Natural Attenuation of Aqueous Arsenic in Weathered Marine Shale

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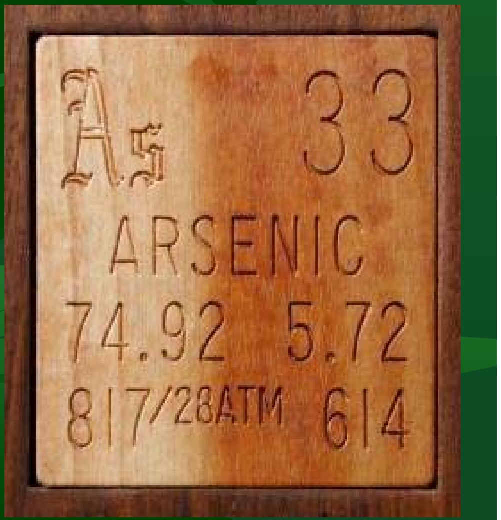

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Presentation Overview

- Introduction/Background
- Objectives of the Study
- Materials and Methods
- Results and Discussion
- Summary/Conclusion

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Background - Arsenic

- Arsenic occurs naturally in geological materials, soils and water
- The average amount of arsenic in the earth's crust is approximately 1.8 mg As/kg crust
- Background concentrations in soil widely vary, with Alberta soils averaging approximately 5 mg As/kg soil

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Background - Arsenic

- Aqueous arsenic exists as a negatively charged oxyanion

- The form depends on the pH and Eh of the system

  - $H_2AsO_4^-$ is the form from pH 0 to 9
  - $HAsO_4^{-2}$ is the form from pH 5 to 14

- Under oxidizing conditions, arsenic exists in the As^{+5} valence state or arsenate

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Background - Arsenic

- Shale of marine origin often contains elevated levels of arsenic concentrated in iron sulfide minerals
  - pyrite FeS_2
  - arsenopyrite FeAsS
- Oxidative weathering breaks down these minerals releasing arsenic into the surrounding pore water

$$4FeAsS(s)+13O_2+6H_2O \rightarrow 4H_3AsO_4(aq) + 4Fe^{+2} + 4SO_4^{-2}$$

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Background – Arsenic in Shale

- Marine shale underlies large parts of the province at varying depths covered in most cases by a thick mantle of glaciofluvial and glaciolacustrine deposits
- Acid sulfate soils are derived from and develop on these marine shale deposits
- The "Boundary Soil" Series found in NW Alberta is an example of one of these acid sulfate soils

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Background – Arsenic in Shale

- In areas where the shale is near the surface it is often covered by and mixed with a thin glacial veneer forming a shale/till mixture

- In Alberta, aquifers composed of marine shale supply water (and potentially arsenic) for human and animal consumption to many rural residents

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Background – Health Risks

- Arsenic accumulates in the body because it is readily absorbed and is slowly eliminated
- A dose as small as 300 mg can be lethal
- Chronic ingestion can cause skin diseases, anemia, diabetes, nerve damage, and digestive disorders
- Approximately 112 million people in Asia and 300,000 people in the U.S drink water with arsenic concentrations above guidelines

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Background – Health Risks

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Goals of the Study

- Determine the equilibrium pore water chemistry, including equilibrium arsenic concentrations, in the weathered marine shale
- Determine the solubility controlling reaction responsible for limiting aqueous arsenic
- Determine how the addition of till and the resulting increase in pH changes the equilibrium pore water chemistry and solubility controlling reactions

Material and Methods

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Material and Methods

Equilibration experiment- marine shale:

- Each sample consisted of 65 g of soil and 130 ml of water (1:2 soil/water ratio)
- Samples were equilibrated for a fixed time and then sacrificed
- Equilibration times were 1, 2, 4, 8, 16, 32, 48, 64, and 128 days
- At the end of each equilibration period samples were analyzed, for pH, EC, Eh (Redox), cations, and anions

Material and Methods

Marine shale and till equilibration experiment:

- This equilibration was run the exact same way as the shale equilibration. The only difference was in the initial starting material
- The samples consisted of 80% marine shale, 20% till, and 130 ml of water

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Material and Methods

Spiking experiments:

- All arsenic spiking was done on the removed solution portion of the samples (shale and shale/till) after varying incubation times
- Arsenic spikes were added in the form of Sodium Hydrogenarsenate Heptahydrate ($Na_2HAsO_4 * 7H_2O$)
- The concentration of aqueous arsenic was measured before and after spiking

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Results and Discussion

- Partial list of the routine chemical/mineral characteristics for the marine shale

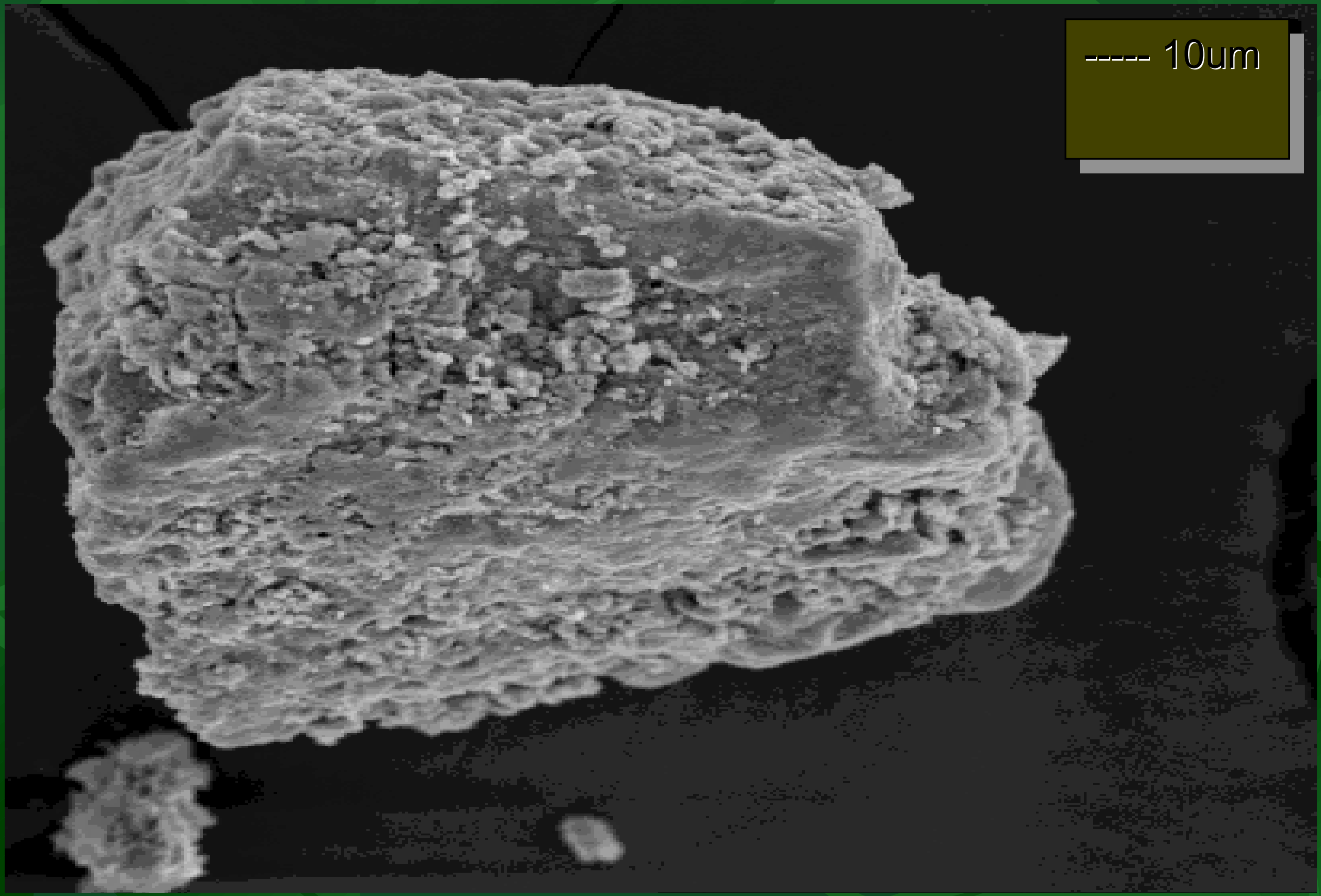
pH	2.63
E.C	2.09 ds/m
Redox	802 mV
Moisture content	26.16%
Clay content	60.10%
Silt content	39.20%
Sand content	0.33%

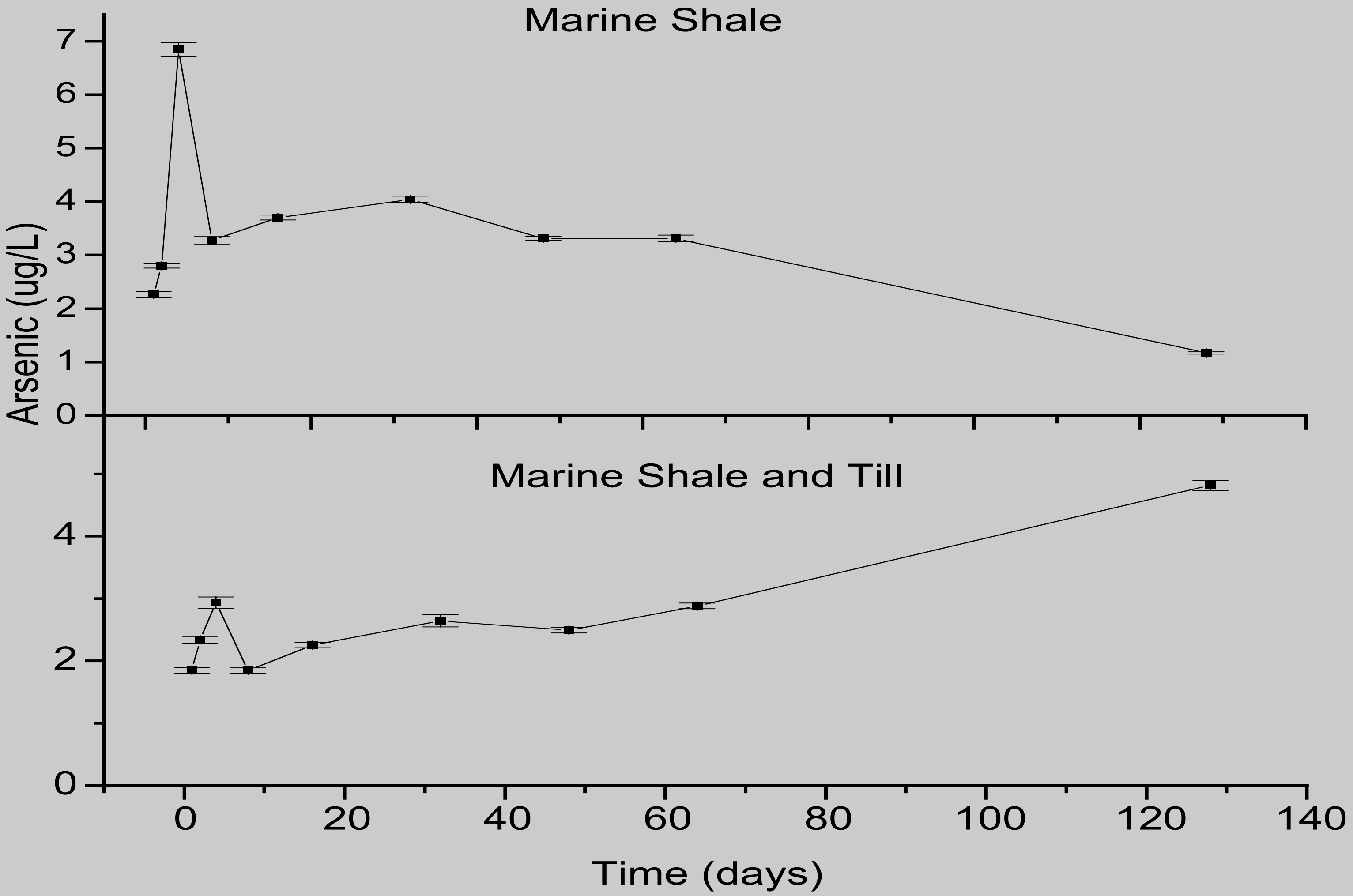
Results and Discussion

- Initial solid phase arsenic concentrations in the marine shale

Fraction	Concentration (mg As/kg soil)
Bulk Sample	34.8
Clay	34.4
Silt	21.8
Sand	382
Iron oxide	305

SEM Micrograph of Weathered Iron Sulfide Particle





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Results and Discussion

- The next step was to experimentally determine if the precipitation of an arsenic solid phase compound is controlling aqueous arsenic concentrations
- A spiking experiment was performed on shale and the shale/till systems

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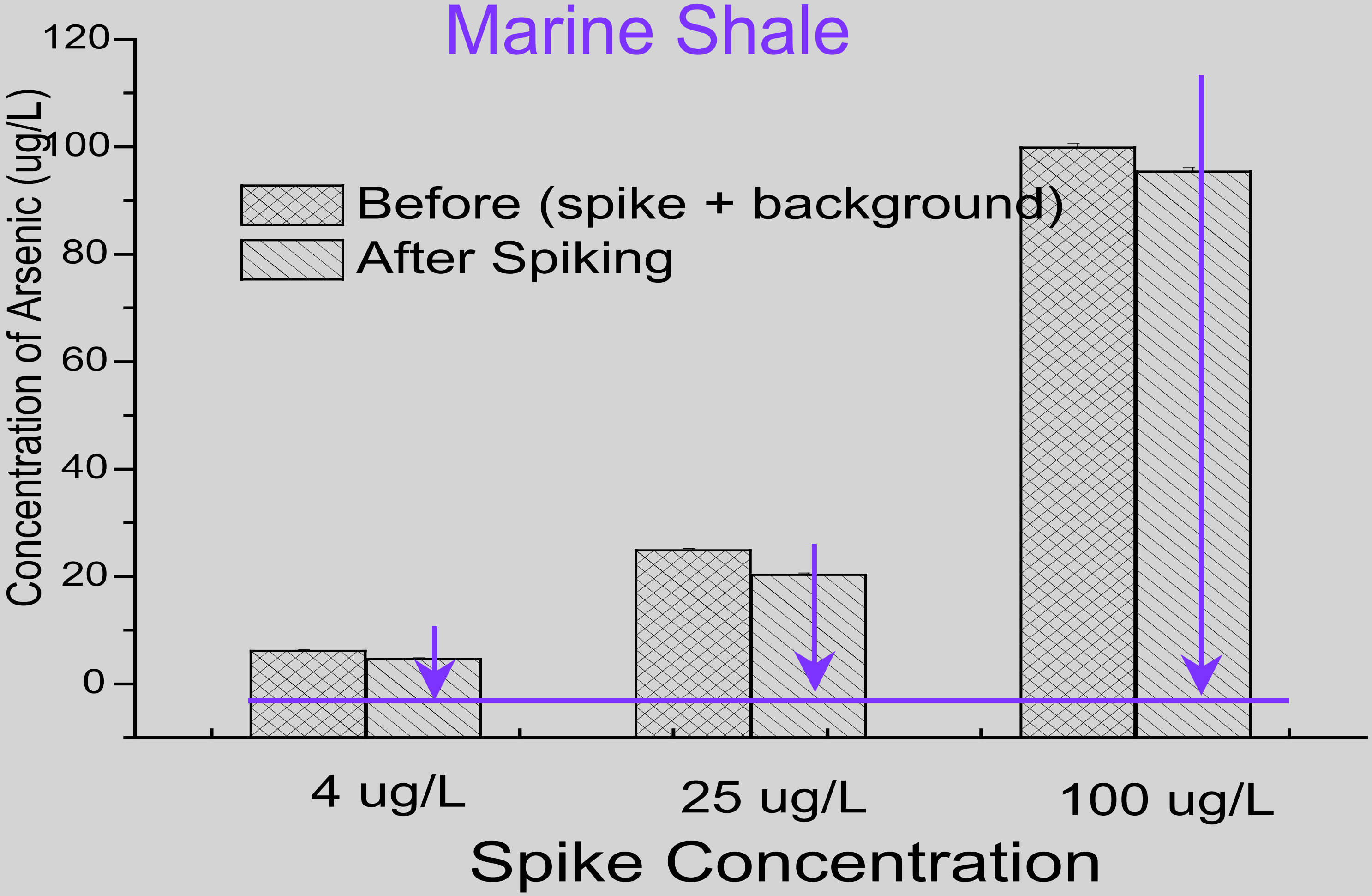
Marine Shale



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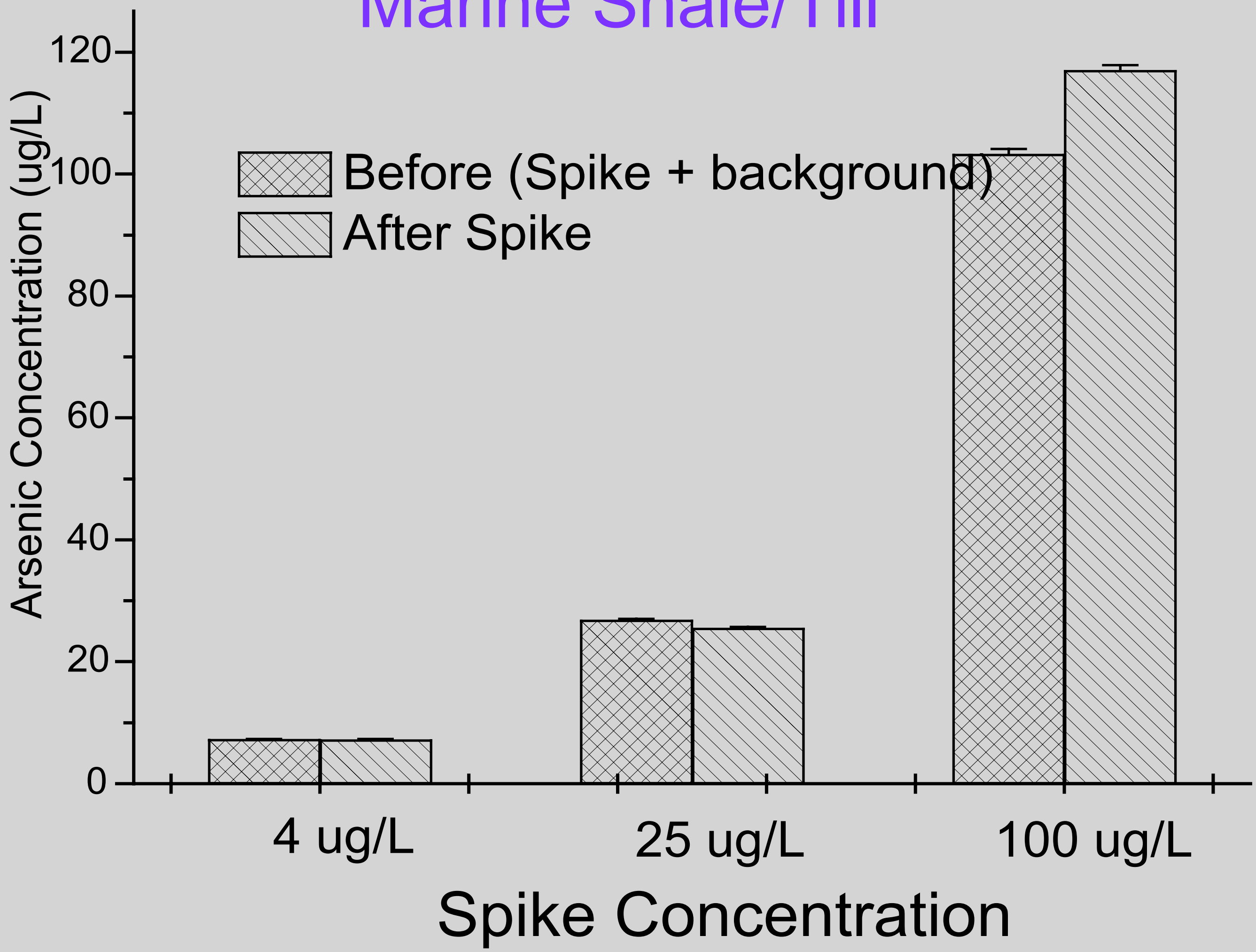
Marine Shale/Till



Summary / Conclusion

- The concentration of solution arsenic released from the marine shale at the end of the 4-month equilibration period was 1.2 μg/L. The predicted value once the system reaches equilibrium is between 1.2 and 0.6μg/L.
- In the shale/till system the value was 4.8 μg/L at the end of the 4-months and between 4.8 and 9.4 μg/L at equilibrium.

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Summary / Conclusion

- The amount of arsenic released from the shale and shale/till systems is low, and should not contribute to the build up of arsenic in the surrounding surface or groundwater provided the system remains oxidized

- More arsenic was released from the higher pH shale/till mixture compared to the shale system alone

- The arsenic spiking experiment indicated that the precipitation of an arsenic solid phase is not occurring and controlling or limiting aqueous arsenic concentrations

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