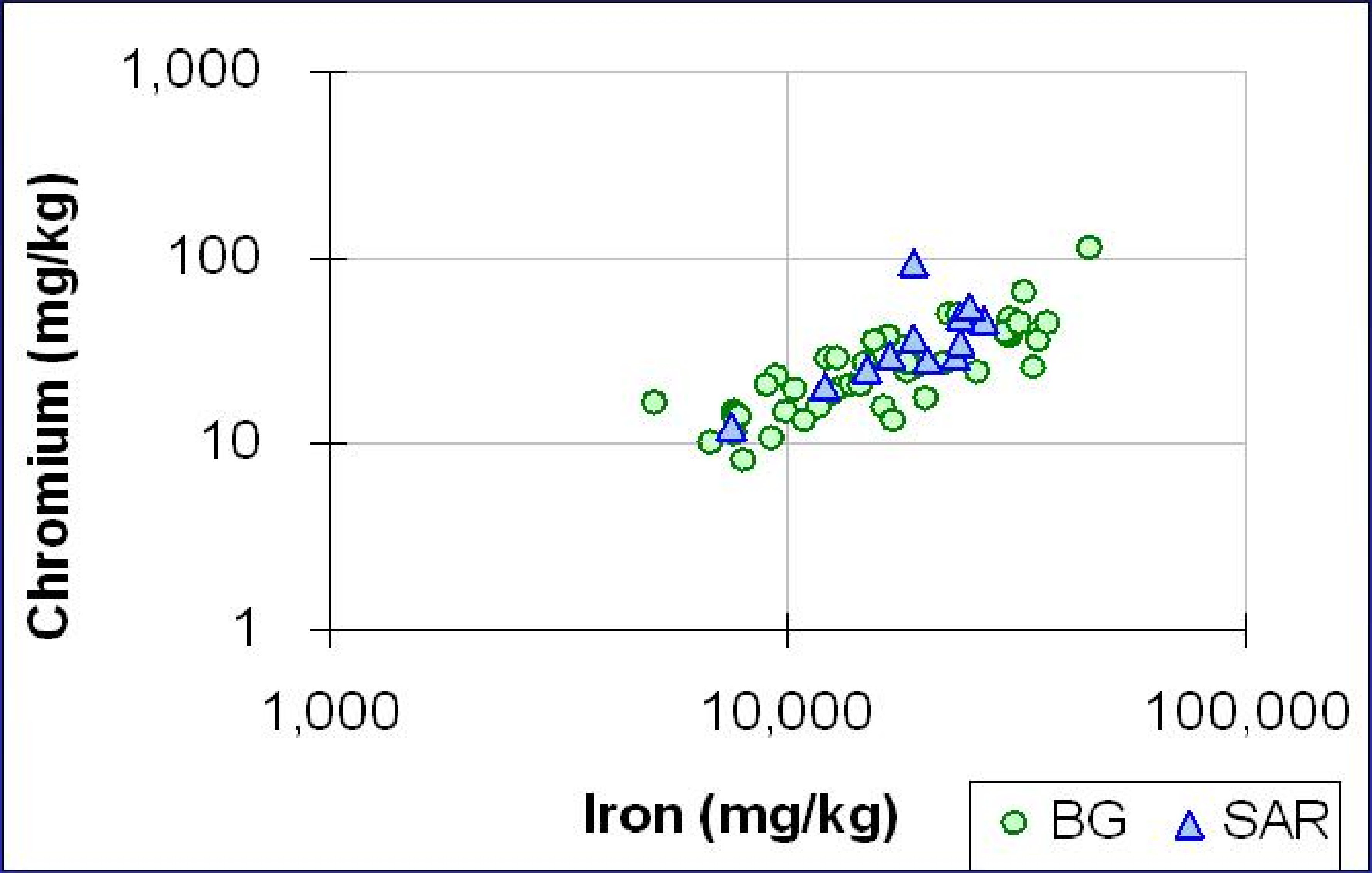
San Juan P.R. NAS, Small Arms Range

- **12 soil samples from Small Arms Range (blue triangles)**
- **46 soil background samples (green circles)**
  - V vs Fe
  - Cr vs Fe
  - Pb vs Fe
  - As vs Fe

San Juan NAS, Small Arms Range



San Juan NAS, Small Arms Range



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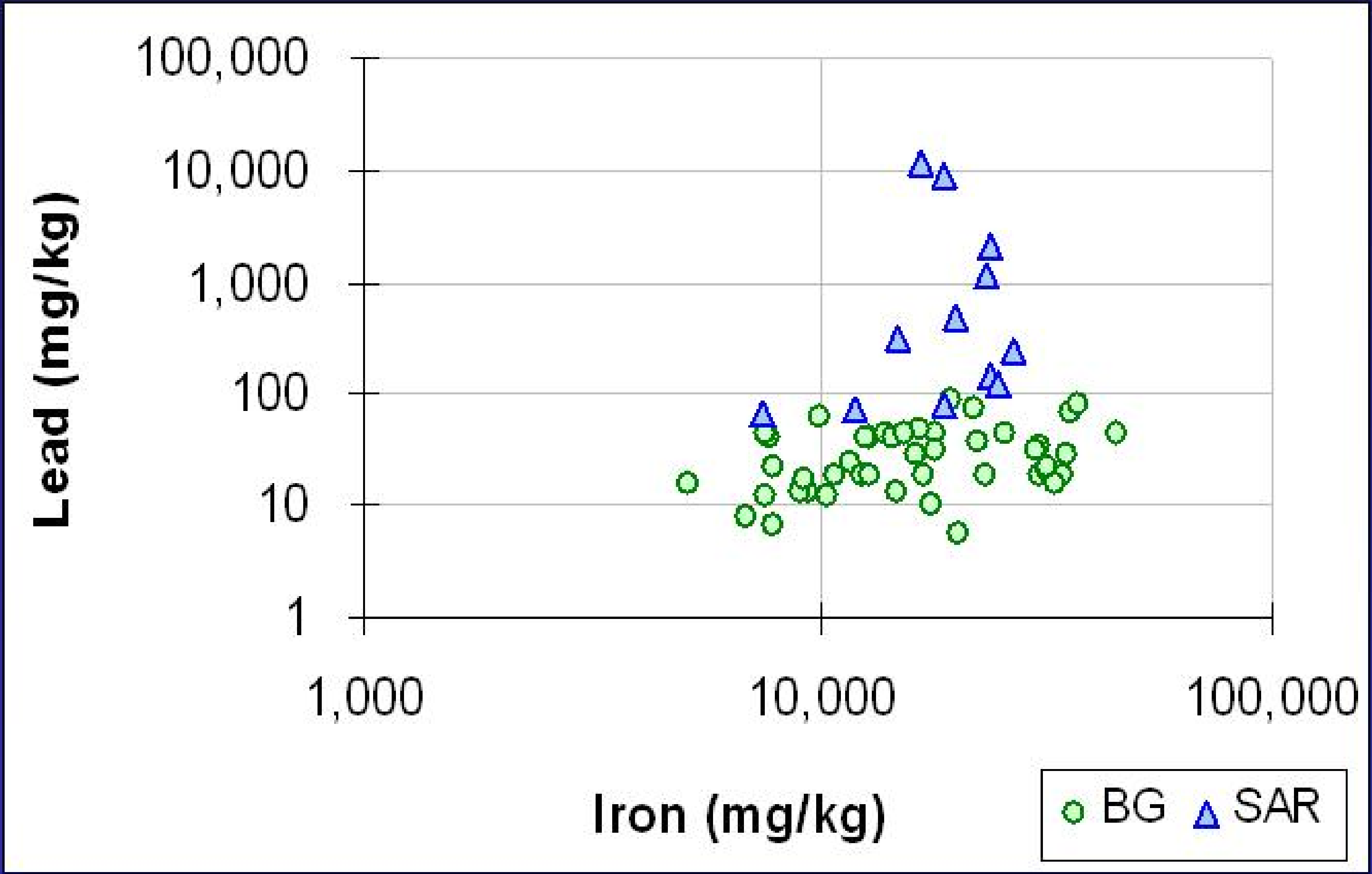
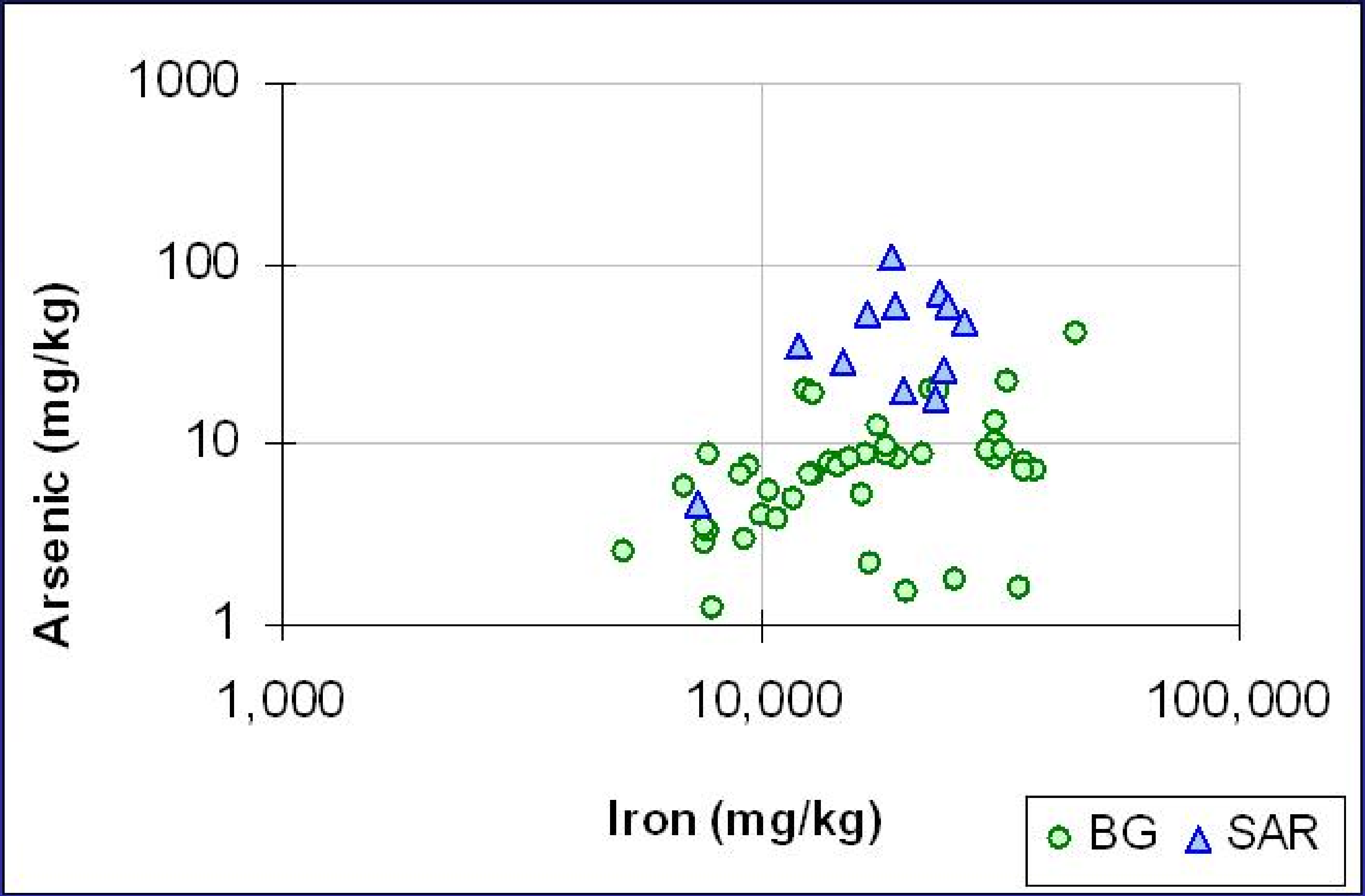


San Juan NAS, Small Arms Range

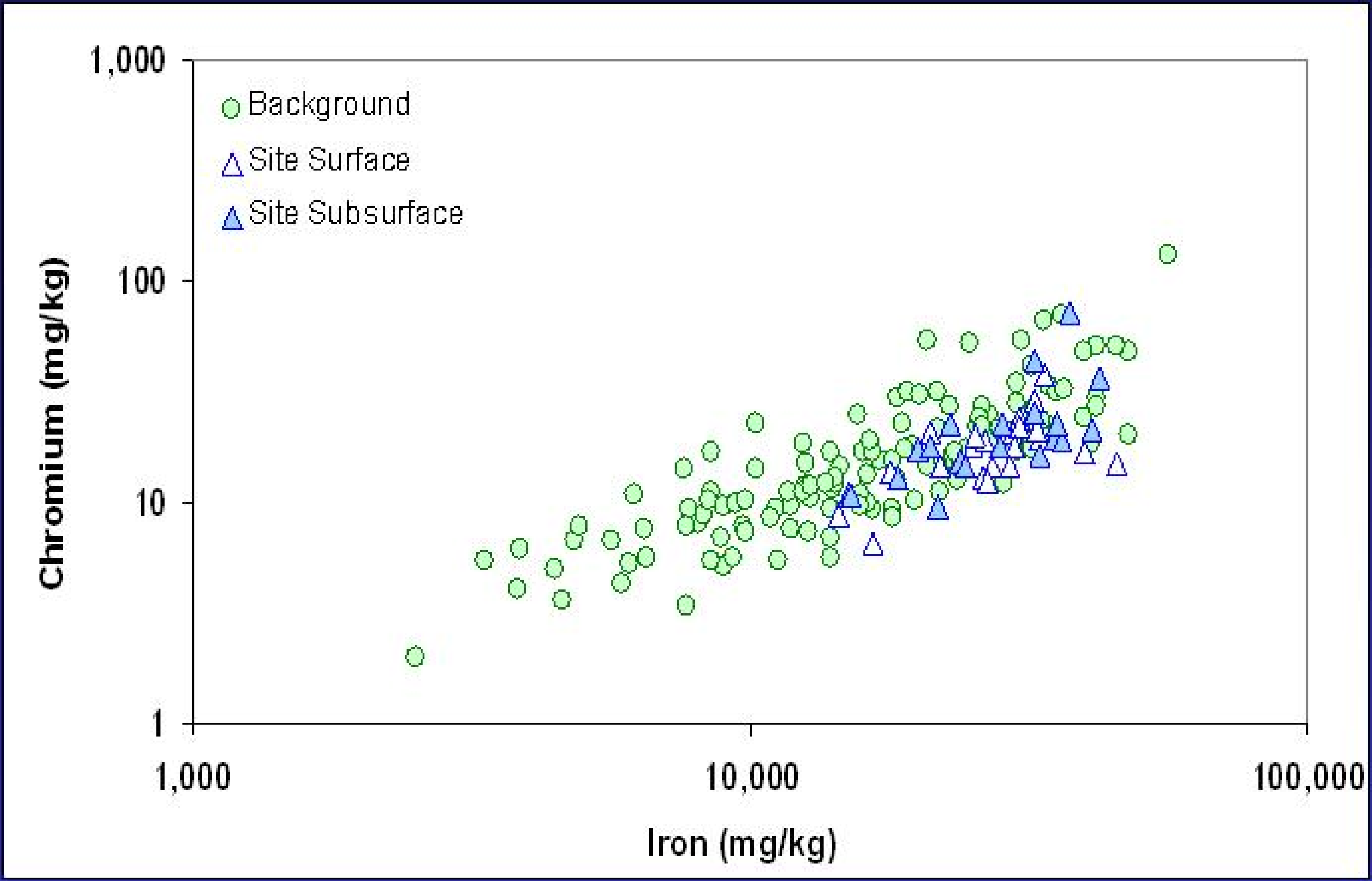


Ft. McClellan AL - Impact Area South

- Artillery firing range
- 22 surface soil samples (0 – 1 foot)
- 20 subsurface soil samples (3 – 4 feet)
- 134 site-wide background samples

  - Cr vs Fe
  - Pb vs Mn
  - Cu vs Fe
  - Cu vs Pb

Ft. McClellan AL - Impact Area South



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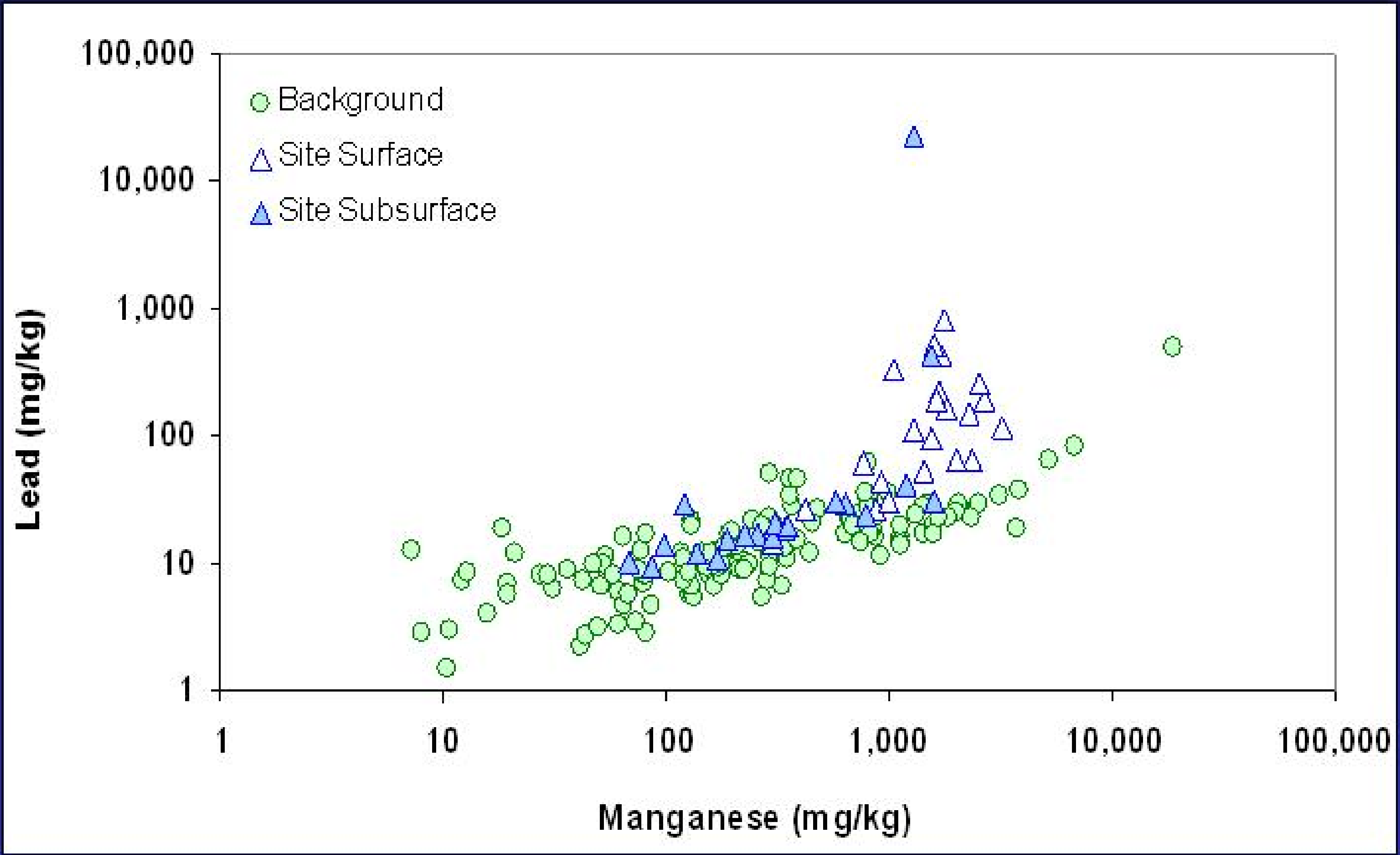

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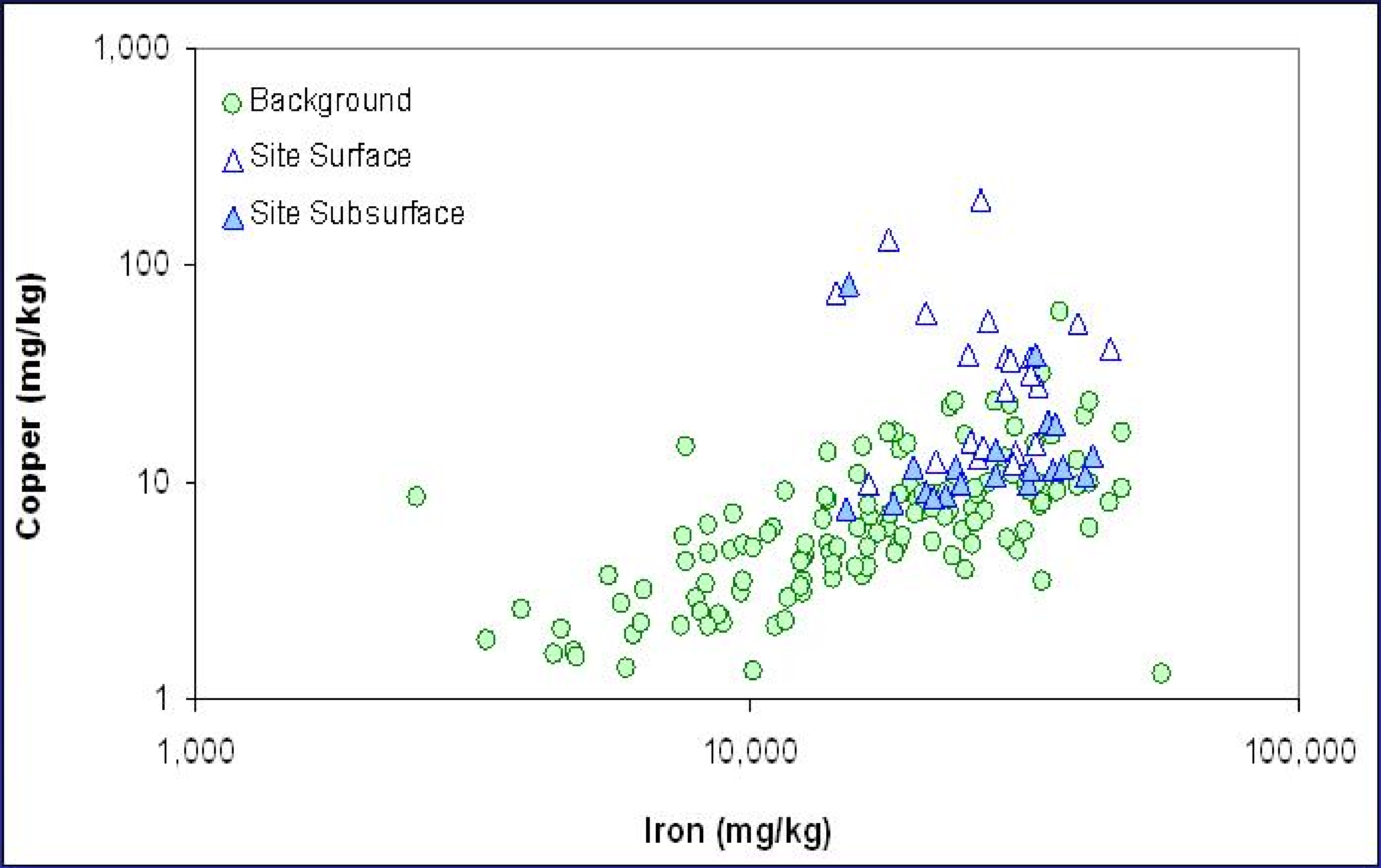

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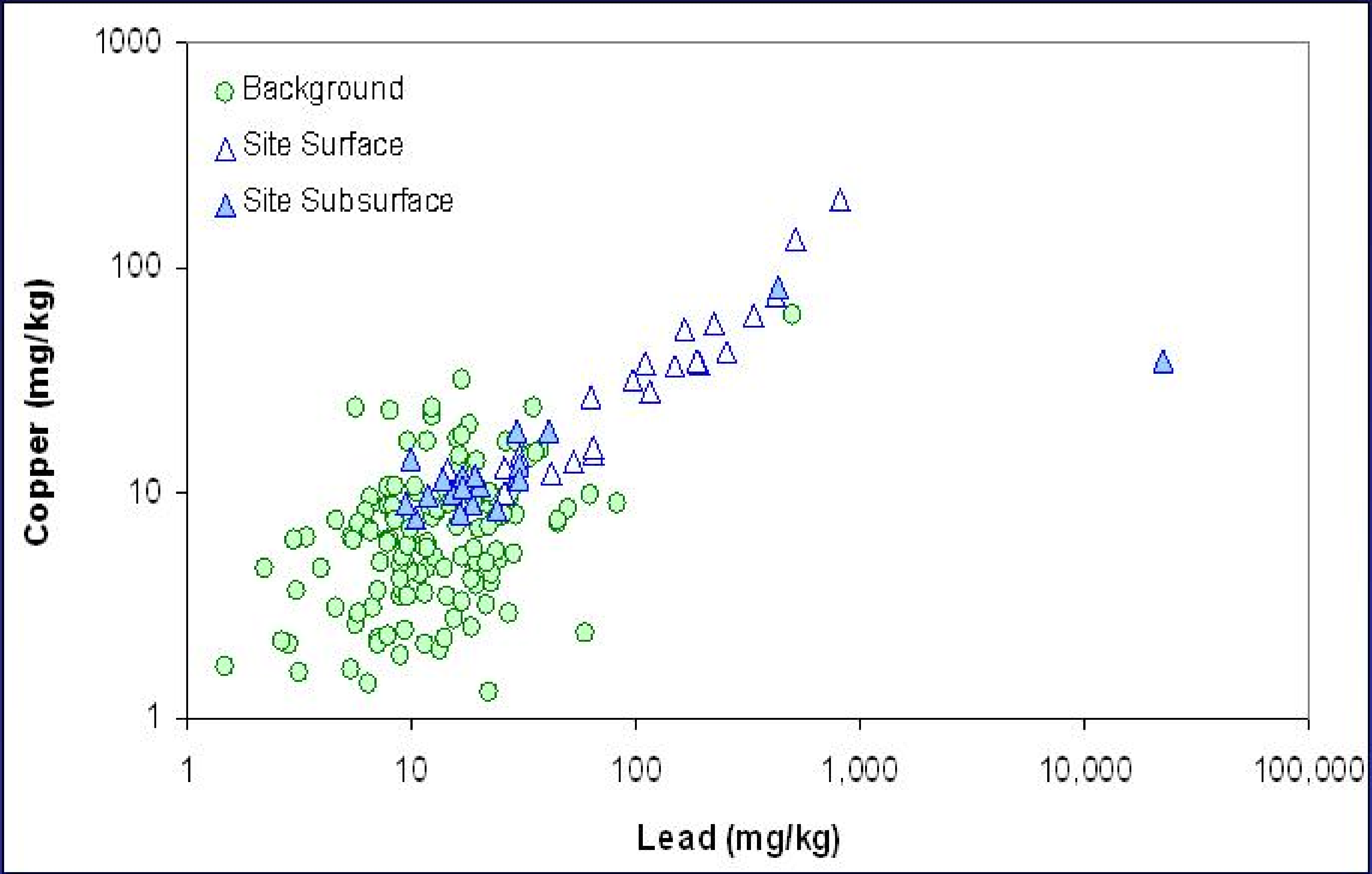
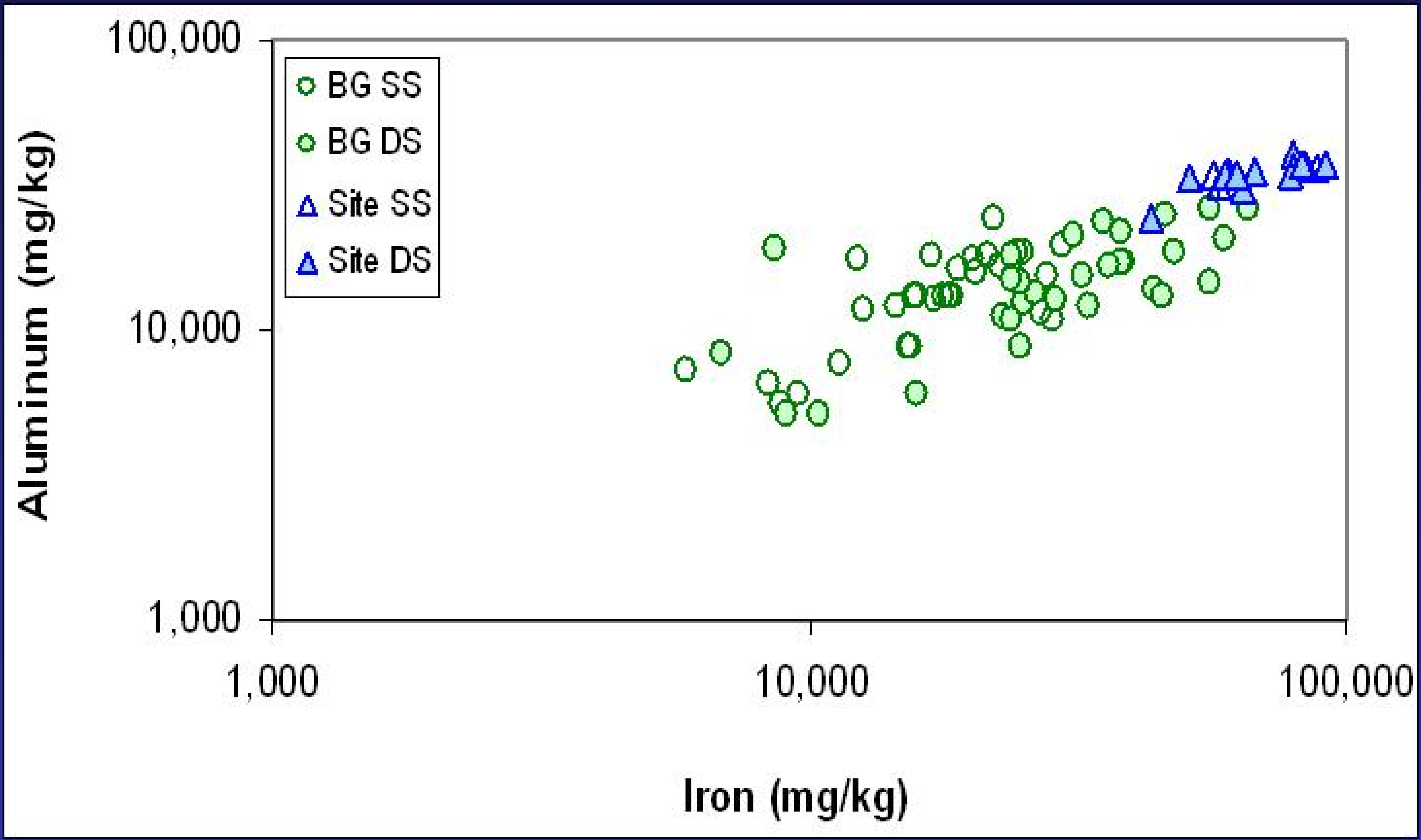


Site 99, Redstone Arsenal, Alabama

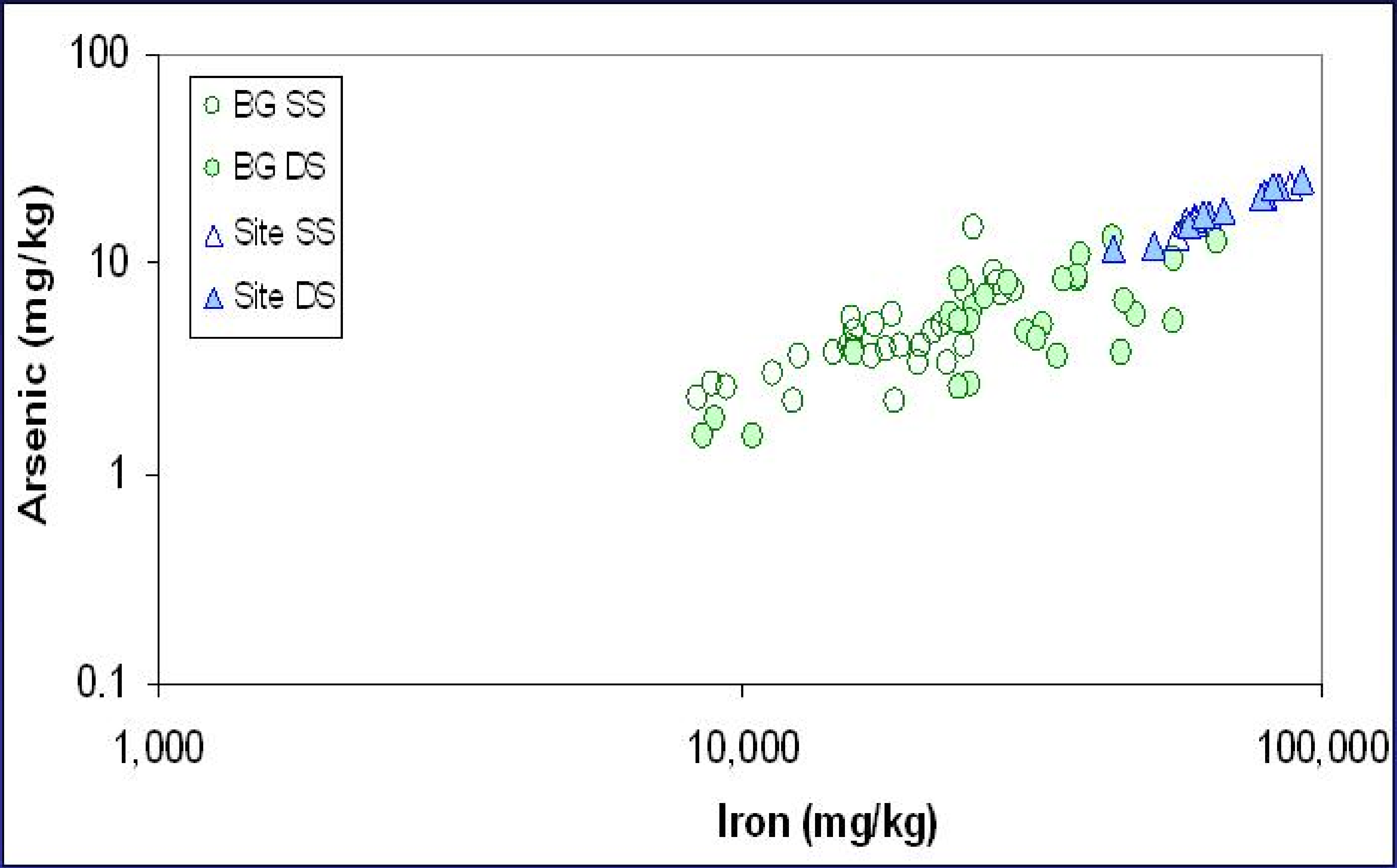
- Chemical weapons and missile development site
- 19 Surface and 43 subsurface site samples
- 30 Surface and 30 subsurface background samples

  - Al vs Fe
  - As vs Fe
  - Cr vs Fe

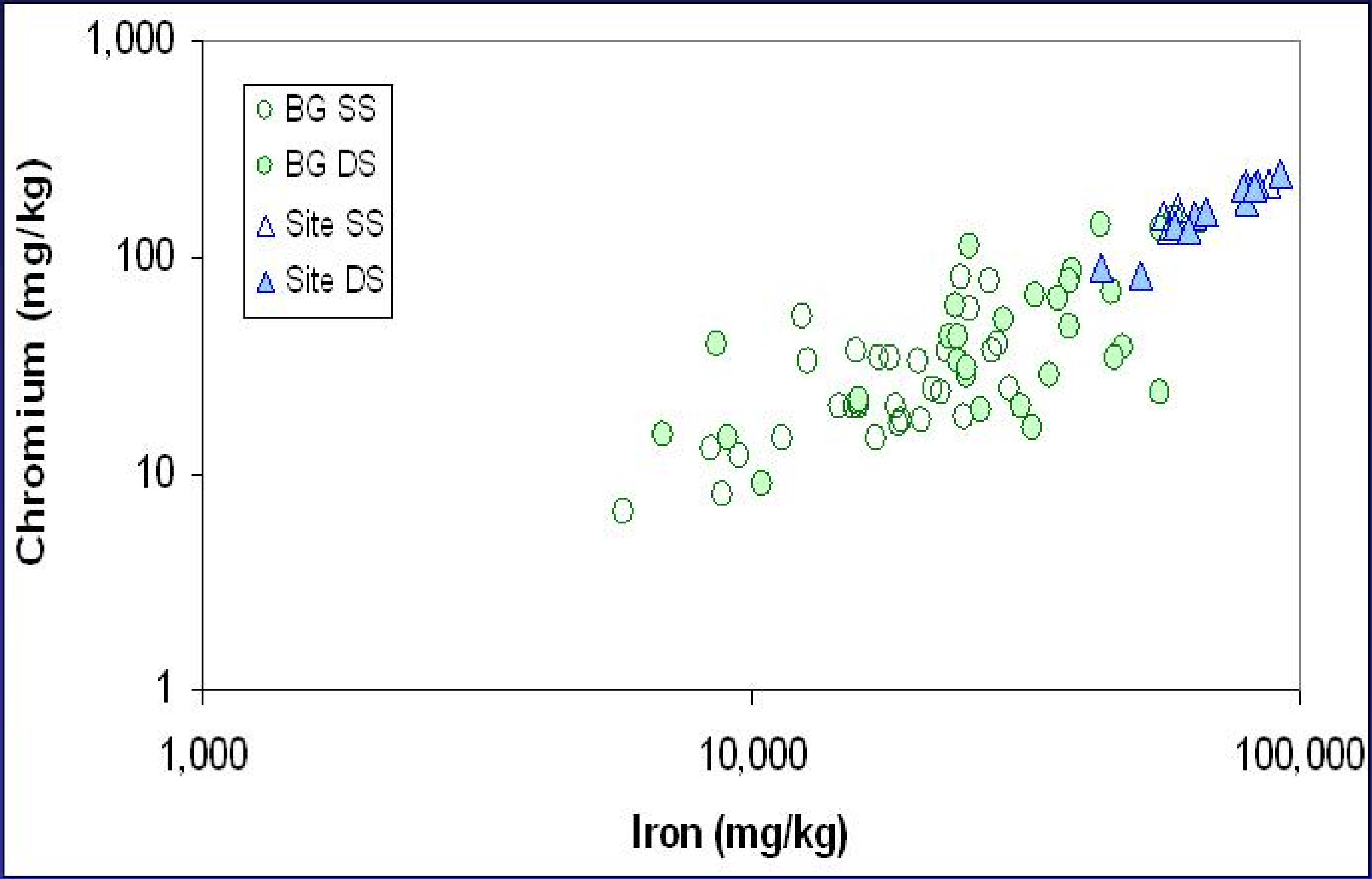
Redstone Site 99 Al vs Fe



Redstone Site 99 As vs Fe



Redstone Site 99 Cr vs Fe



Dugway Proving Ground, Utah

Site 168

Chemical and biological weapons development

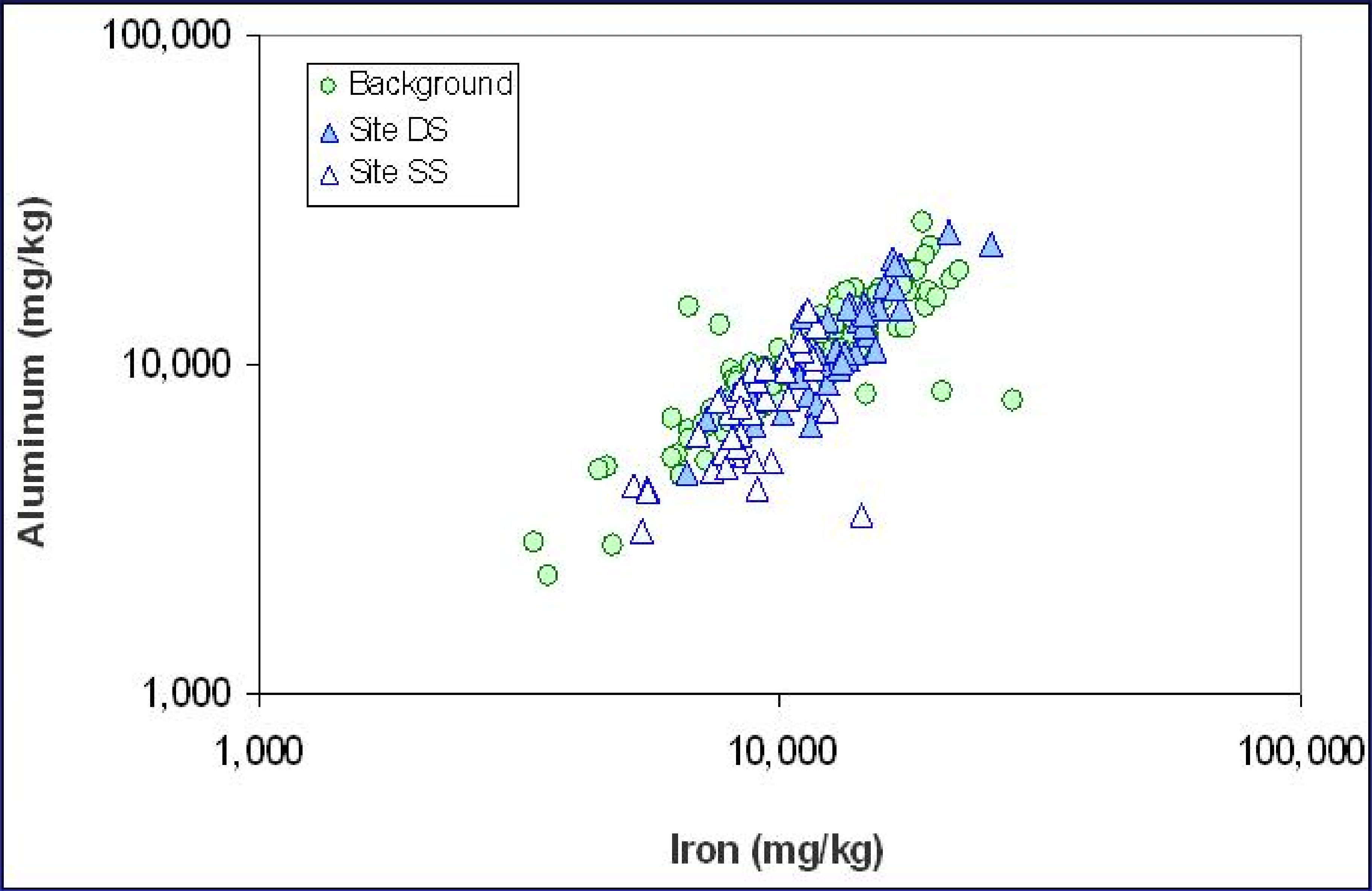
39 Site soil samples (0 to 1 ft.)

42 subsurface (1 to 21 ft.)

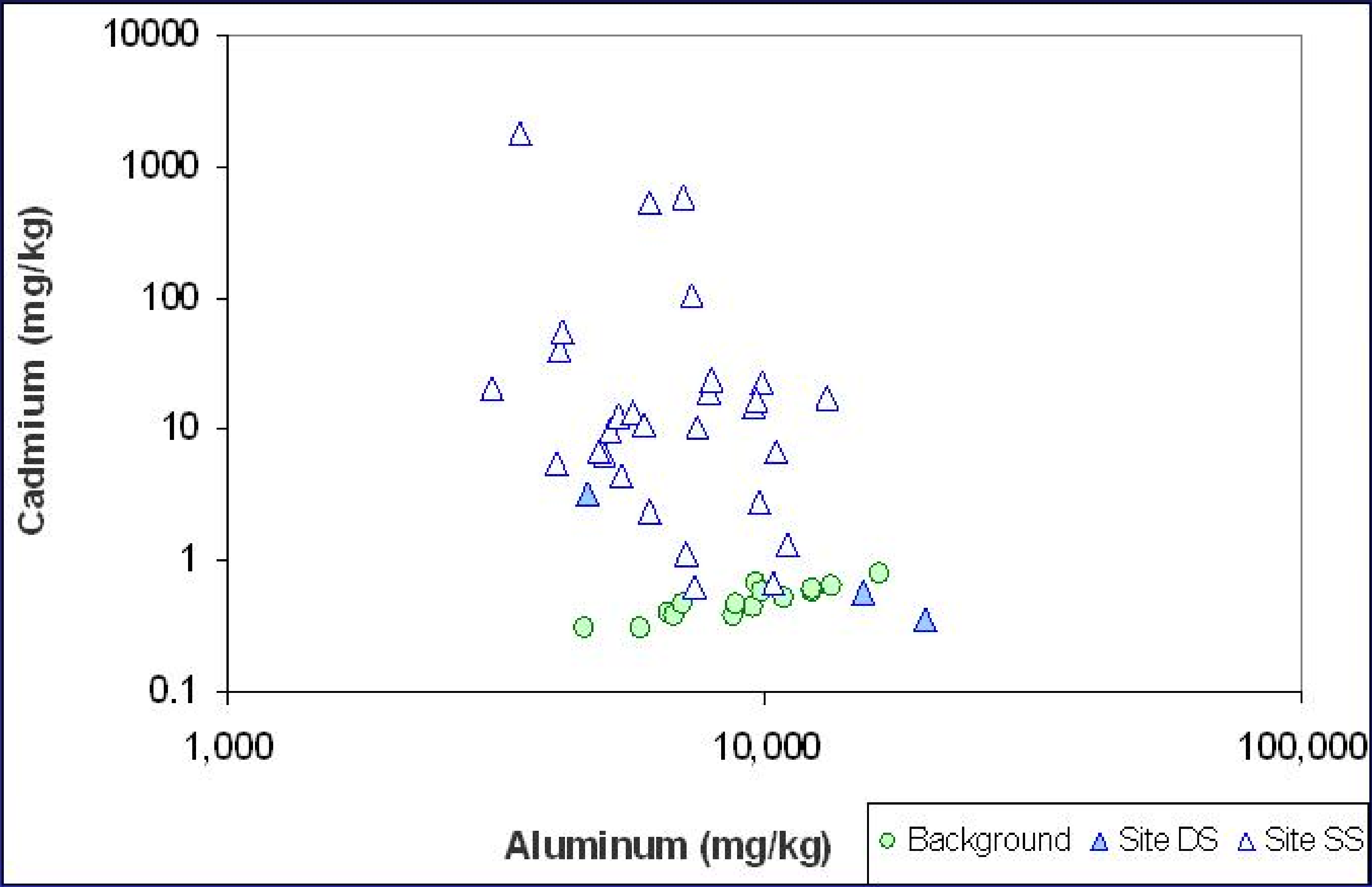
141 site-wide background samples

- Al vs Fe
- Cd vs Al
- Zn vs Al
- Cd vs Zn

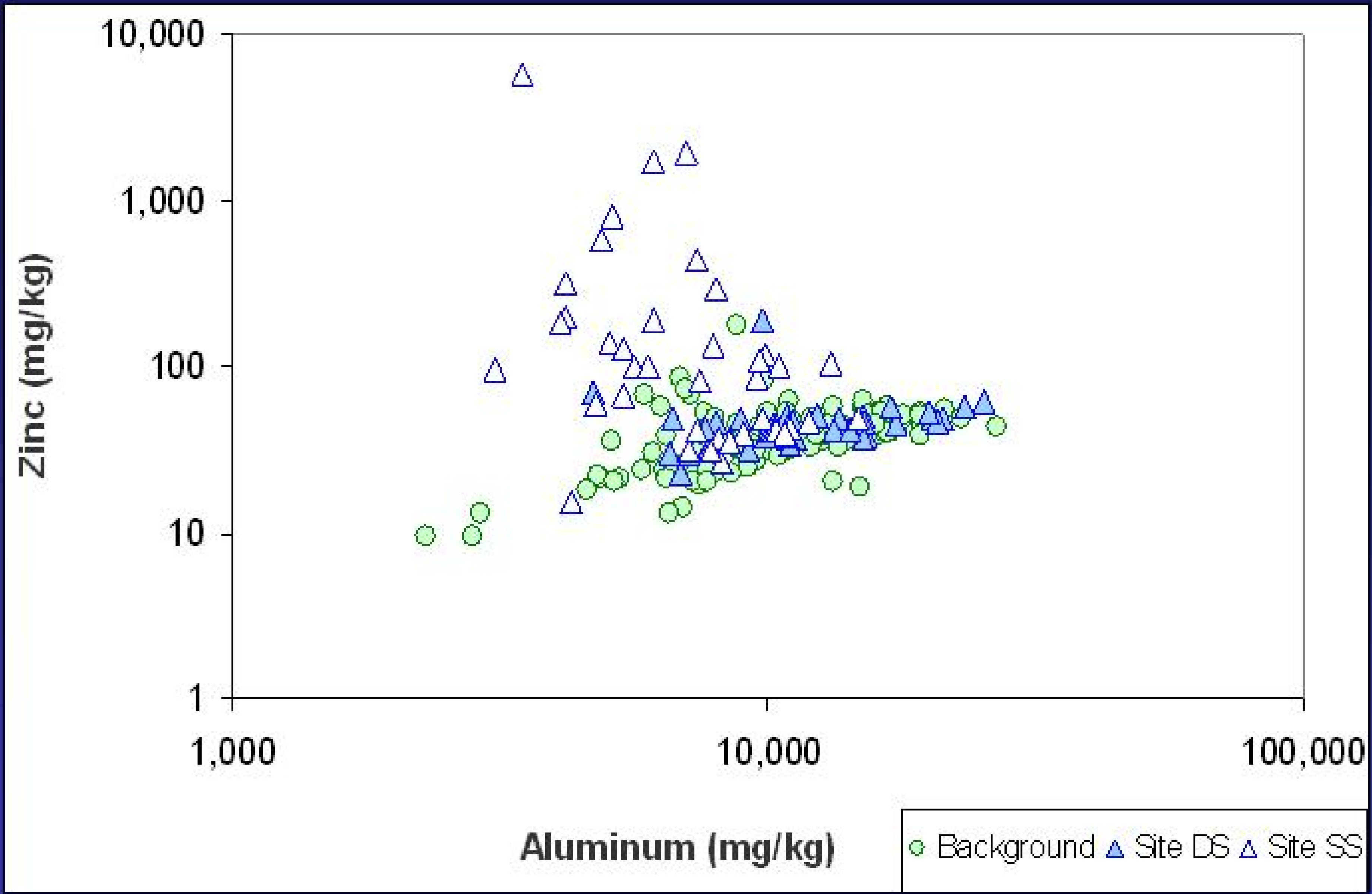
Dugway PG Site 168, Aluminum vs. Iron



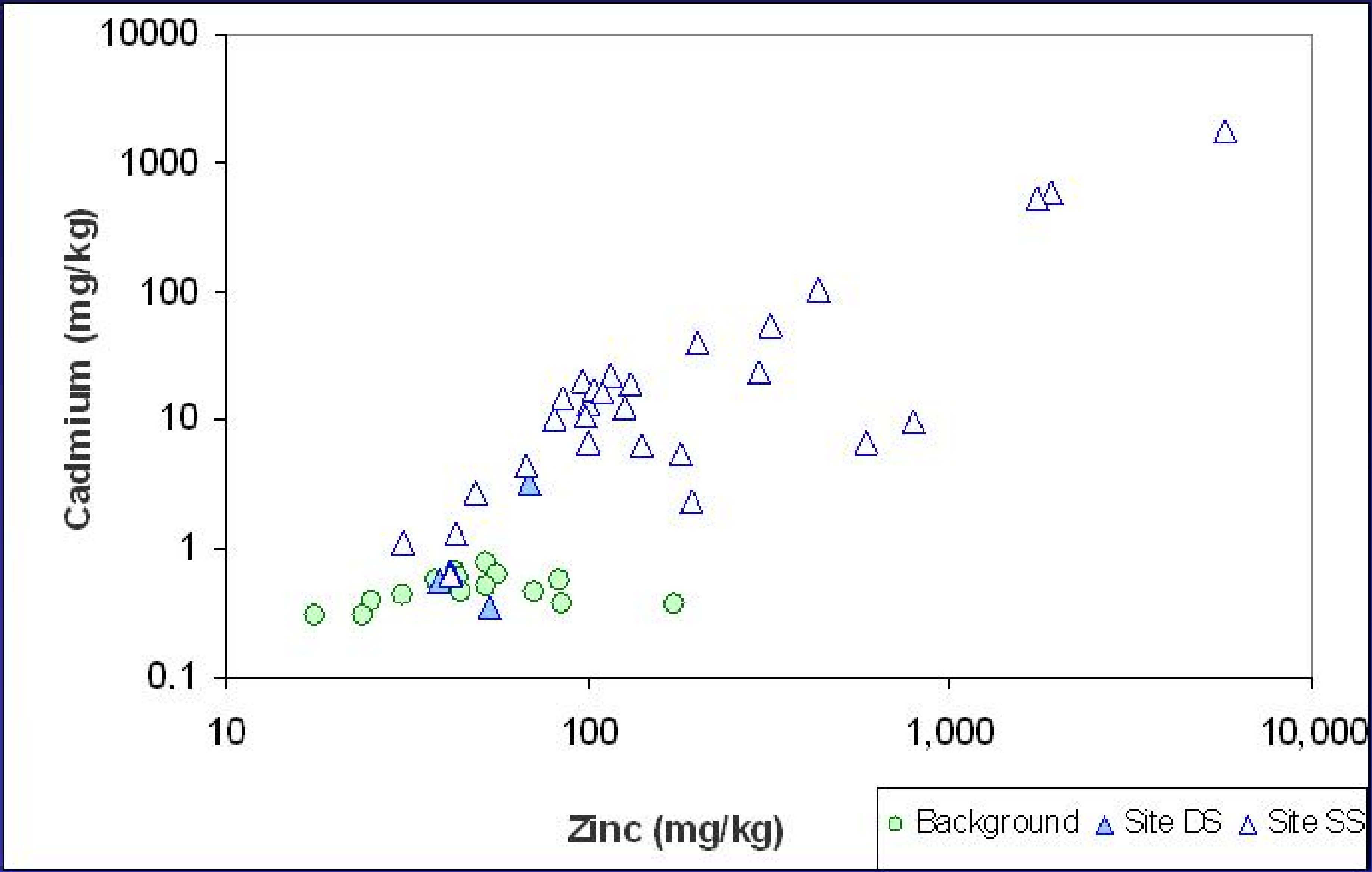
Dugway PG Site 138, Cd vs. Al



Dugway PG Site 138, Zn vs. Al



Dugway PG Site 138, Cd vs. Zn



Knolls Atomic Power Lab, Connecticut

- **Naval nuclear propulsion training center (DOE/Navy)**
- **72 background samples**
- **335 Site samples**
- **0 to 12 foot depths**

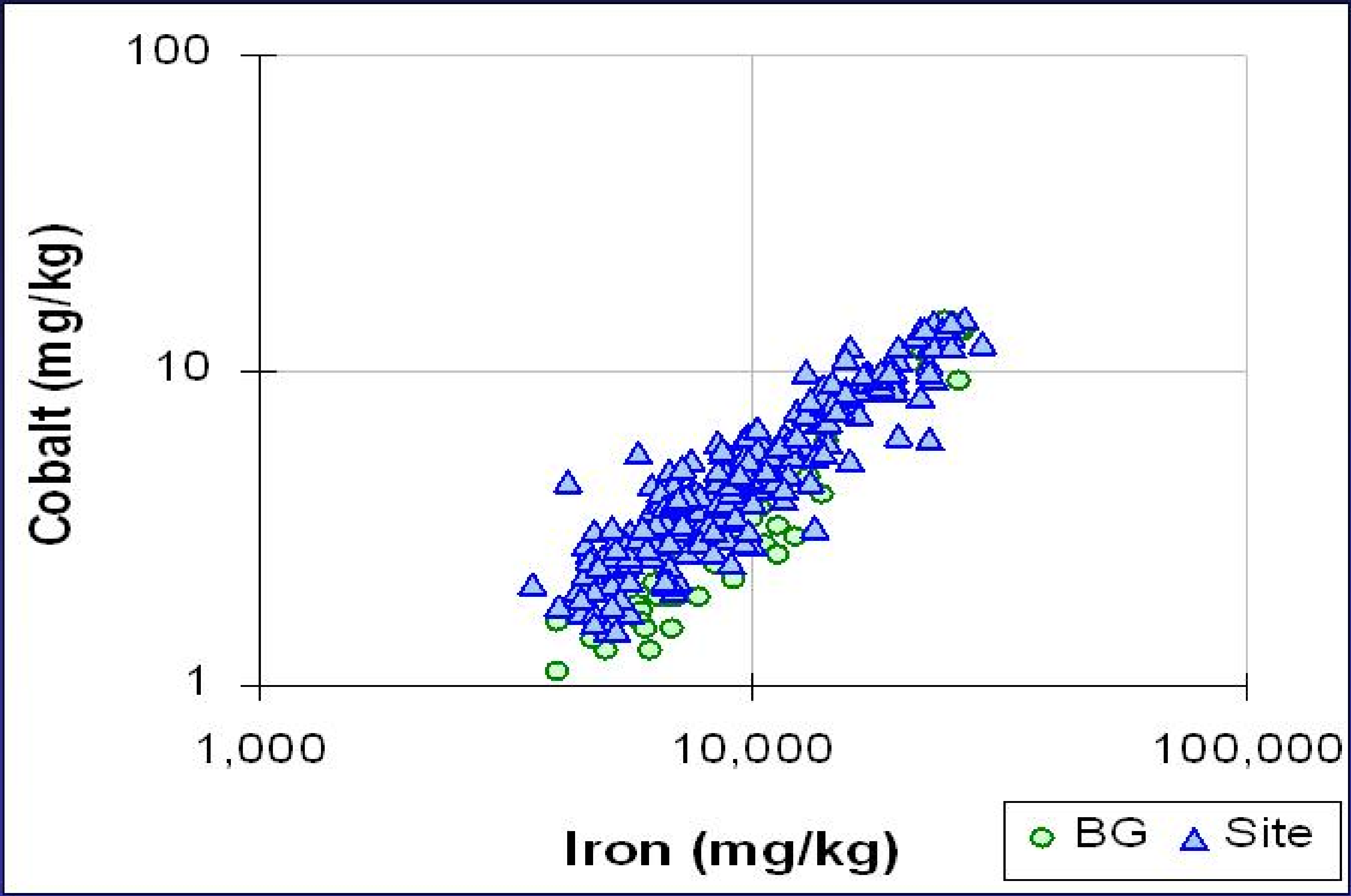
    Co vs Fe

    Se vs Fe

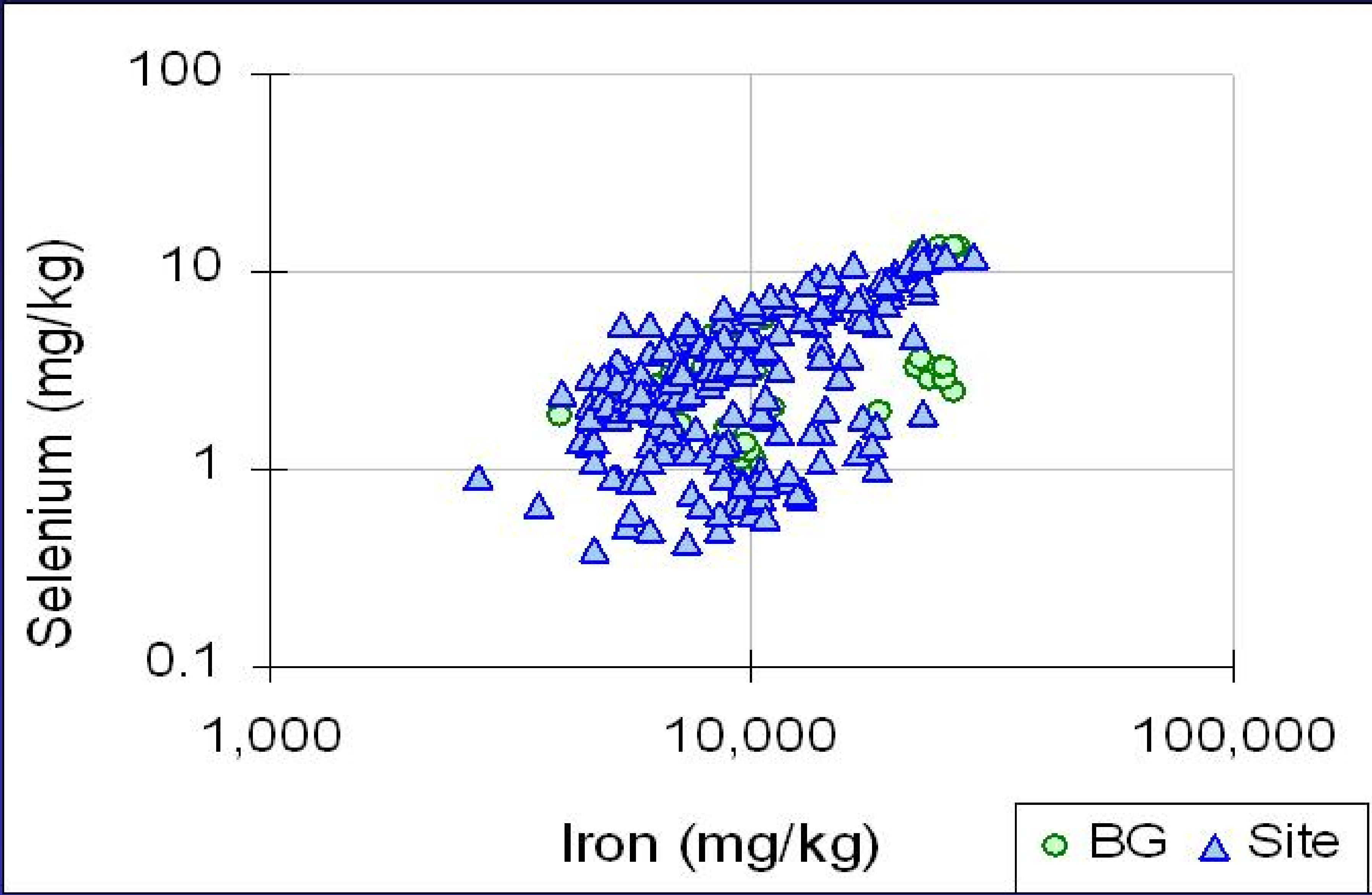
    Ag vs Fe

    Pb vs Fe

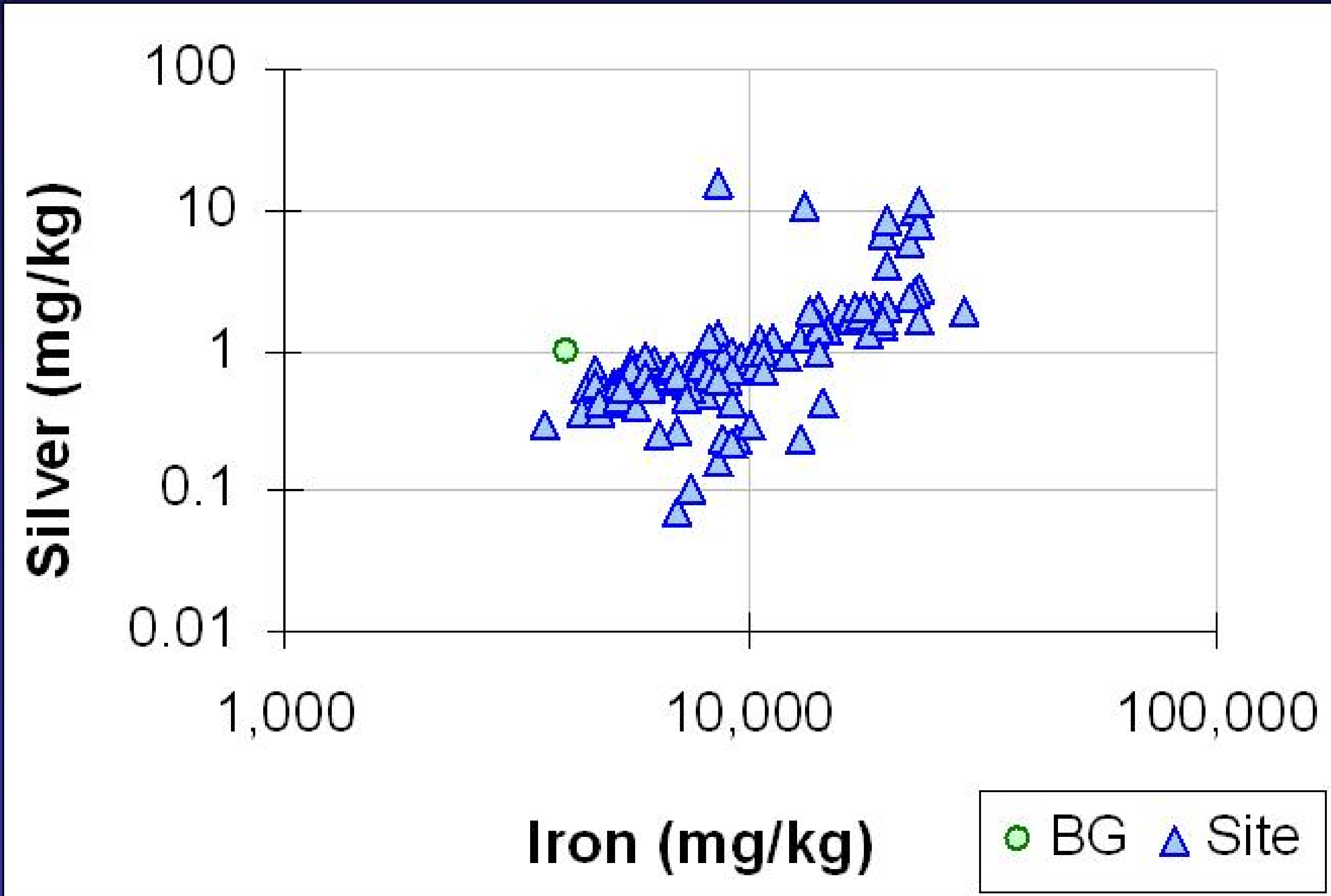
Knolls APL, Co vs. Fe



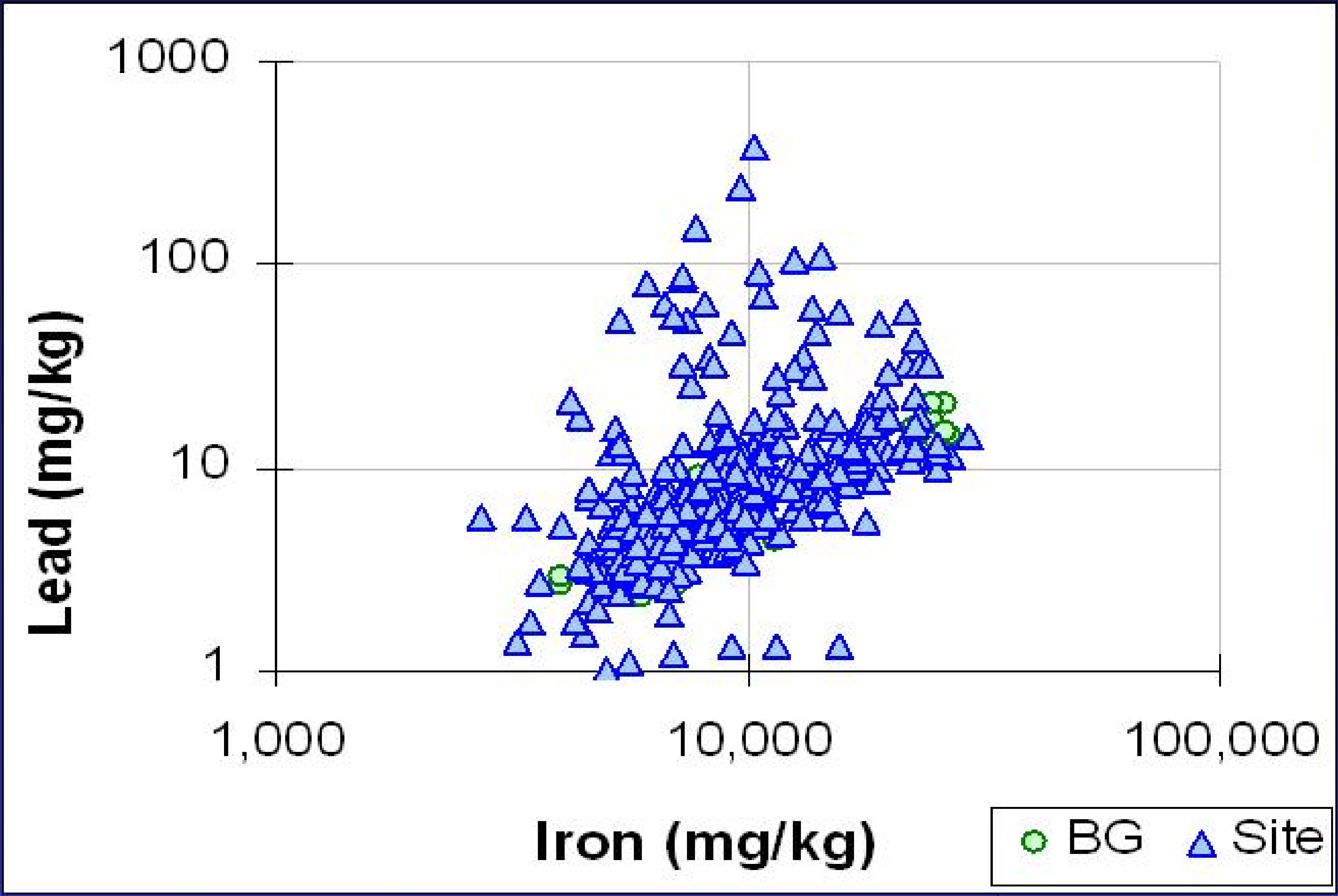
Knolls APL, Se vs. Fe



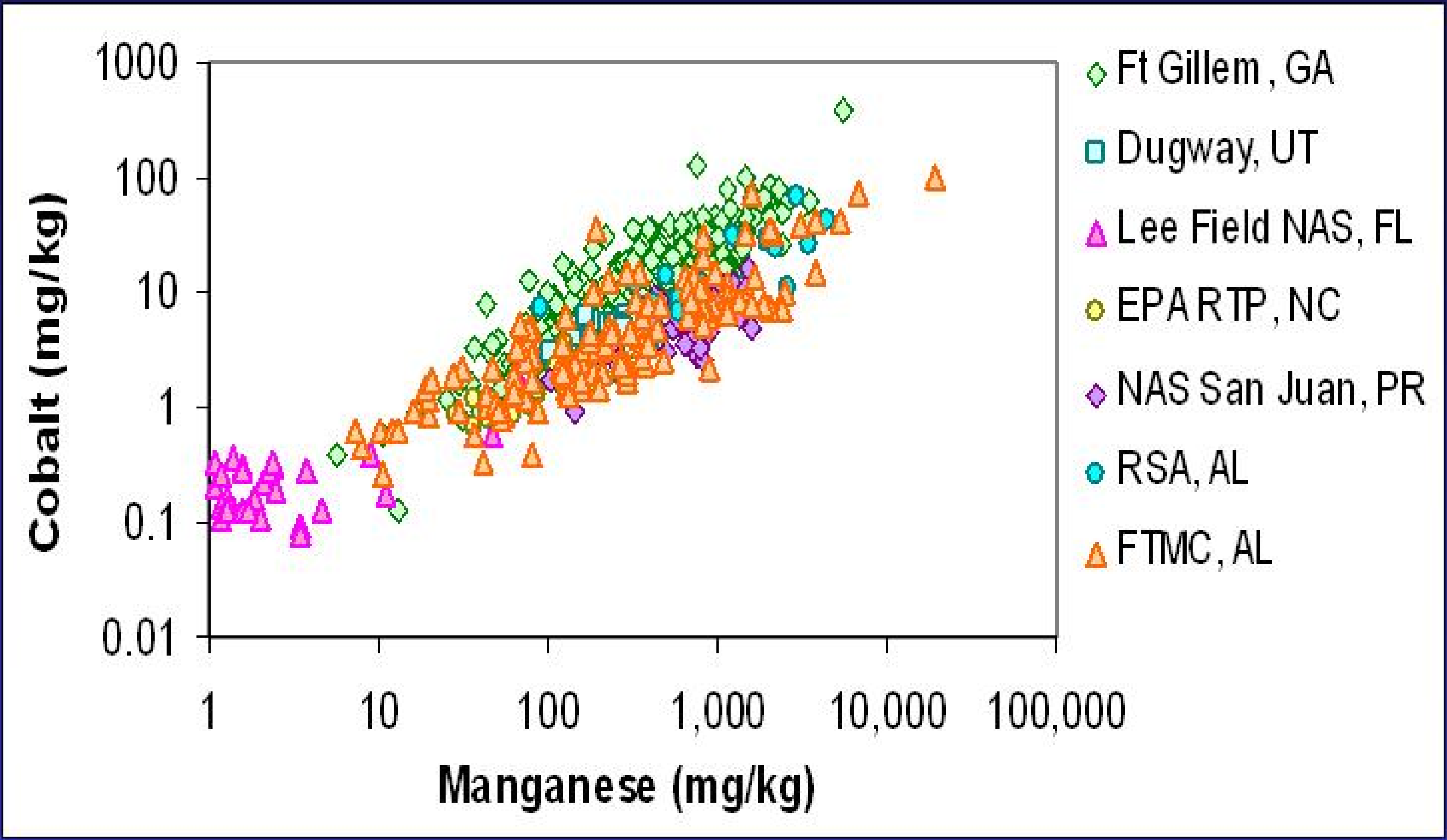
Knolls APL, Ag vs. Fe



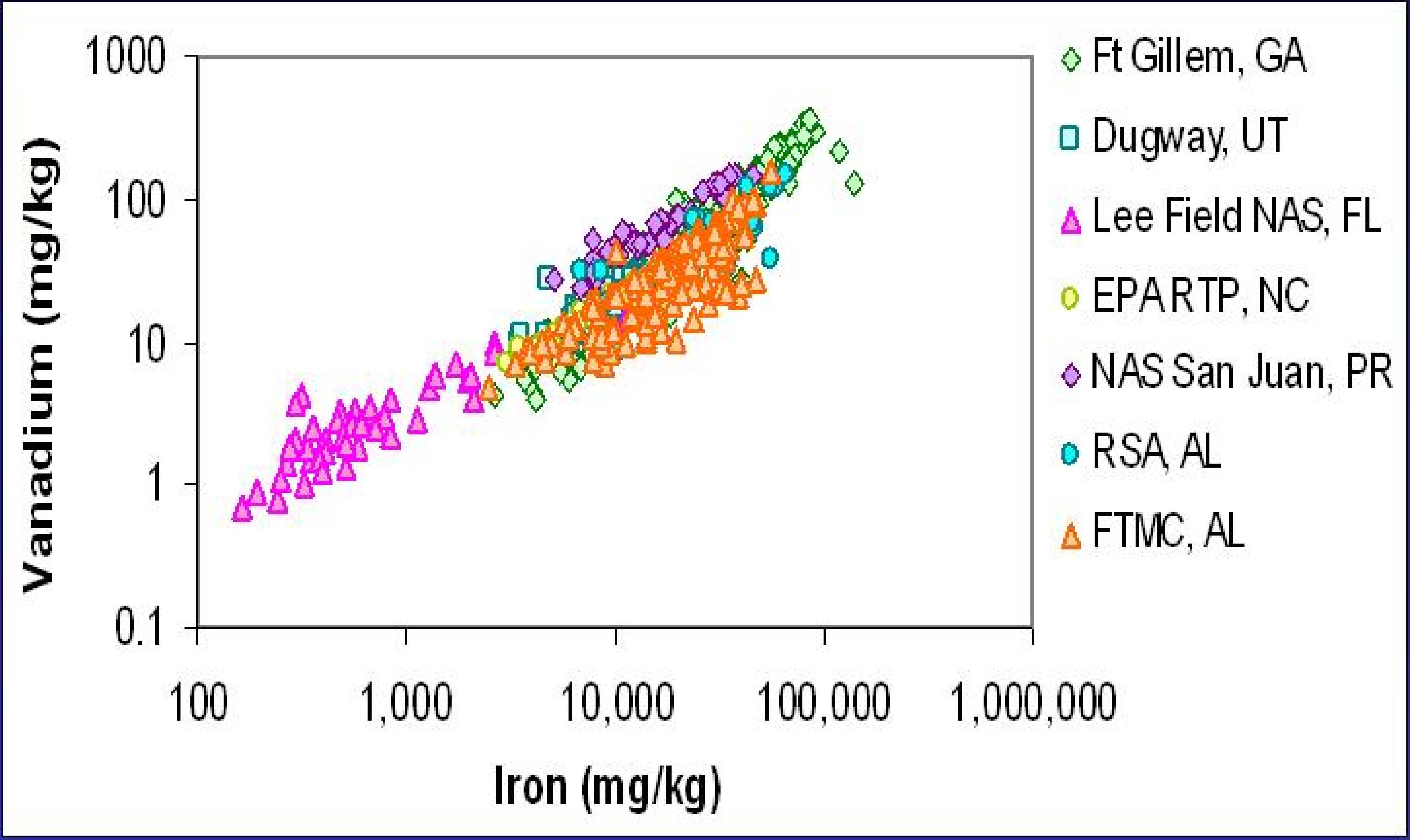
Knolls APL, Pb vs. Fe



Multi-Site Correlations – Cobalt vs. Manganese in Background Soils



Multi-Site Correlations – Vanadium vs. Iron in Background Soils



Conclusions

- Geochemical evaluations are a cost-effective approach to determining if metals contamination of soil has occurred.
  - Valid background set is not required
  - Lower probability of false positive results
  - Analyses of Al, Fe, Mn, and Ca are required
  - The mechanisms responsible for the observed concentrations can be identified
- Approach can be used with statistical methods
  - If site-to-BG comparison fails for an element, then do a geochemical evaluation.