Geochemical Evaluation of Arsenic in Groundwater: Interaction of Organic-Rich Sediments and Underlying Beach Sands at a Former Petroleum Release Site

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GEOCHEMICAL EVALUATION

Why Use It?

- Distinguish contamination from naturally high background concentrations
- Combines observations with the known geochemical behaviors of the elements
- Not a statistical technique; complements statistical evaluations
- Determines if statistical outliers should be included or rejected
- Can identify contaminated samples, even if the component of contamination is insignificant
- Identifies processes controlling element concentrations

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SORPTION OF METALS

Most important sorptive surfaces are:

- Clays
- Organic material
- Iron and manganese “oxides”
  - Oxides, hydroxides, oxyhydroxides, hydrous oxides, amorphous oxides, etc.

SORPTION OF METALS

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-}

Attracted to positively charged surfaces – FeO_x

SITE BACKGROUND

- Former military service station at a base along the Gulf Coast
- Groundwater plume from a hydrocarbon release has naturally attenuated to undetectable concentrations
- Arsenic in groundwater ranges from 0.44 µg/L to 729 µg/L
- Highest well arsenic concentrations ranged from 120 µg/L (2018) to 729 µg/L (2020) to 320 µg/L (2023)
- Hydrocarbons (TPH-DRO) were never detected at the location with highest arsenic
- Twelve new background wells installed; Soil and GW collected Fall 2023
- Six existing background wells also sampled for GW

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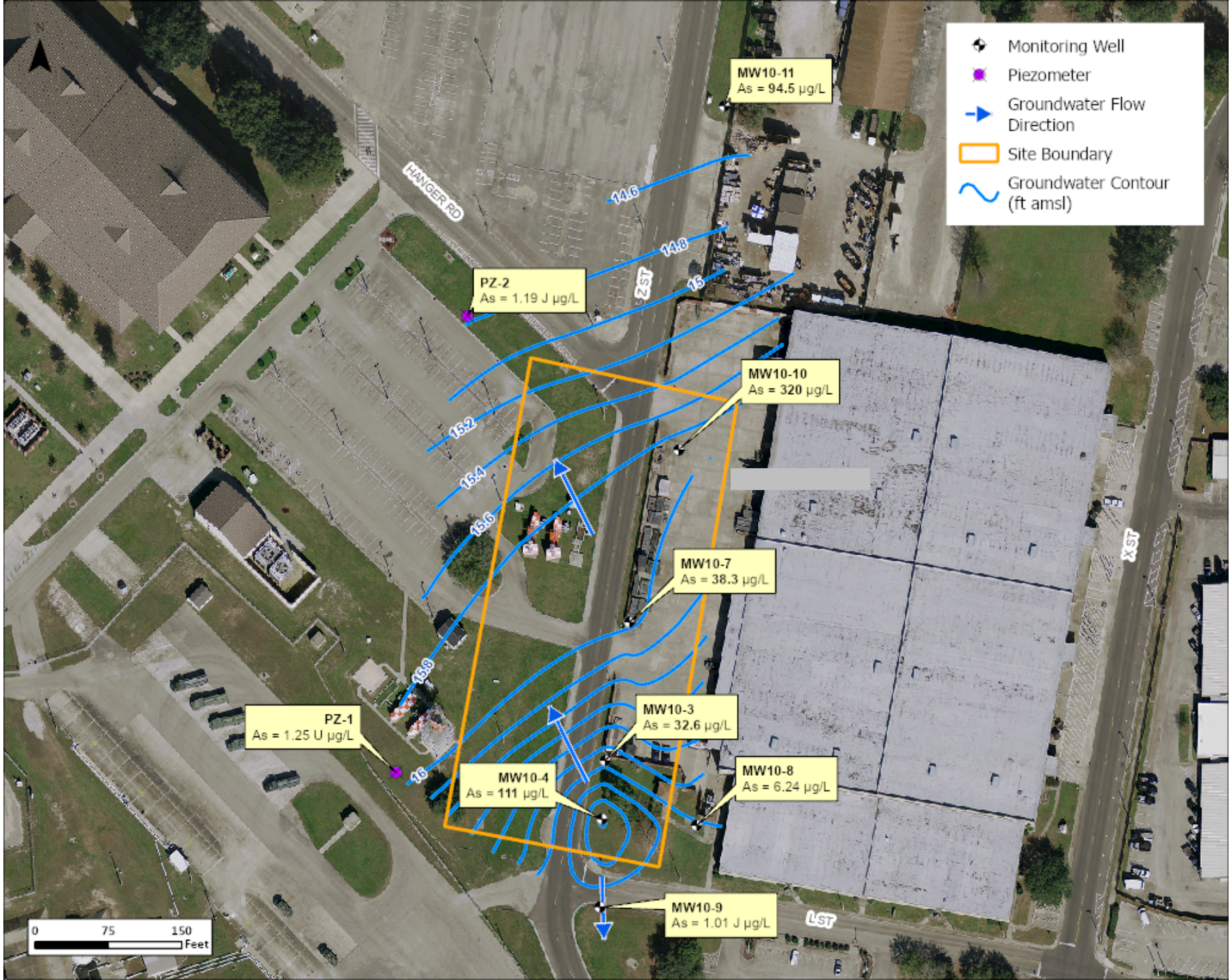
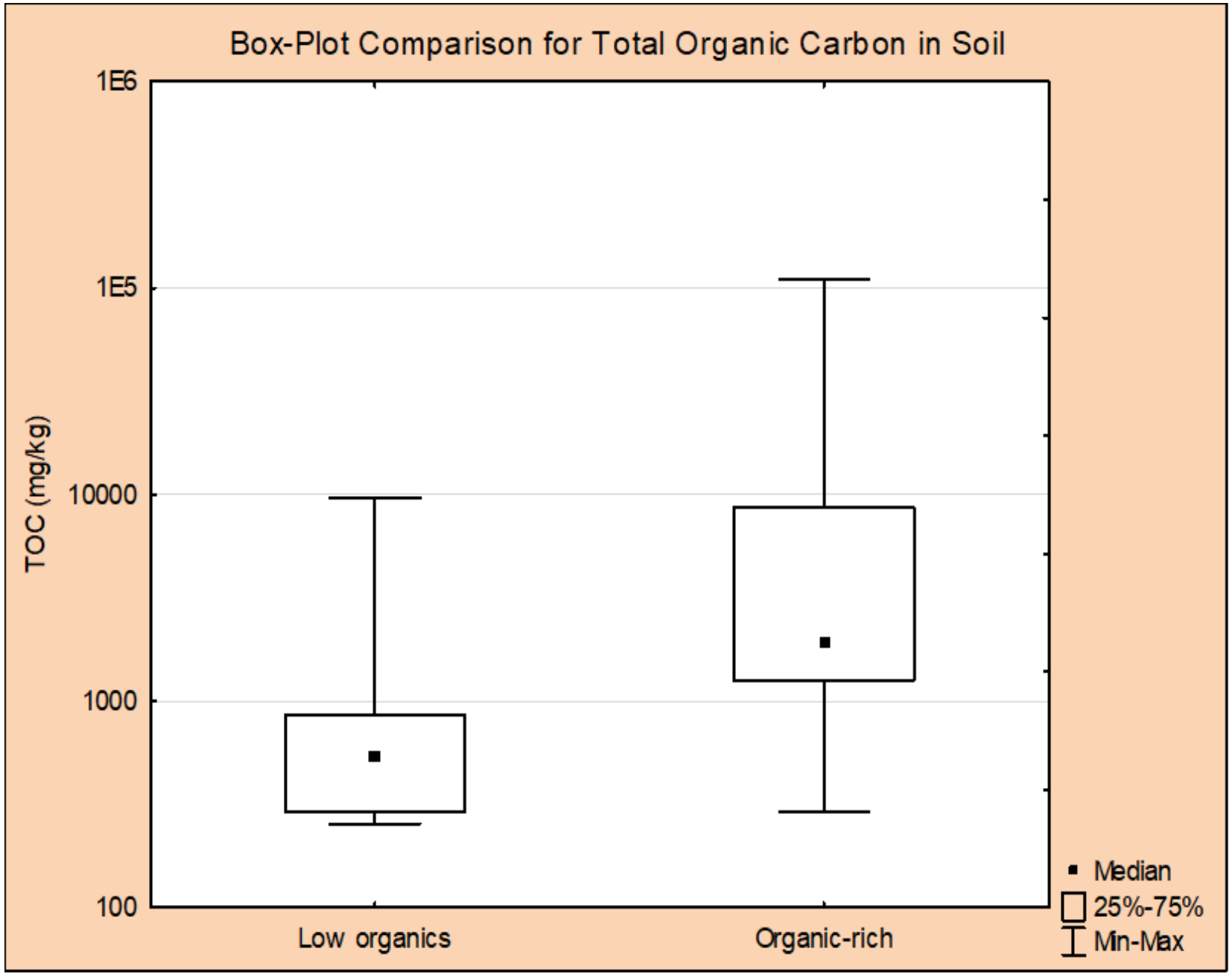

Monitoring Well
Piezometer
Groundwater Flow Direction
Site Boundary
Groundwater Contour (ft amsl)
MW10-11
As = 94.5 µg/L
PZ-2
As = 1.19 J µg/L
MW10-10
As = 320 µg/L
MW10-7
As = 38.3 µg/L
MW10-3
As = 32.6 µg/L
MW10-8
As = 6.24 µg/L
MW10-4
As = 111 µg/L
PZ-1
As = 1.25 U µg/L
MW10-9
As = 1.01 J µg/L
14.6
14.8
15
15.2
15.4
15.6
15.8
16
HANGER RD
ZST
XST
LST
0
75
150
Feet

- Two soil samples per boring analyzed for TOC and Arsenic
  - One from organic-rich layer (if present)
  - Other from clean sand below water table
- No surprise that organic-rich layer has considerably higher TOC



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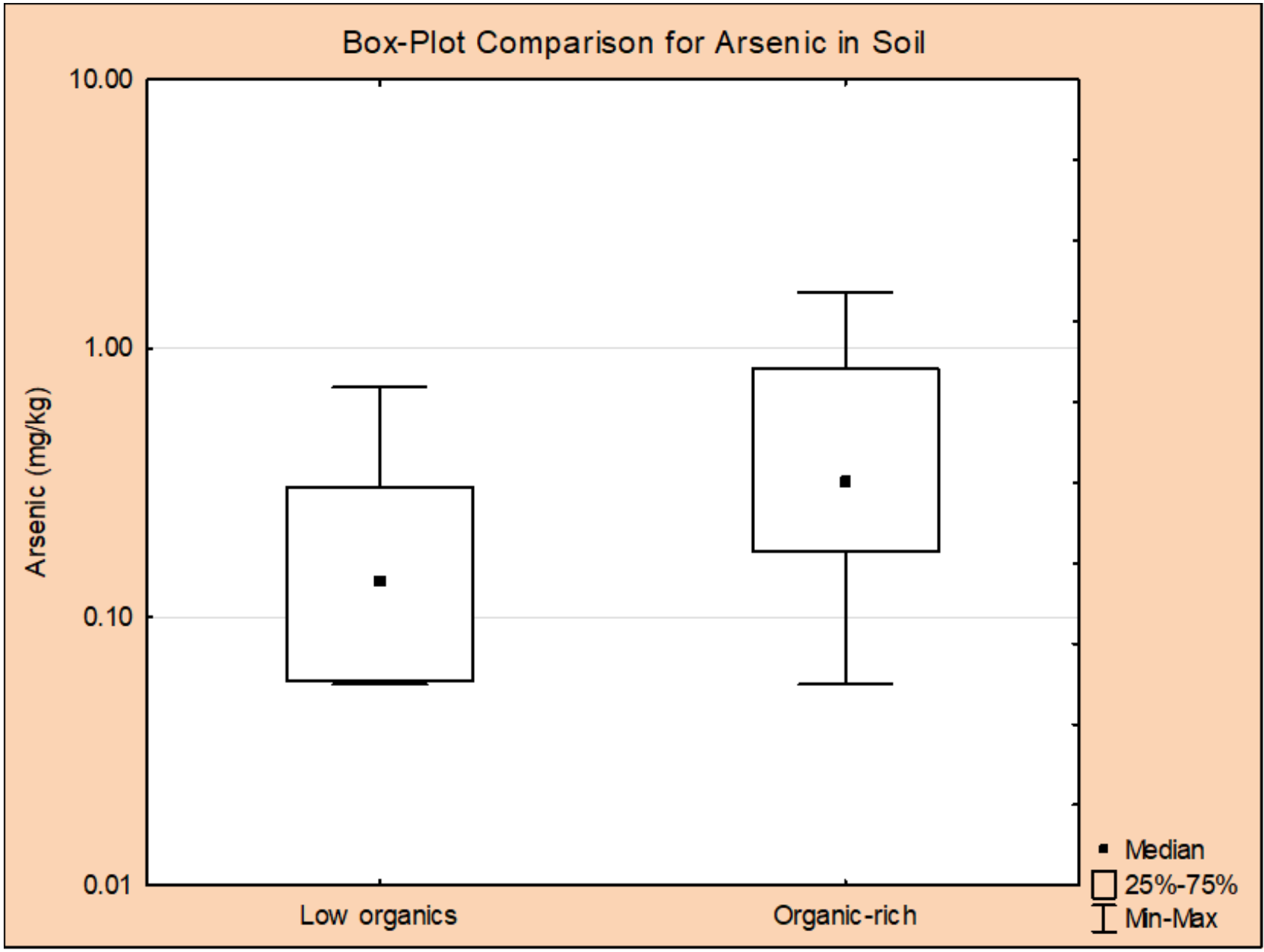
- Upward shift in arsenic also visible in organic-rich samples
- Overall arsenic concentrations are relatively low



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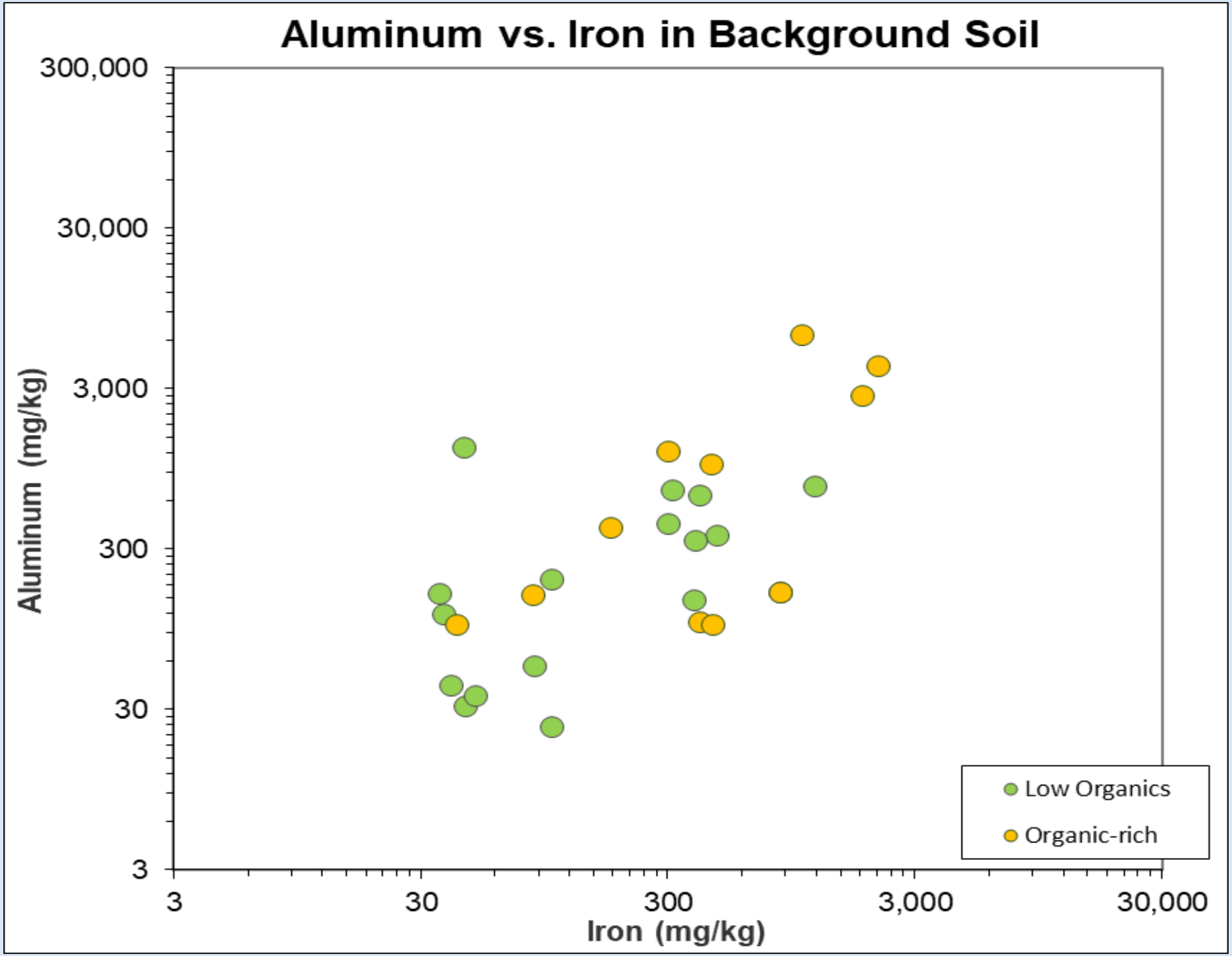
Aluminum vs. Iron in Background Soil
300,000
30,000
3,000
300
30
3
Aluminum (mg/kg)
3
30
300
3,000
30,000
Iron (mg/kg)
Low Organics
Organic-rich

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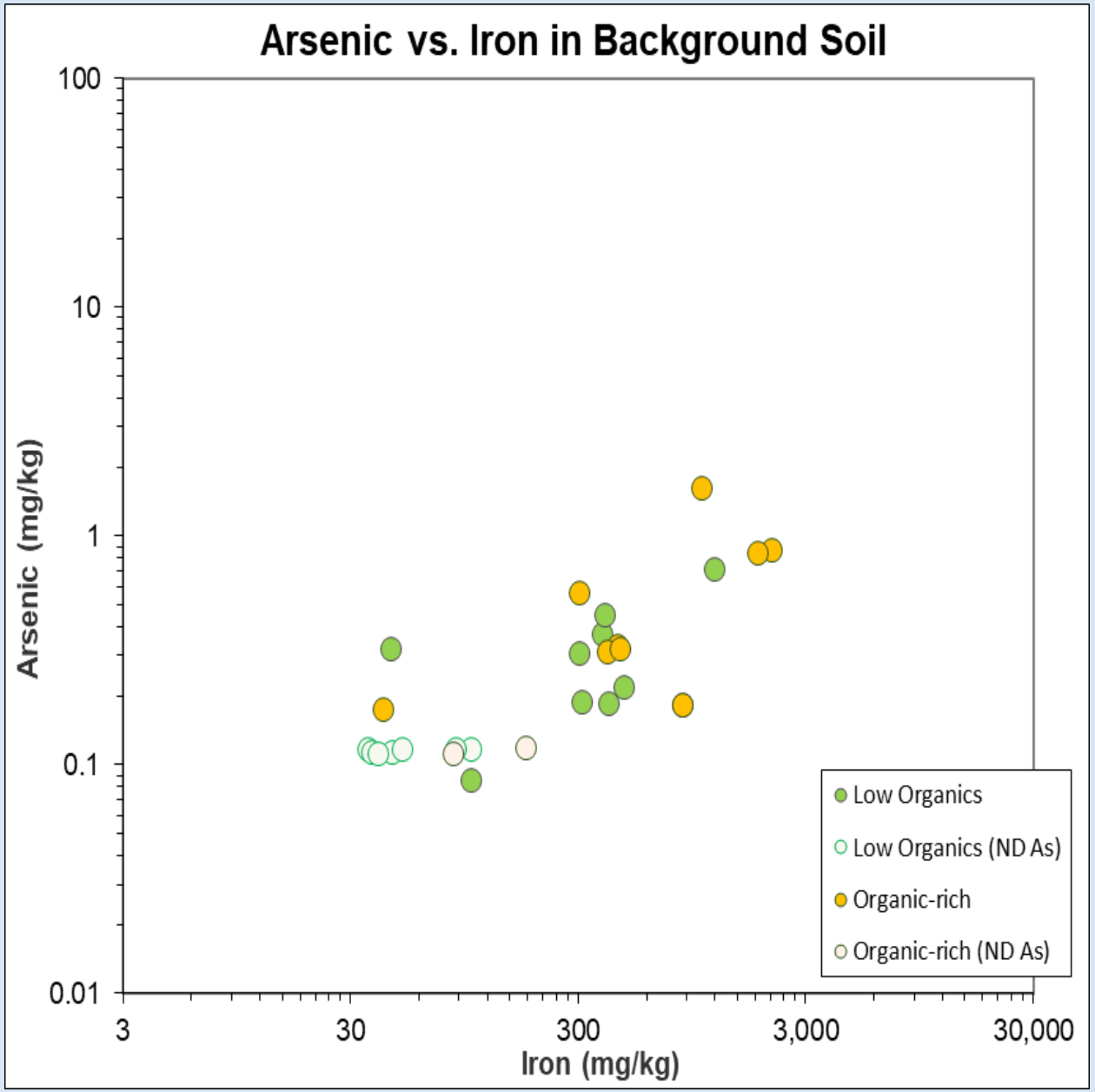
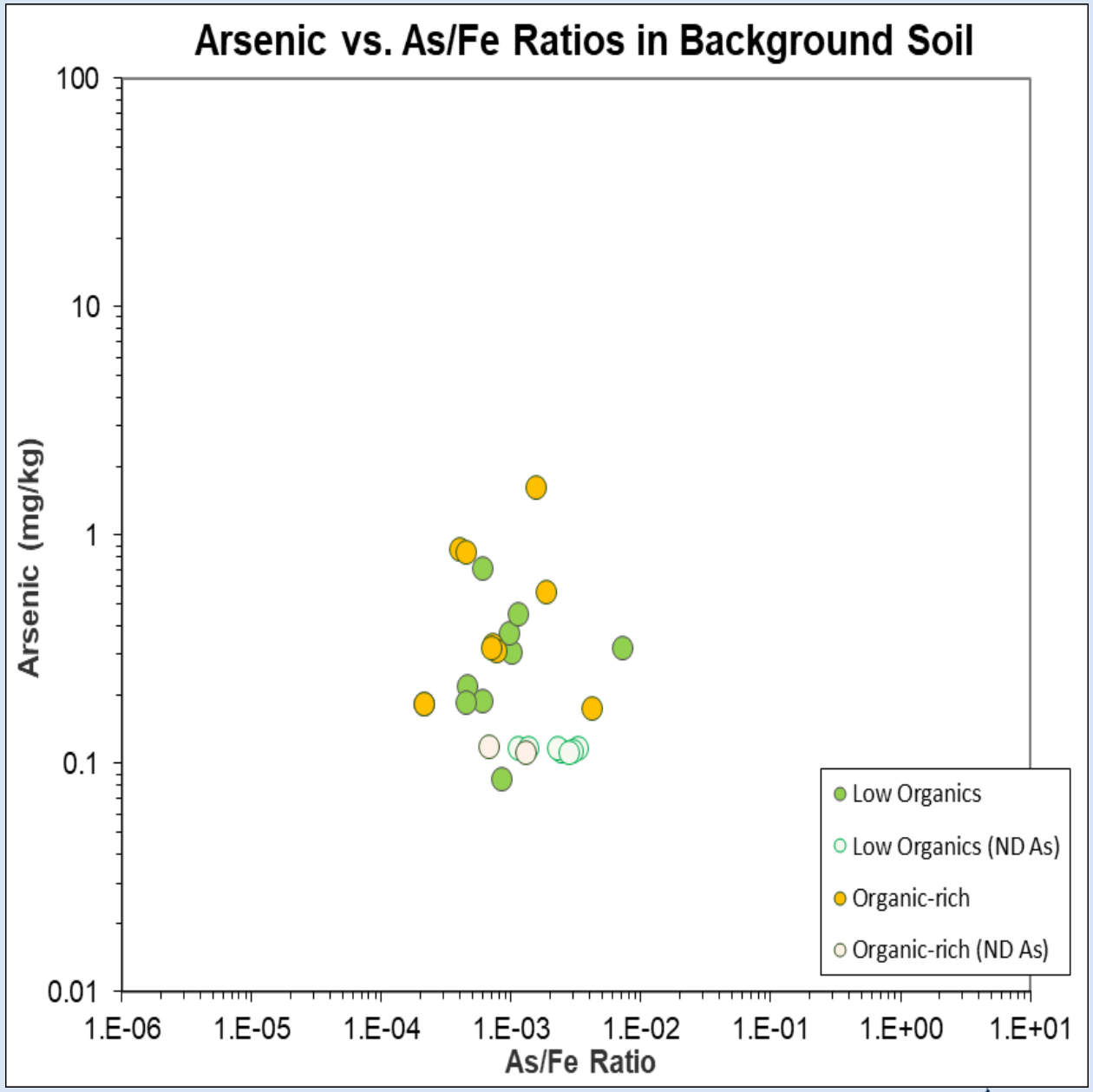

Arsenic vs. Iron in Background Soil
100
10
1
0.1
0.01
Arsenic (mg/kg)
3
30
300
3,000
30,000
Iron (mg/kg)
Low Organics
Low Organics (ND As)
Organic-rich
Organic-rich (ND As)


Arsenic vs. As/Fe Ratios in Background Soil
100
10
1
0.1
0.01
Arsenic (mg/kg)
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
1.E+01
As/Fe Ratio
Low Organics
Low Organics (ND As)
Organic-rich
Organic-rich (ND As)

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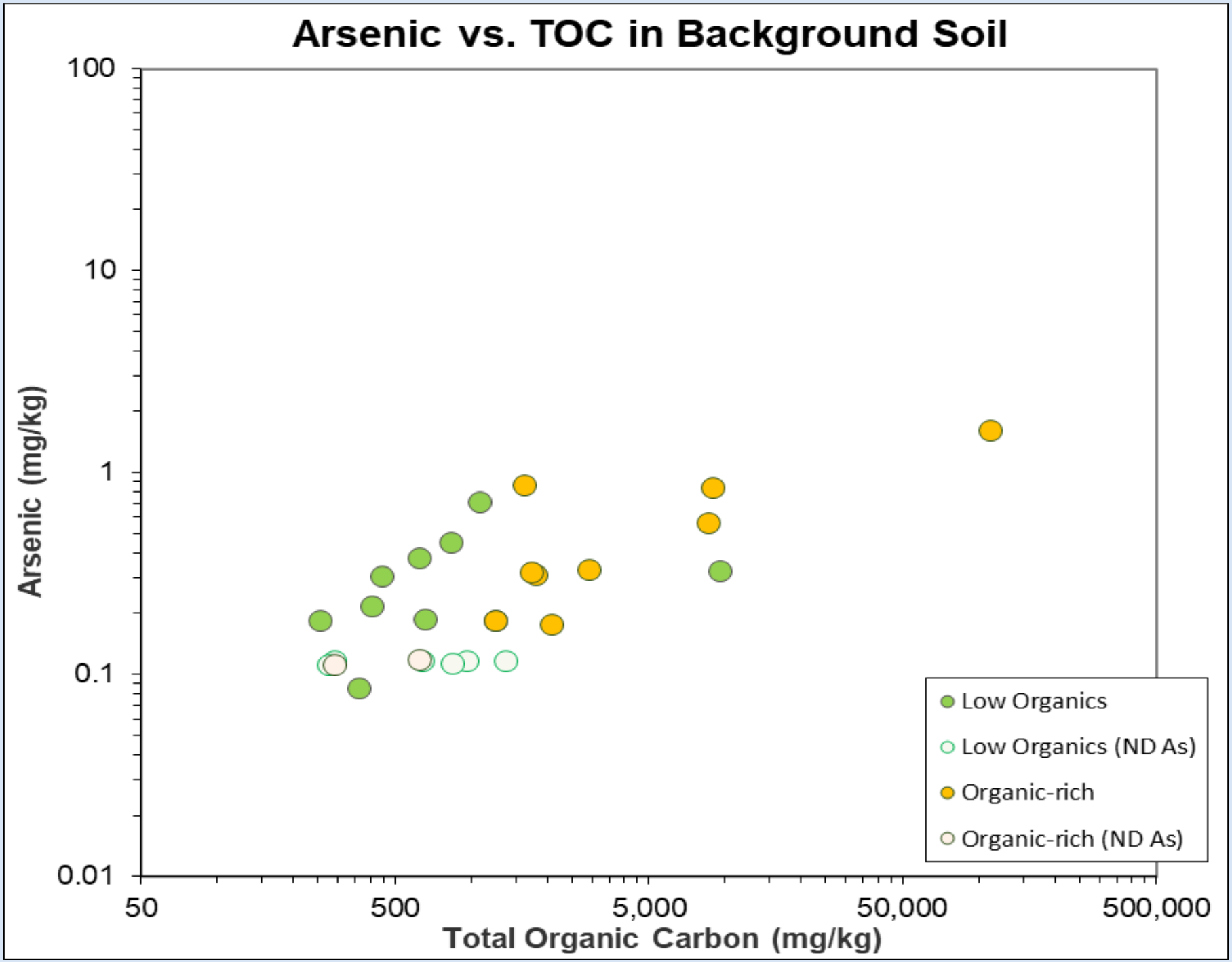
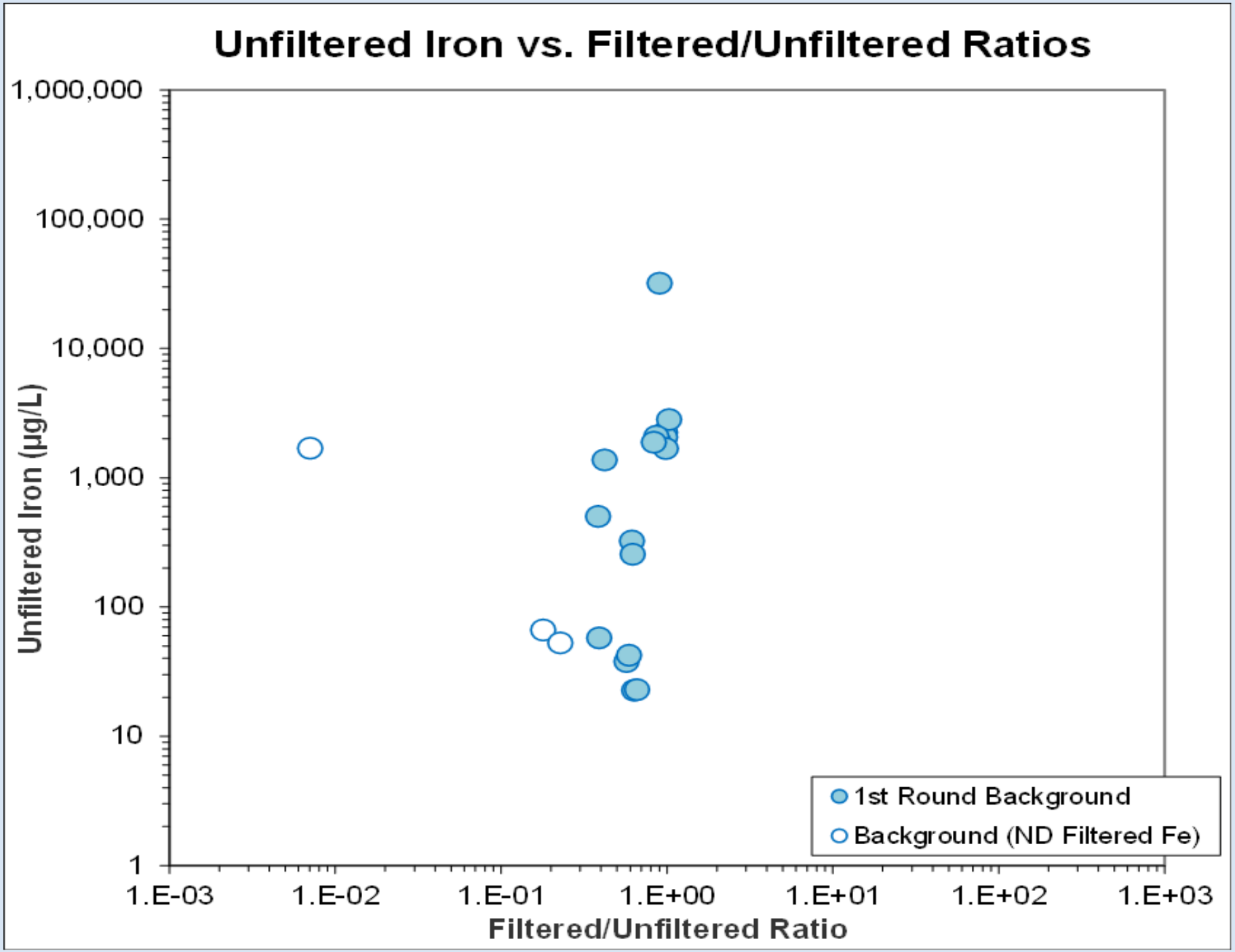
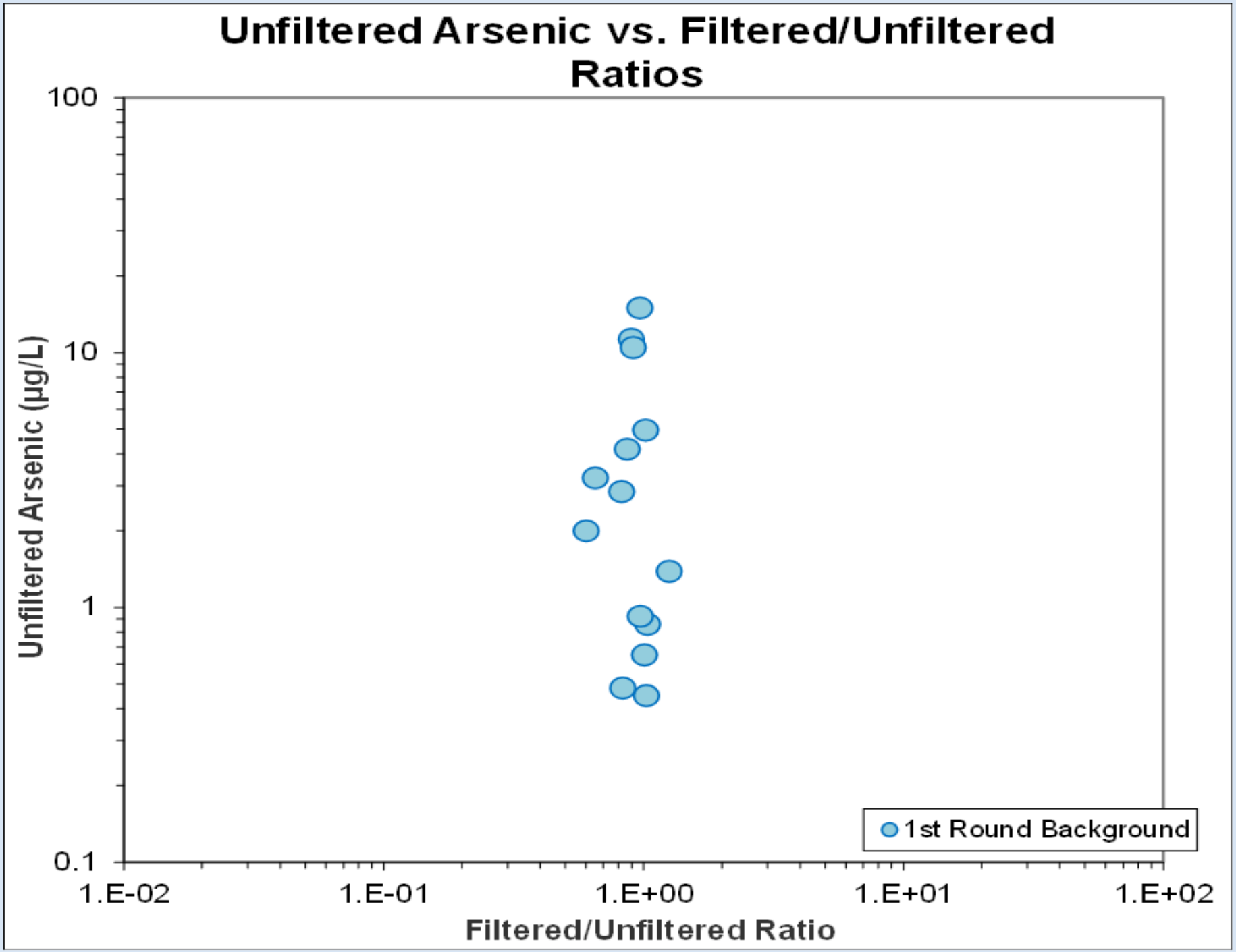

Arsenic vs. TOC in Background Soil
100
10
1
0.1
0.01
Arsenic (mg/kg)
50
500
5,000
50,000
500,000
Total Organic Carbon (mg/kg)
Low Organics
Low Organics (ND As)
Organic-rich
Organic-rich (ND As)

EVALUATION OF METALS IN GROUNDWATER

Possible reasons for elevated metals concentrations in groundwater:

- Suspended particulates
- pH effects
- Redox effects
- Reductive dissolution
- Evaporation (concentration) in arid climates
- TDS and complexation effects (seawater mixing)
- Contamination


Unfiltered Iron vs. Filtered/Unfiltered Ratios
1,000,000
100,000
10,000
1,000
100
10
1
Unfiltered Iron (µg/L)
1.E-03
1.E-02
1.E-01
1.E+00
1.E+01
1.E+02
1.E+03
Filtered/Unfiltered Ratio
1st Round Background
Background (ND Filtered Fe)


Unfiltered Arsenic vs. Filtered/Unfiltered Ratios
100
10
1
0.1
Unfiltered Arsenic (µg/L)
1.E-02
1.E-01
1.E+00
1.E+01
1.E+02
Filtered/Unfiltered Ratio
1st Round Background

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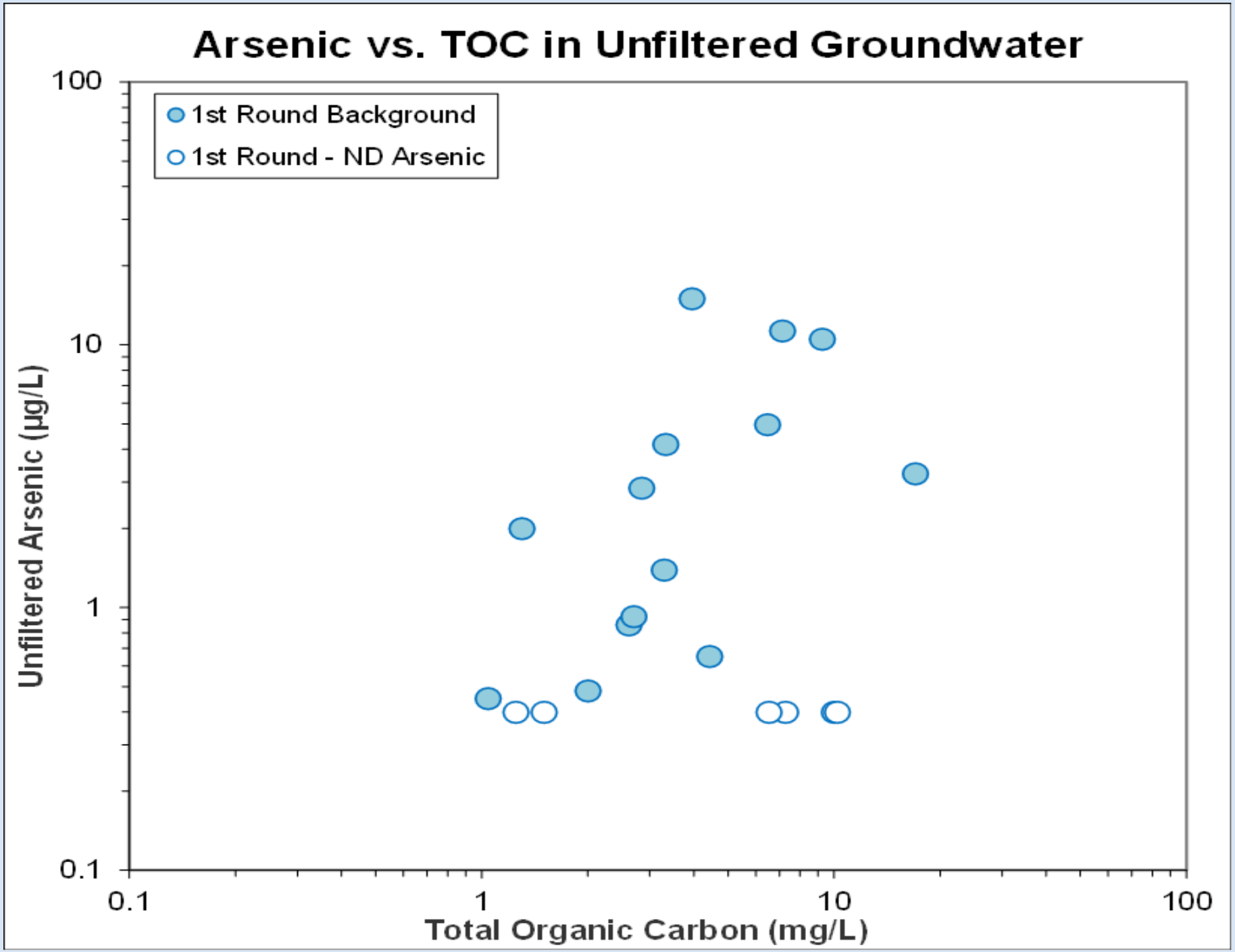
Arsenic vs. TOC in Unfiltered Groundwater
1st Round Background
1st Round - ND Arsenic
Unfiltered Arsenic (µg/L)
100
10
1
0.1
0.1
1
10
100
Total Organic Carbon (mg/L)

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REFERENCES

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