Using bromide tracer to measure uranium diffusivity in ground water sediments

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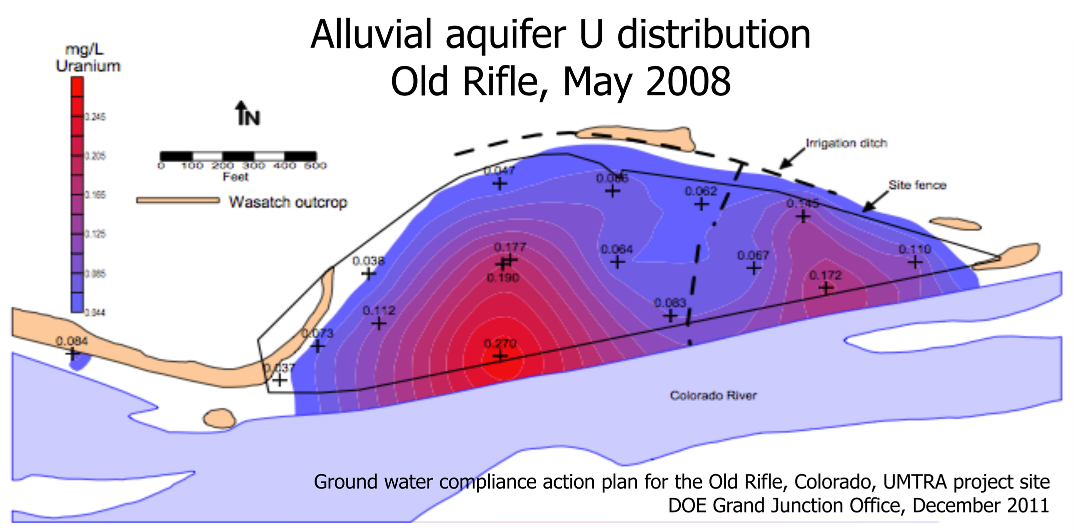
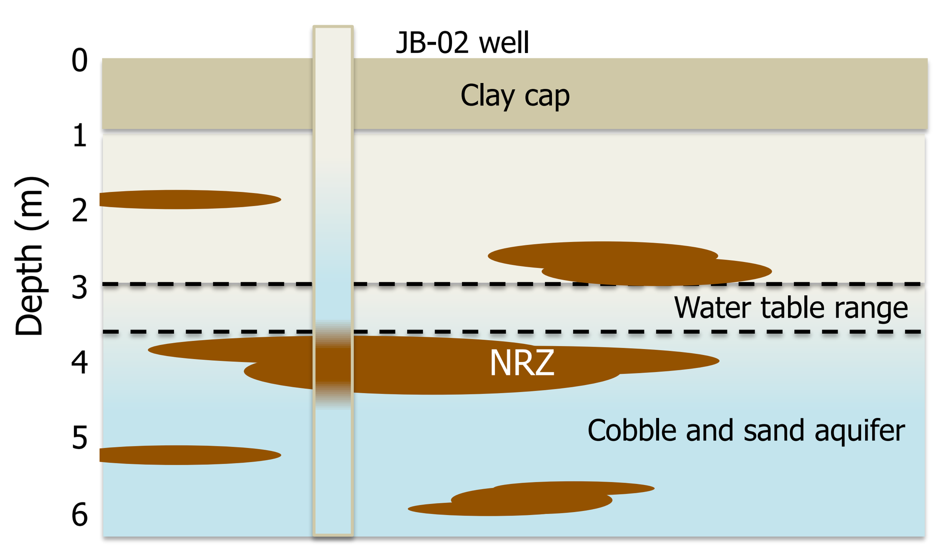


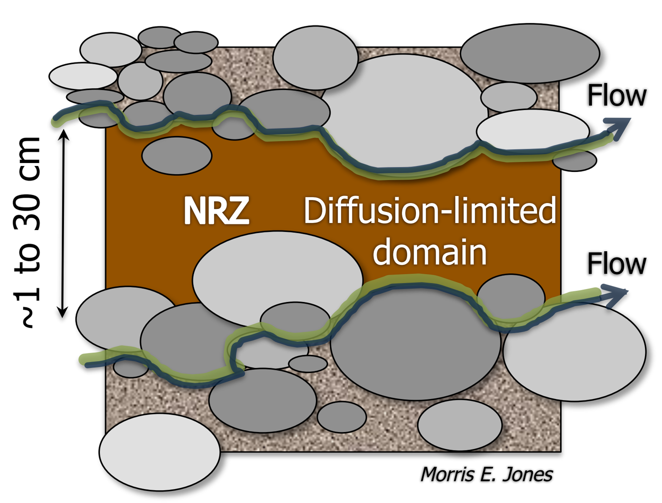
Background

- The Old Rifle site in western CO covers an area of 52.6 m^2 and has over 129 million liters of uranium-contaminated groundwater
- Naturally reduced zones (NRZs) are thin pockets of silt-, clay-, and organic-rich sediments that contain reduced uranium
- NRZs can act as both sinks and sources, contribute to plume persistence, and appear to be diffusion-limited controlled

Objective

- Although it has been stated that NRZs are diffusion-limited controlled, those numbers have not been expressed explicitly
- The objective of this study is to better understand the diffusivity of U by using bromide tracer to calculate the net flux (J), effective diffusivity (D*) and tortuosity effect (m).

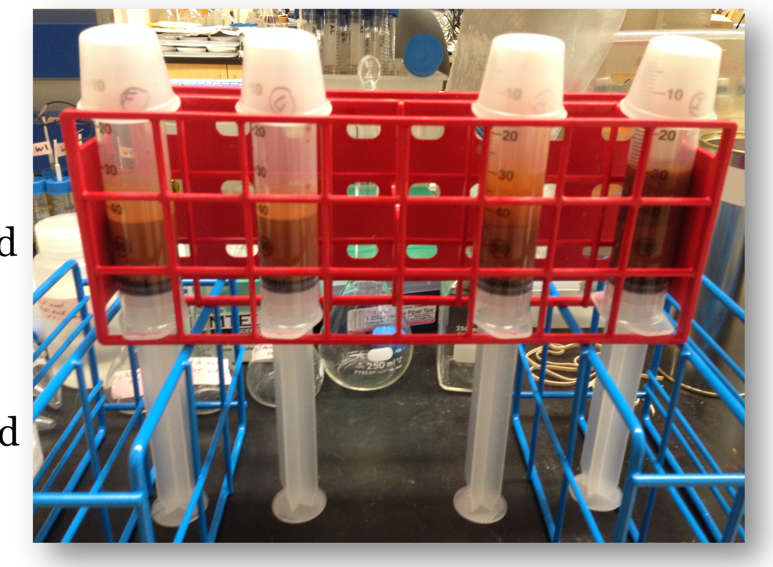


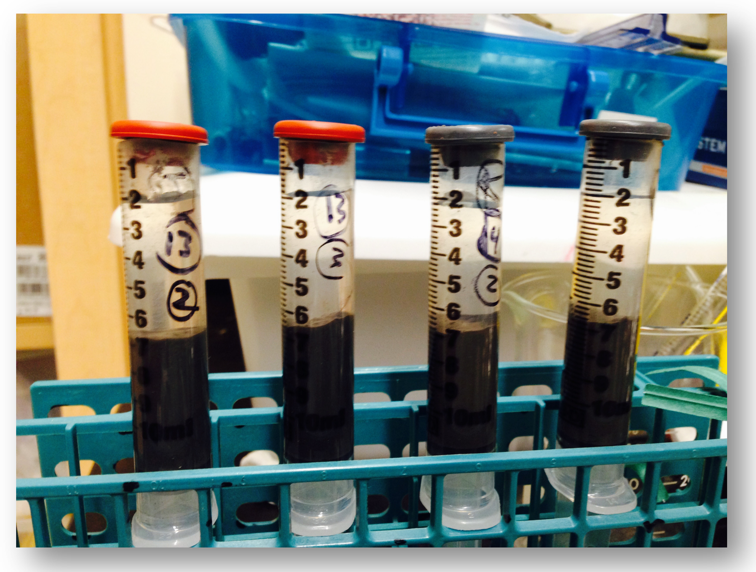


Methods

I. Ferrihydrite coated sand

1. Different grain sizes and porosity
2. 60 mL syringe tubes, 15 mL sand saturated with 800 ppm NaCl, and reservoir of 400 ppm NaCl and 400 ppm NaBr solution.
3. 140 hours diffusion, two 0.5 mL samples per day.
4. Sediments sectioned and water extracted at 0.6 g sediment per 1 mL water, one hour in end-over-end shaker, centrifuged at 3500 rpm for 10 minutes.
5. Br concentration analyzed using inductively coupled plasma mass spectroscopy (ICP-MS)





II. JB-02 well sediments

1. Middle of the NRZ (4.0 m, 41% porosity) and bottom edge of the NRZ (4.4 m, 37% porosity)
2. 10 mL syringe tubes, 4 mL water-saturated JB-02 sediments, reservoir of 6 mL of 1000 ppm NaBr and 1000 ppm NaCl solution
3. 7-9 day diffusion, two 0.25 mL samples per day
4. Sediments sectioned and water extracted at 1.5 g sediment to 5 mL water, orbit shaker for one hour, centrifuged at 3500 rpm for 10 minutes.
5. Br concentration analyzed using ICP-MS

Calculations

$$J = \frac{\partial C/\partial t}{A}$$

Equation 1, where net flux (J) equals the change in concentration (dC) over the change in time (dt) divided by the reservoir-surface interface area

$$D^* = -J \bullet \partial C/\partial x$$

Equation 2 is a rearrangement of Fick's First Law, where the effective diffusivity (D) equals negative net flux (J) multiplied by the change in concentration (dC) over the distance from the reservoir-surface interface*

$$D^*_{Br} = D_{Br}\phi^m$$

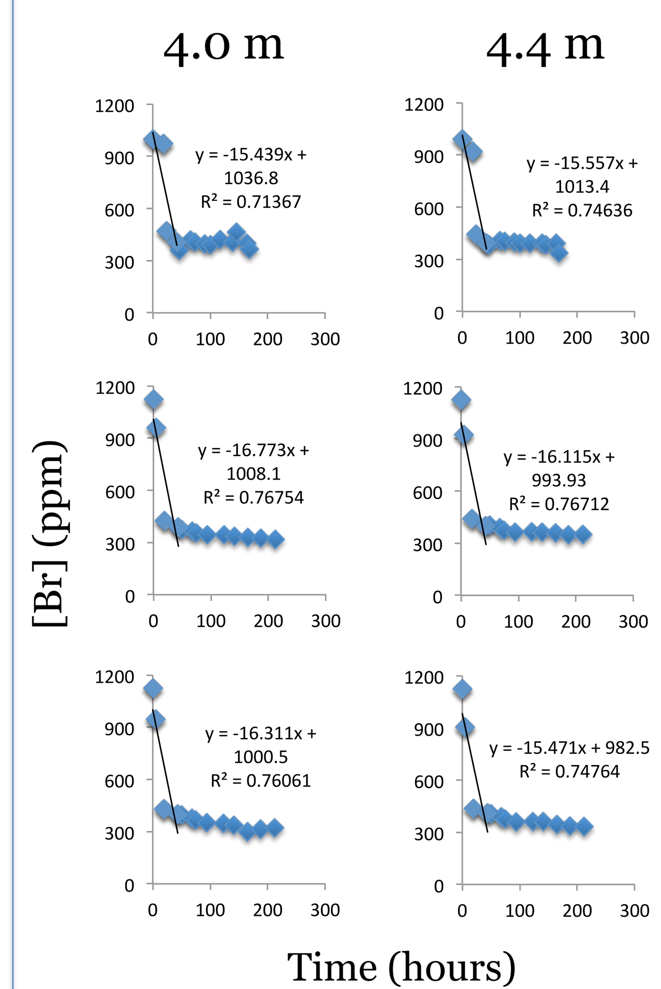
Equation 3, where the effective diffusivity of bromine ($D_{Br}{}^*$) equals the literature diffusivity value of bromine multiplied by the porosity (Φ) raised to a tortuosity factor (m)

Results

I. Ferrihydrite coated sand

Grain size, Porosity	J x 10^{-7} (ug/s/cm²)	D* x 10^{-9} (cm²/s)	Tortuosity effect	Average tortuosity
74 um, 42%	2.61	7.05	2.05	1.76 ± 0.41
74 um, 42%	3.39	4.24	1.47	
104 um, 38%	2.95	7.57	1.93	1.60 ± 0.46
104 um, 38%	3.37	4.05	1.28	
149 um, 39%	2.73	8.26	2.08	1.88 ± 0.29
149 um, 39%	3.75	5.60	1.67	
250 um, 37%	2.82	8.30	1.95	1.69 ± 0.37
250 um*, 37%	10.2	4.92	1.43	

*Second trial of 250 um, 37% porosity sand had an initial reservoir concentration 1000 ppm NaBr rather than 400 ppm

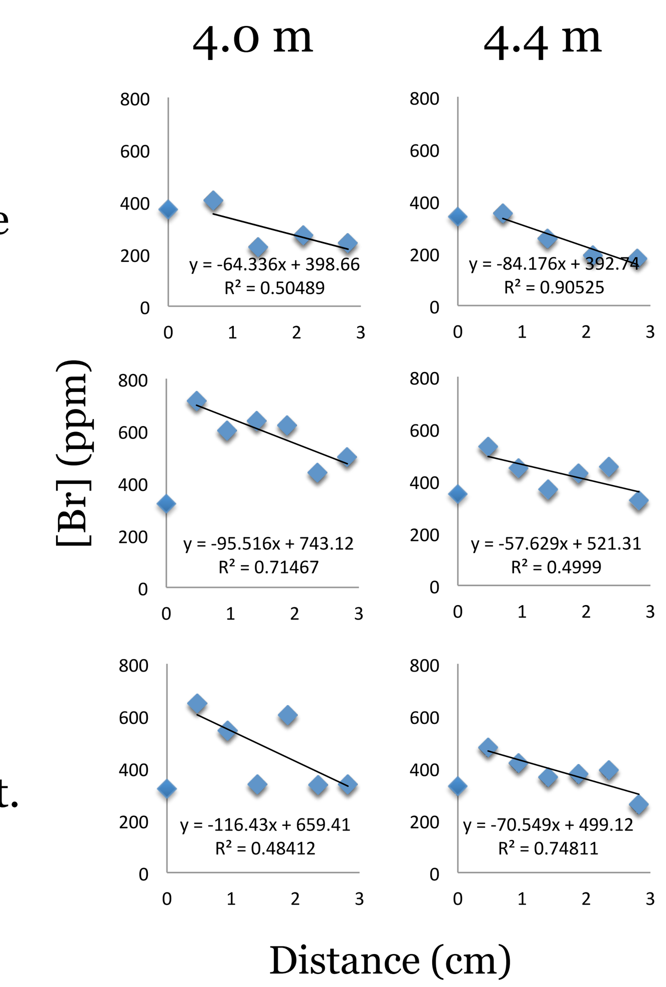


II. JB-02

The graphs on the left show the change in concentration over time (dC/dt).

The graphs on the right show the change in concentration over distance (dC/dx).

Together these values help us determine net flux, effective diffusion and the tortuosity effect.



Br values

Depth, Porosity	J x 10^{-7} (ug/s/cm²)	D* x 10^{-9} (cm²/s)	Tortuosity effect
4.0 m, 41%	70.5 ± 3.1	80.8 ± 2.2	4.76 ± 0.31
4.4 m, 37%	60.8 ± 1.2	88.1 ± 1.8	4.28 ± 0.21

U estimates

U net flux is 1.3 x 10^{-7} ug/s/cm².
U diffusivity is 37.2 x 10^{-12} cm²/s in the middle of the NRZ and 43.1 x 10^{-12} cm²/s at the bottom edge of the NRZ.

Conclusions

- Porosity is dependent on the packing of sediments and is best measured on undisturbed sediments, preferably fresh core samples at field sites. Accurate measurements of porosity are important for determining the tortuosity effect (equation 3).
- There is no significant difference in tortuosity between the four sands tested, nor is there significant difference in tortuosity between the two depths of JB-02 well sediments tested, which were measured to be 4.76 in the middle of the NRZ and 4.28 for the bottom edge of the NRZ.
- There is however a significant difference in the net flux of Br between the two depths of JB-02 well sediments ($P = 0.05$), which we then used to estimate U diffusivity at 37.2 x 10^{-12} cm²/s in the middle of the NRZ and 43.1 x 10^{-12} cm²/s at the bottom edge of the NRZ.

Further studies

- How does the diffusivity compare at other DOE legacy sites such as Riverton, Wyoming and Shiprock, New Mexico?
- How can we use this data in crunch-flow models?

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