Simulating and Predicting Arsenic Mineralogy Controlling Arsenic Solubilization into Groundwater in Semi-Arid Environments

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Abstract

Elevated arsenic (As) concentrations in groundwater used for drinking water have been seen throughout the United States, with generally higher concentrations in the Rocky Mountain and Interior Plains regions. Long term exposure to arsenic concentrations over the Maximum Contaminant Level (MCL) of 10 µg/L can cause skin and lung cancer, along with several other adverse health effects. Previous studies have looked into the tragic As poisoning of millions of people in West Bengal, Bangladesh, and Southeast Asia; focusing only in these humid regions. There are limited data evaluating the fate of As and its mineral speciation in groundwater in semi-arid environments. At our study site, groundwater concentrations of As exceed the MCL, mineralogy is dominated by carbonates, and groundwater recharge is controlled by high evapotranspiration rates. The objective of this study is to determine As mineralogy that controls the solubility of As. Two cores were collected from the soil surface to the depth of groundwater. Cores were sectioned under anaerobic conditions based on observed redoximorphic features. Pore water was analyzed for As and Fe redox species and general water quality parameters and solid phase As, Fe and Mn have been described using sequential extractions. We have evidence that redox transition soils contain As associated with iron oxides and carbonates. Most of the As in all zones is associated with mineral surfaces or incorporated into non-crystalline minerals as defined by sequential extractions. To evaluate solid phase associations of As, parameters from pore water analysis from the various layers within the cores will be modeled using MINEQL+. The model results will be compared to bulk As concentration data from soil sequential extractions. Results will be used to simulate field conditions and understand and predict As retention and solubilization.

Introduction

- Arsenic levels exceeding MCL measured in monitoring wells throughout Cache County, Utah[1] (Fig. 1)

- Arsenic is naturally occurring in geologic material from soil surface to 1.5 m below depth of groundwater

- Recent USGS [2] study predicts 42.7% of the area underlain by basin-fill aquifers in the western US equals or exceeds the MCL for As

- Arsenic concentrations were higher in basins with low recharge and basins surrounded by volcanic rocks [2]

- Study area is on the eastern edge of the Great Basin

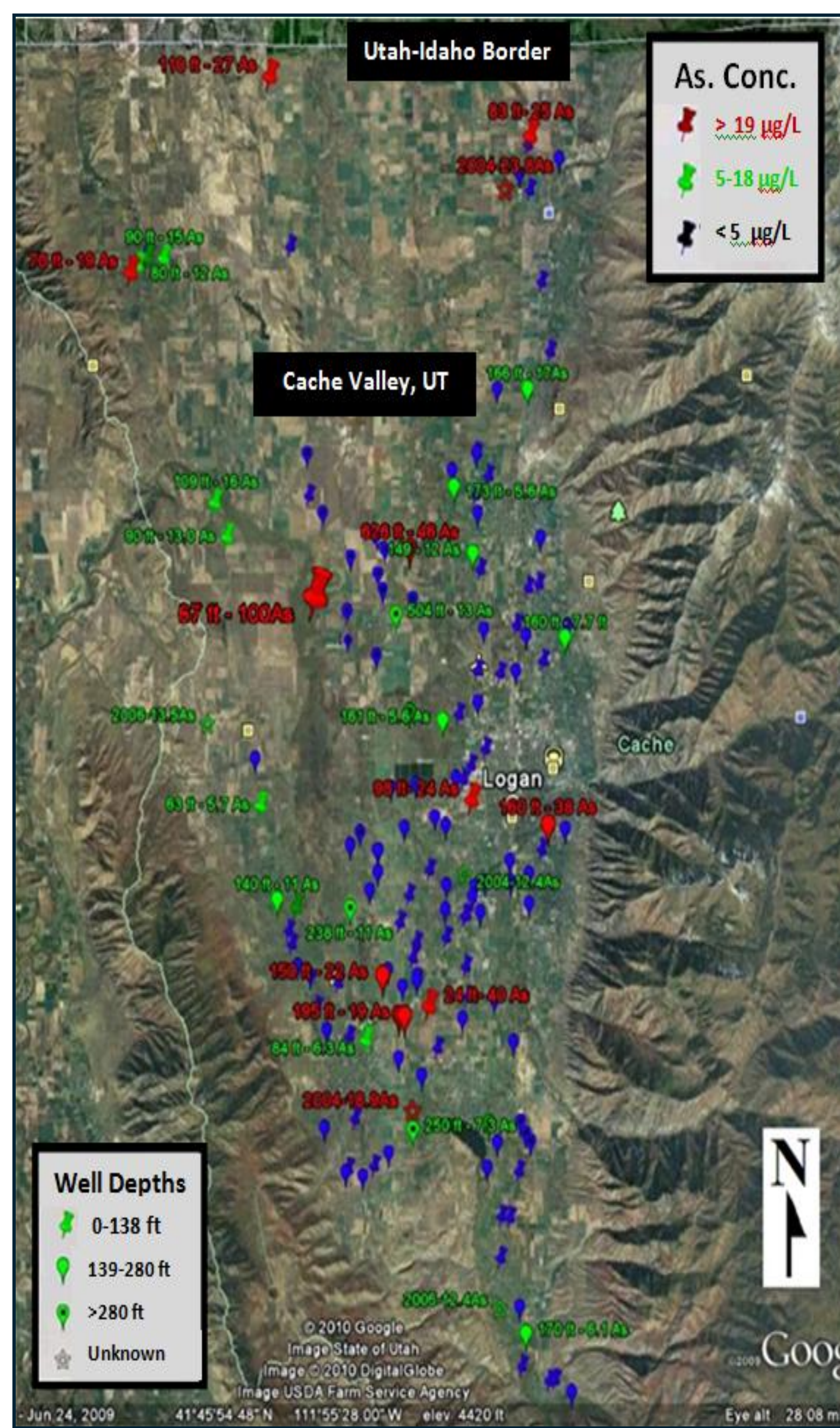- Mechanisms and prediction of retention and solubilization of As and groundwater chemistry not yet fully understood

Fig. 1: Groundwater wells sampled for arsenic in Cache Valley and Northern Utah. (Pin notation: Blue: As conc. <5 µg/L, Green: As conc. from 5 µg/L to 18 µg/L, Red: As conc. > 18 µg/L)

Objectives

(1) Determine arsenic mineral phases controlling arsenic solution chemistry down the soil profile

(2) Determine if arsenic is retained through sorption and precipitation onto iron oxides

Methods

- Soil core from soil surface to 1.5 m below water table collected from the center of the Cache Valley Basin

- Core sectioned into three zones and 16 layers, determined by color, texture, and redoximorphic features under anaerobic conditions

- Pore water analyzed for As(III), As(V), Fe(II), and Fe(III) and general water quality parameters

- Seven step sequential extraction[3,4] used to determined As associated with soluble and insoluble mineral phases

- Use pore water data for equilibrium modeling (MINEQL+)

Vadose Zone
108 cm
Redox Transition Zone
430 cm
Saturated Zone
610 cm
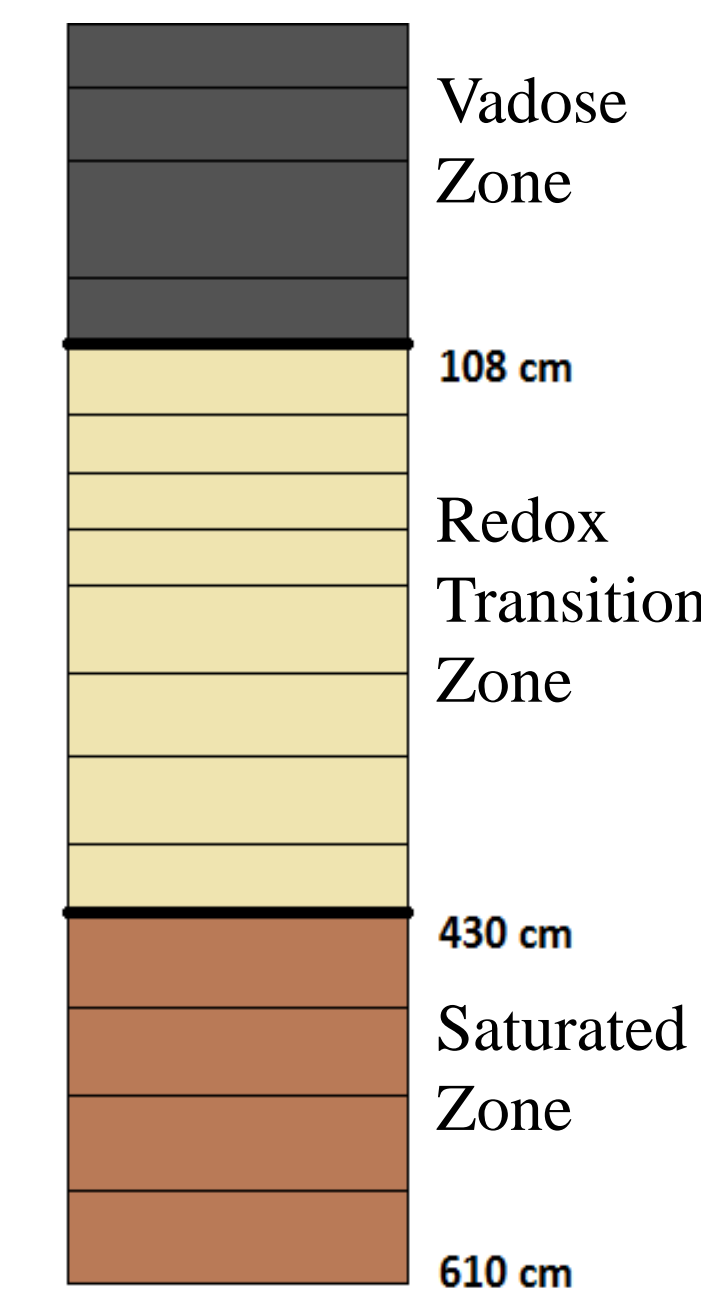
Results and Discussion

Pore Water Analysis

- As concentration in pore water increases with depth throughout vadose zone

- As(V) dominates in vadose and redox transition zones

- Maximum concentration of As near groundwater (GW) table, the area of seasonal fluctuating groundwater influencing redox conditions

- Lowest concentration of As in the depletion zone where As(III) is the dominant species

- Fe(II) is the dominant oxidation state of iron below the surface soil; ranging from 54-66% of the total iron
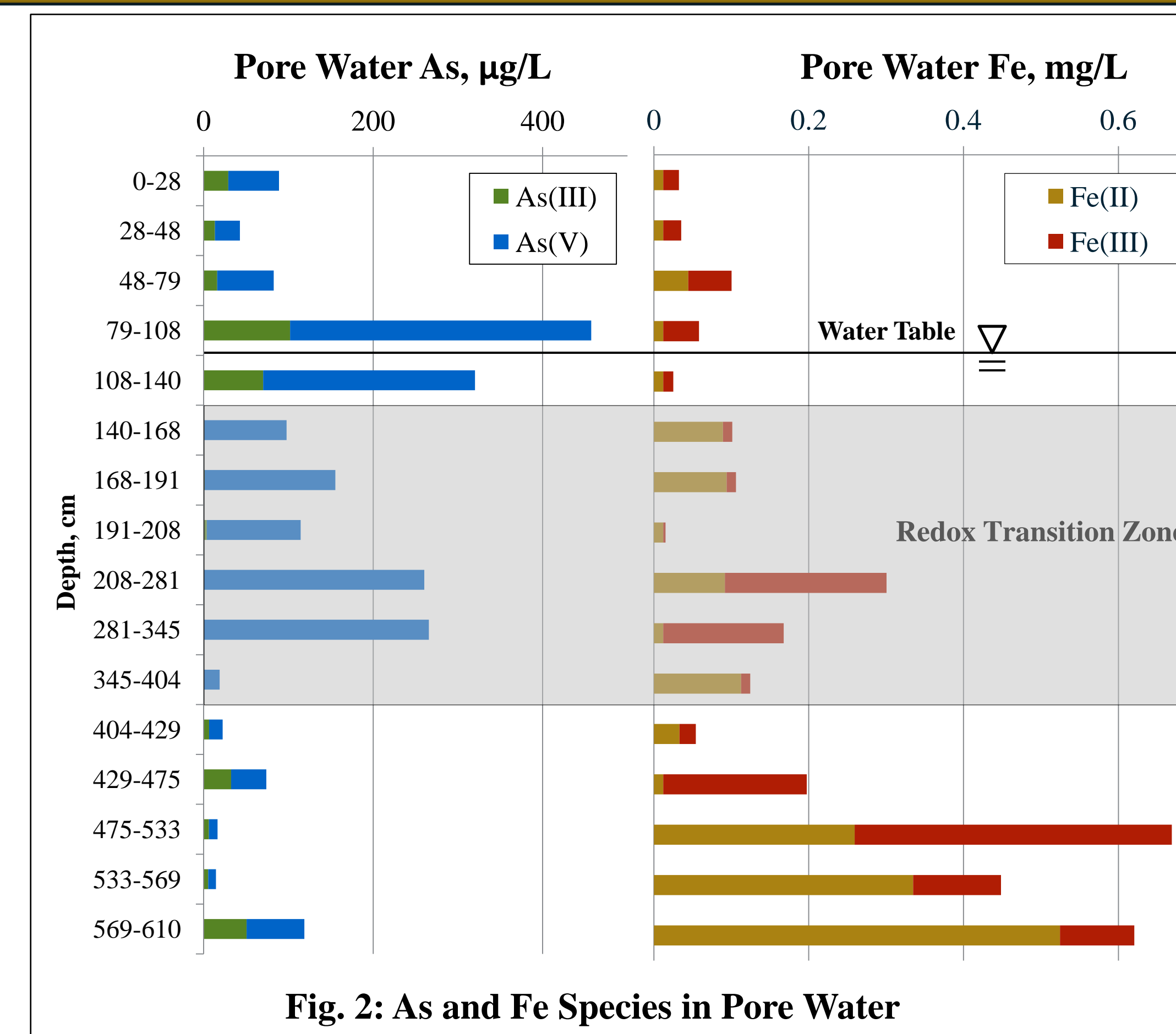
Fig. 2: As and Fe Species in Pore Water

Modeling Results

Vadose Zone:
- Average As distribution: 31% As(III), 69% As(V)
- 100% of As(III) in solid phase as orpiment (As_2S_3)
- 32% of As(V) sorbed onto Fe(III) oxyhydroxides (Fe-OH), remaining 68% in solution or unknown solid phase (Fig. 3)

Redox Transition Zone:
- Average As distribution: 1% As(III), 99% As(V)
- 100% of As(III) in solid phase as orpiment (As_2S_3)
- Unstable redox conditions
- 9% of As(V) sorbed onto Fe-OH, remaining 91% in solution or possibly sorbed to carbonates (Fig. 3)

Saturated Zone:
- Average As distribution: 55% As(III), 45% As(V)
- Redox stable groundwater conditions
- 100% of As(III) in solid phase as orpiment (As_2S_3)
- Fe-OH does *not* play role in As sorption (Fig. 3)
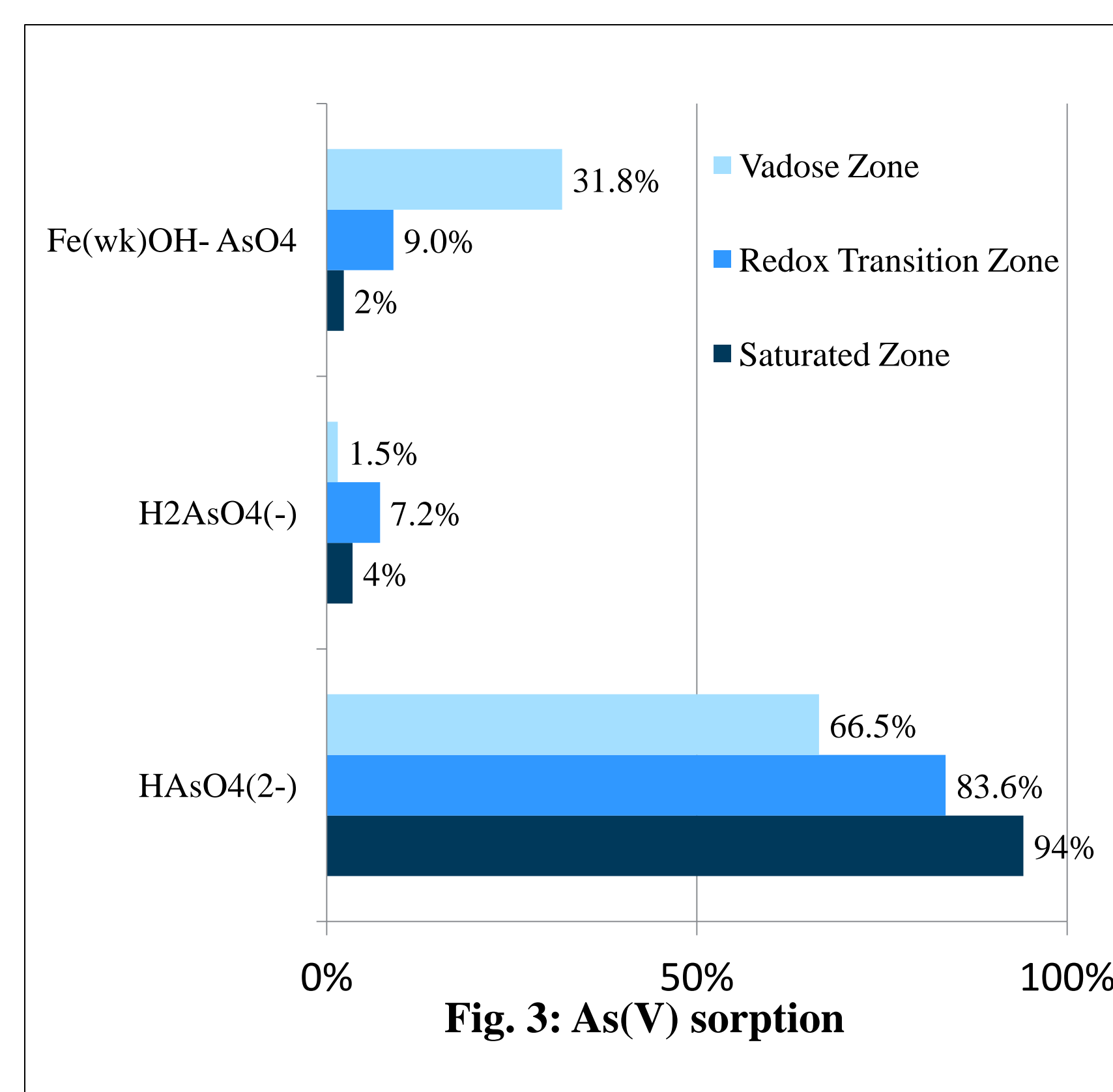- As(V) may be associated with carbonate sorption

Fig. 3: As(V) sorption

	Vadose Zone	Redox Transition Zone	Saturated Zone
Fe(wk)OH- AsO4	31.8%	9.0%	2%
H2AsO4(-)	1.5%	7.2%	4%
HAsO4(2-)	66.5%	83.6%	94%

Sequential extraction: Arsenic in the solid phase

% As Extracted

- Ligand Exchangeable As
- Carbonate Minerals
- Mn oxides, very amorphous Fe oxides
- Amorphous Fe oxides
- Sulfides, Crystalline Fe oxides, Residuals

- Arsenic distribution in defined mineral phases varies with depth (Fig 4)

- A high % of As in the redox transition zone is associated with soluble minerals (ligand exchangeable As, carbonates, Mn oxides), corresponding to higher pore water concentrations (Fig. 2)
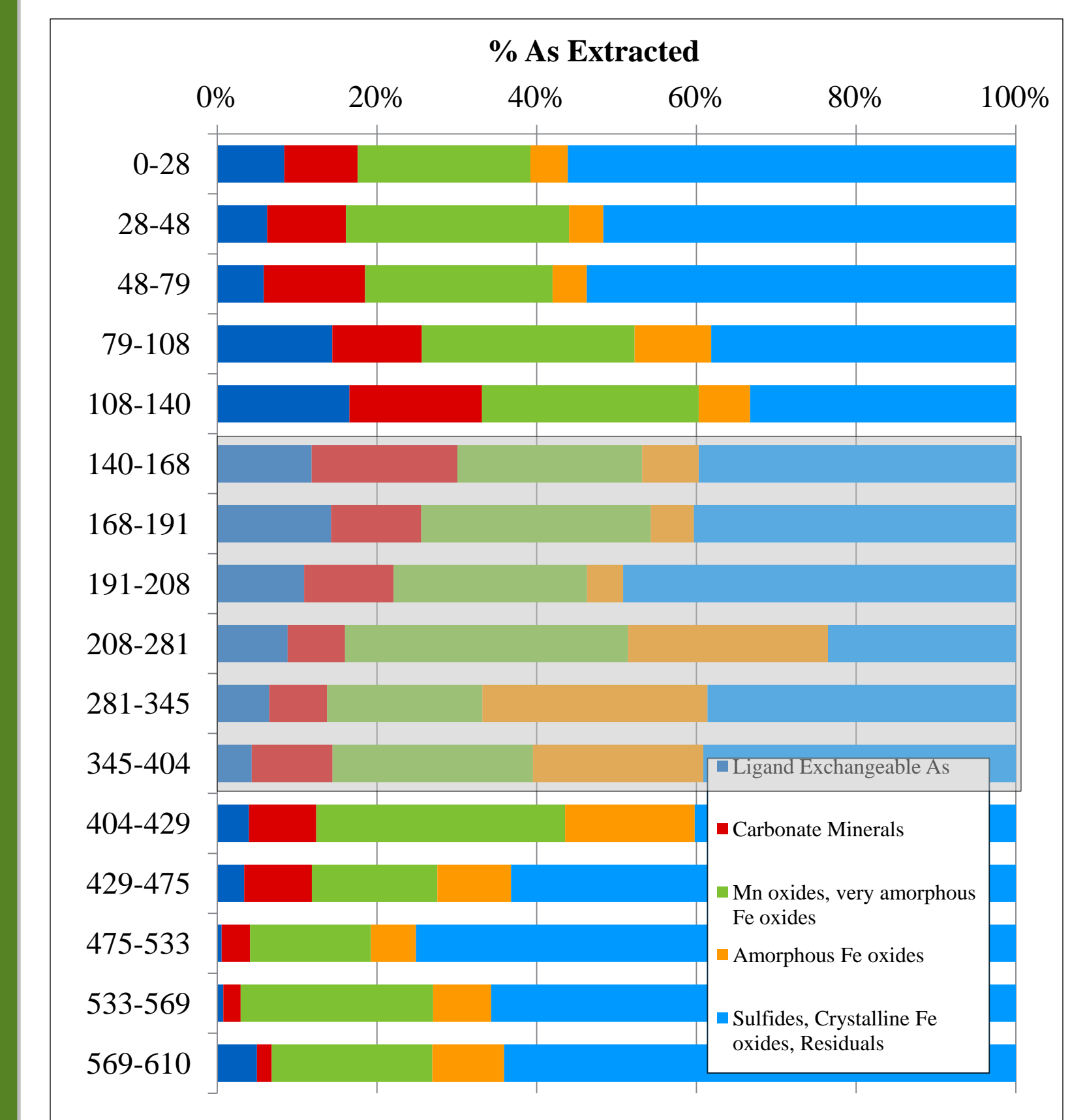
Fig. 4: Distribution of As in different mineral phases, as defined by sequential extraction (Shaded area=redox transition zone)

- Transition zone exchangeable and carbonates not included in model

- With depth more of the As is precipitated with insoluble minerals (sulfides, crystalline iron oxides, residuals)

Continuing Research

- Determine the role of carbonate minerals in sorption/desorption of arsenic

- Predict effect of changing redox conditions on As mineralogy

- Compare geochemical modeling results to sequential extraction data

- Simulate and predict As solubilization and retention with geochemical modeling

Conclusions

- Solid phases controlling arsenic concentration in the pore water change with changes in mineralogy and redox conditions down the soil profile

- Fe-OH accounts for only a portion of the arsenic associated with solid surface

Contributions

- Properly assess and select groundwater sources by understanding aquifer susceptibility and vulnerability to arsenic contamination

- Identify high-quality groundwater supplies in semi-arid climates, where there is generally limited supply of surface-water resources in the region

- Estimate the potential of As and other heavy metals to mobilize from sediments through geochemical modeling

- Avoid adverse health effects by selecting low-risk groundwater sources where arsenic release is not likely to occur

- Understand other oxyanions release, like selenium, phosphorus, and molybdenum in similar geological environments since the processes controlling arsenic solubilization may be similar

Key References

[1] Sanderson, I. D., and Lowe, M. (2002). *Ground water sensitivity and vulnerability to pesticides, Cache Valley, Cache County, Utah*, Utah Geological Survey.
[2] Anning, D. W., Paul, A. P., McKinney, T. S., Huntington, J. M., Bexfield, L. M., and Thiros, S. A. (2012). "Predicted Nitrate and Arsenic Concentrations in Basin-Fill Aquifers of the Southwestern United States."
[3] Huang, J.H., Kretzschmar, R., 2010. Sequential Extraction Method for Speciation of Arsenate and Arsenite in Mineral Soils. Analytical Chemistry 82, 5534-5540
[4] Keon, N., Swartz, C., Brabander, D., Harvey, C., and Hemond, H. (2001). "Validation of an arsenic sequential extraction method for evaluating mobility in sediments." *Environmental Science & Technology*, 35(13), 2778-2784.

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