



***A Simple Diffusion Sampler for Pore-
Water Hydrogen as a Tool for
Understanding Redox Conditions in
Saturated Sediment***

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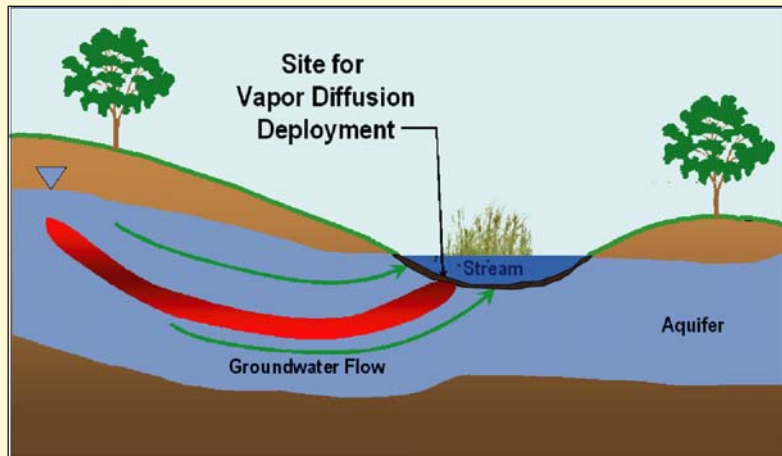
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When determining fluxes across the ground-water/surface-water boundary, determination of concentration is important.

This talk concentrates on determining solute concentrations as a component for determining fluxes.

VOCs from ground water transported through bottom sediment



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Contaminated GW discharging to a stream passes through bottom sediment that often are sites of substantial contaminant degradation.

PEEPERS



- ★ Hesslein, R.H., 1976, *Limnology and Oceanography*, [Membrane: polysulfone. Parameters: inorganics.
- ★ Mayer, L.M., 1976, *Limnology and Oceanography*, [Membrane: Not specified. Parameters: inorganics.

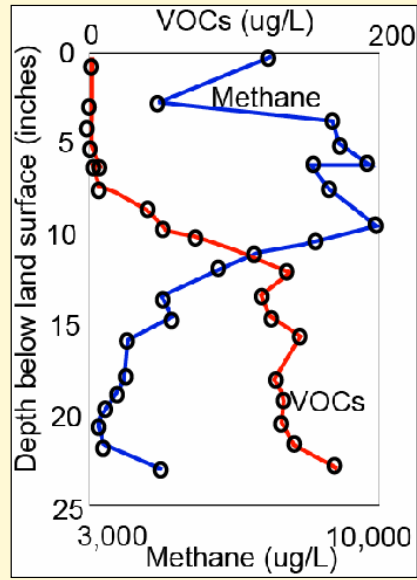
•Rigid body with openings that are typically hold about 1 to 20 mL of water.



•Originally used to examine inorganics in bottom sediment in limnology studies.

CVOCs and methane in streambed peepers

(modified from Lorah et al., 1997)



Degradation of CVOCs under different TEAPs (Bradley, 2003)



Reduct.	O2 Red.	Mn(IV) Red.	Fe(III) Red.	SO4 Red.	Methano-genesis
TCE	No	Fair	Good	Good	Excellent
DCE	Poor	Poor	Poor	Fair	Good
VC	Poor	Poor	Poor	Fair	Fair

Oxidation	O2 Red.	Mn(IV) Red.	Fe(III) Red.	SO4 Red.	Methano-genesis
TCE	A CoM	No	No	No	No
DCE	Excellent	Good	Poor	Poor	Poor
VC	Excellent	Excellent	Excellent	Good	H. acid red.

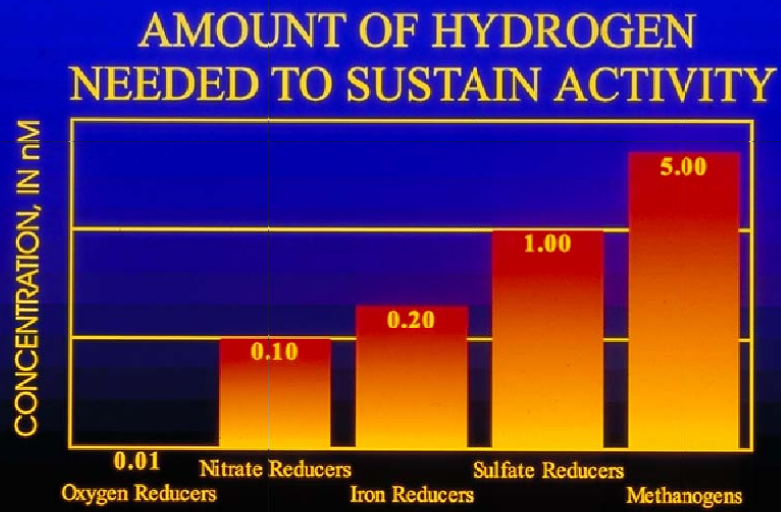
Importance of Terminal Electron Accepting Processes (TEAPS)



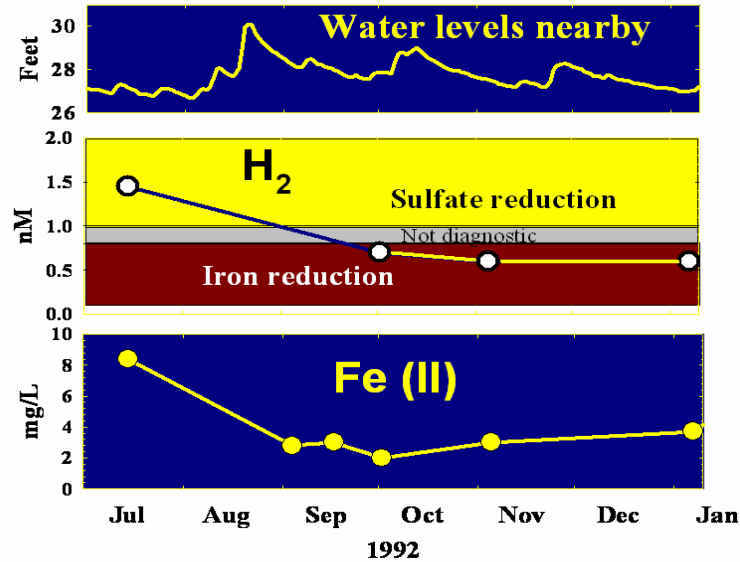
- ★ TEAPS influence CVOC degradation rates
- ★ TEAPS influence MTBE degradation rates:
SO₄, Fe(II), Mn(IV) < NO₃ < O₂
- ★ Nitrate concs. in a stream can be influenced by daily, storm-event, and seasonal variations in TEAP conditions (Grimaldi et al., 2004).
- ★ TEAP zones can shift spatially and temporally depending on seasonal and other influences.

Competition among microbes controls the redox.

Order of microbial competition: O₂>Fe(III)>SO₄>CH₄



Microbial shift from sulfate reduction to iron reduction



8

8

Here is an example of a shifting TEAP. The data show a shift from sulfate reduction to iron reduction in response to FeIII precipitation and initiation of iron reduction. We would expect the same near the GWSWI from changes in stream stage levels.

But TEAPs are not always easy to identify



Presence of oxygen means oxygenated conditions. But:

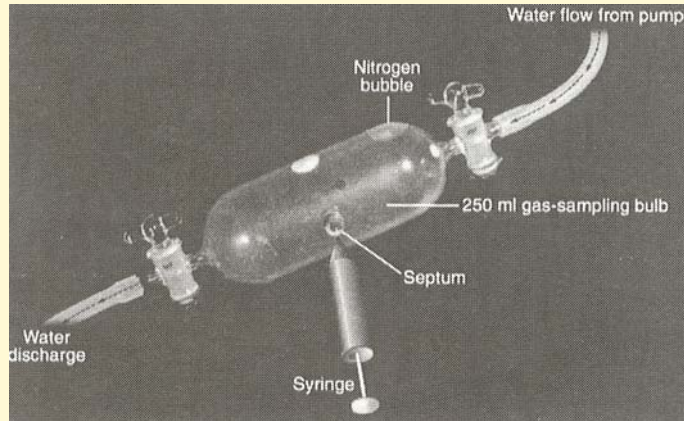
- **Presence of dissolved Fe(II) may not mean iron reduction. Fe(II) could have been transported or the Fe(III) may be depleted.**
- **Presence of sulfide and methane not diagnostic of sulfate reduction or methanogenesis because of transport.**
- **Presence of sulfate does not mean sulfate reduction because when iron(III) is present, iron reducers can outcompete sulfate reducers for available substrate**

***Dissolved hydrogen in pore water as
an indicator of the terminal electron
accepting process***



Predominant TEAP	H₂ concentration (nM)
Nitrate reduction	<0.1
Mn reduction	0.1-0.2
Fe(III) reduction	0.1-0.8
Sulfate reduction	1-4
Methanogenesis	5-30

The commonly used bubble-strip method for H₂ is not usually appropriate for GWSWI



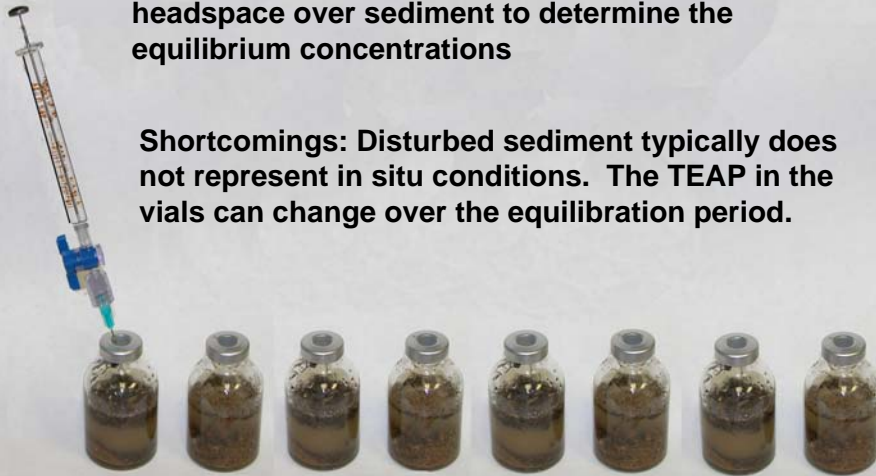
**Chapelle, Vroblesky, Woodward, and Lovley,
1997, ES&T, v. 31, p. 2873-2877**

Typical determination of H₂ in stream sediment



Method: Observe H₂ changes over time in headspace over sediment to determine the equilibrium concentrations

Shortcomings: Disturbed sediment typically does not represent in situ conditions. The TEAP in the vials can change over the equilibration period.



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12

Previous H₂ Samplers



*(Chapelle et al.,
ES&T, 1997)*



*(Spalding and Watson,
ES&T, 2006)*



*(Vroblesky et al.,
USGS WRI 01-4242, 2001)*

13

13

H₂ Syringe Sampler ***(Vroblesky et al., in press, Ground Water)***



A. Plunger; not deployed



B. Syringe and stopcock



C. Deployed syringe in two LDPE sleeves

14

14

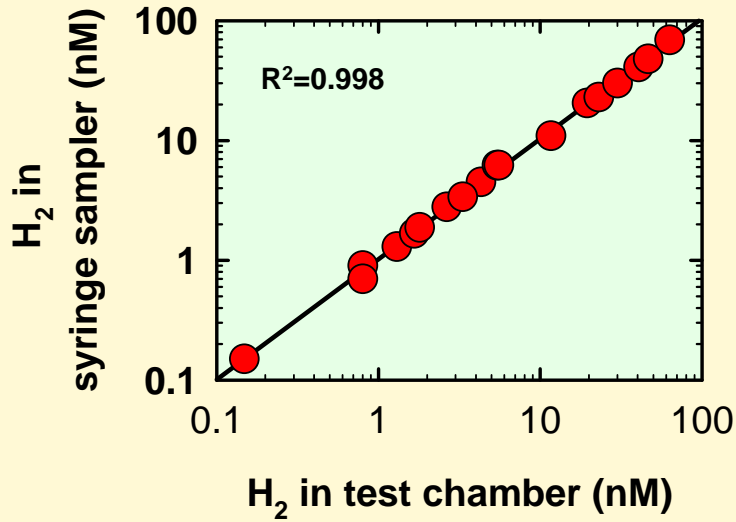
Good to depths up to 17-22 ft below the water surface

Inject 15 mL of gas into a sealed serum vial filled with nitrogen

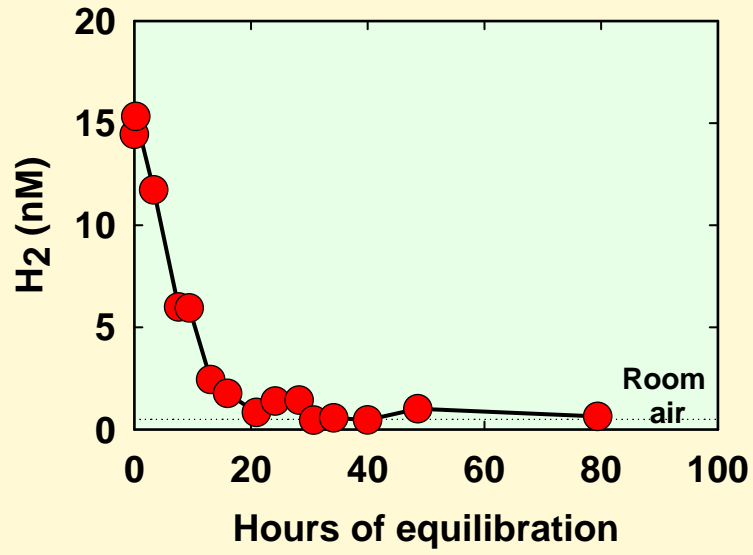


(Vroblesky et al., in press, Ground Water)

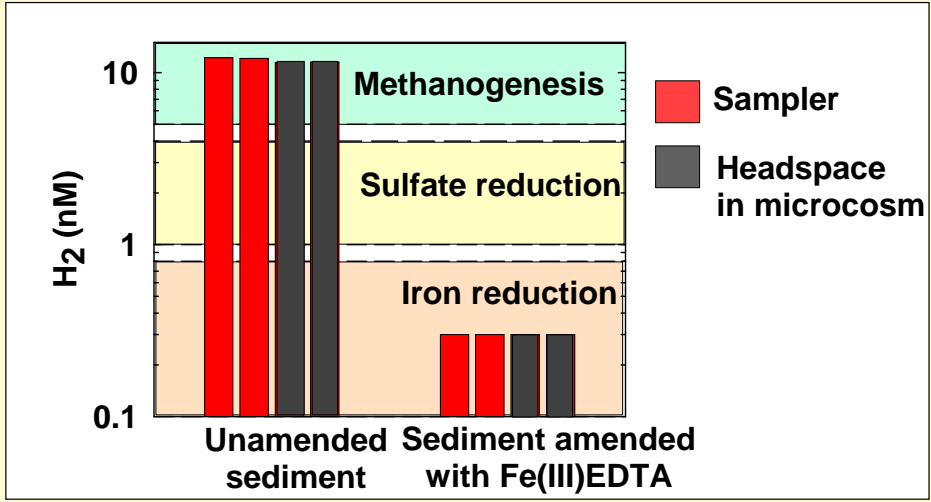
Comparison of passive H_2 samplers to ambient H_2

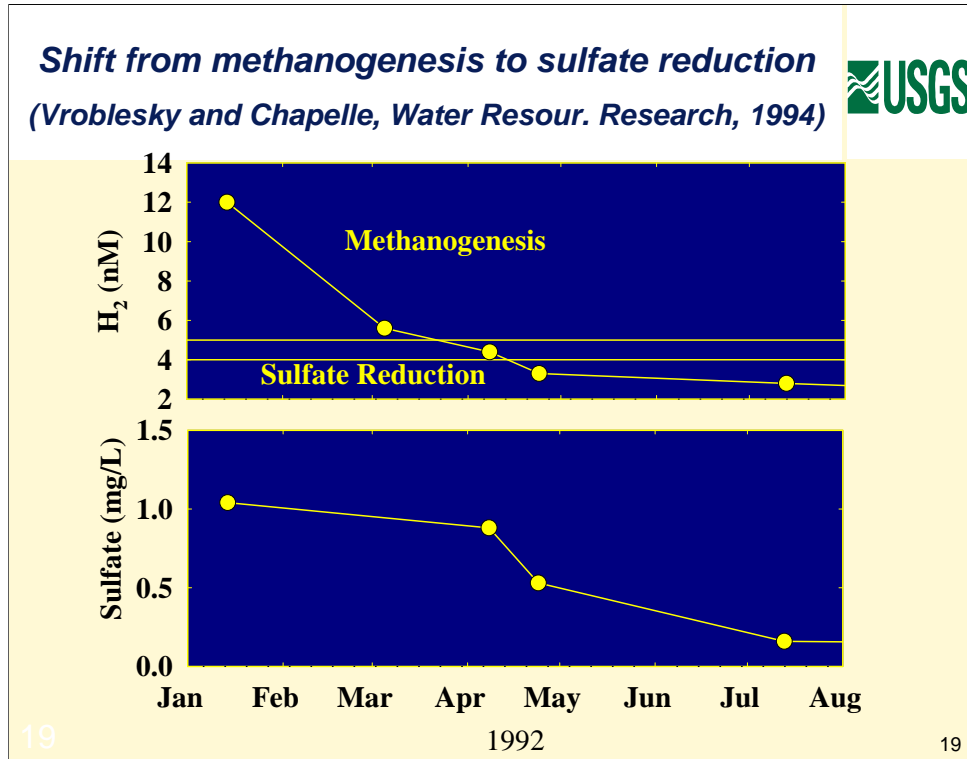


Equilibration of 20-mL H₂ syringe samplers



Comparison of H₂ in microcosms and passive samplers





Field test of the diffusion sampler in a swamp took advantage of the fact that methanogens can be outcompeted by sulfate reducers when sulfate is present.

Syringe sampler attached to gypsum

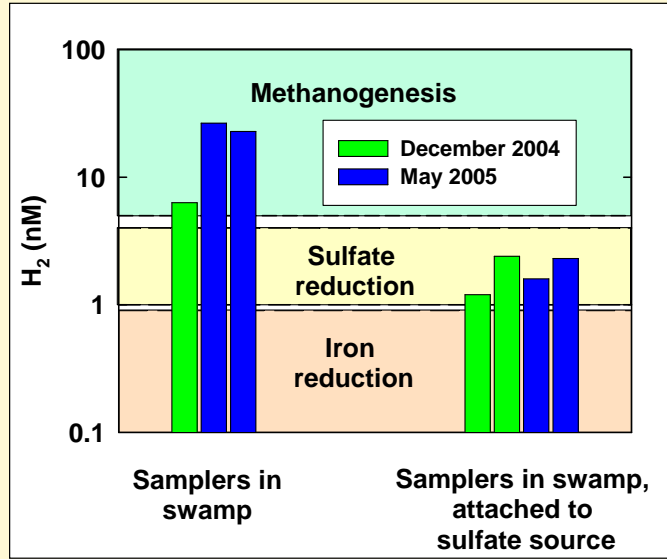


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This shows a pair of hydrogen diffusion samplers strapped to a cage containing gypsum, to provide a sulfate source in the methanogenic swamp mud.

H₂ in passive samplers deployed in swamp



Robust H₂ Diffusion Sampler for Deep Environments



A. Exploded view of bag-less syringe H₂ sampler



B. Assembled bag-less syringe H₂ sampler

Tested down to about 100 ft below water.

Comparison of syringe H₂ sample and bubble-strip sample



[m, meters; nM, nanomoles per liter; ns, not sampled]

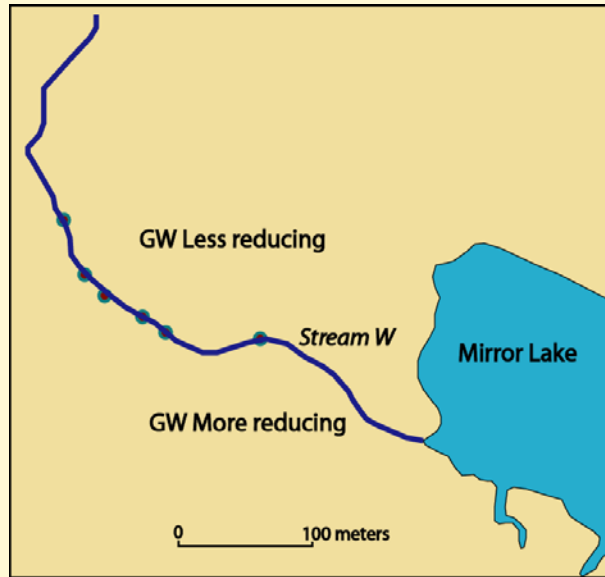
Sampled Depth (m)	H ₂ concentration (nM)	
	Syringe Sampler	Bubble Strip
15.5 (unpacked)	0.86±0.27	1.1±0.0
18 (packed interval)	1.0±0.45	ns
21 (packed interval)	0.70±0.25	ns
24 (packed interval)	0.93±0.12	ns
46.6 (packed interval)	ns	1.7±0.1

23

23

These are results for the unbagged syringe sampler

Flow-through stream, Mirror Lake, NH

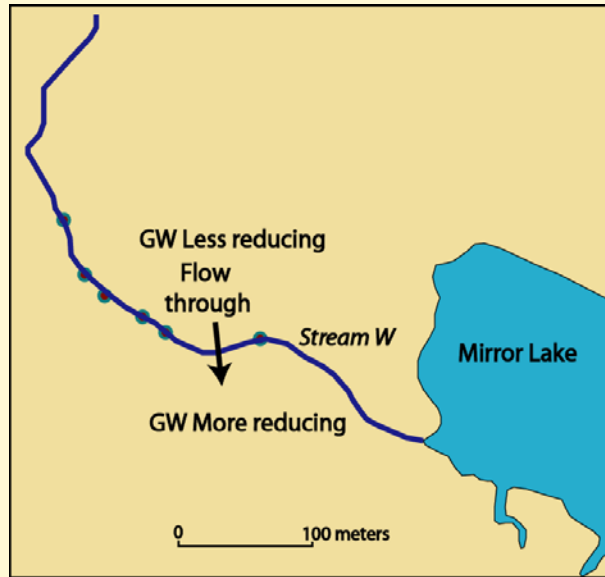


24

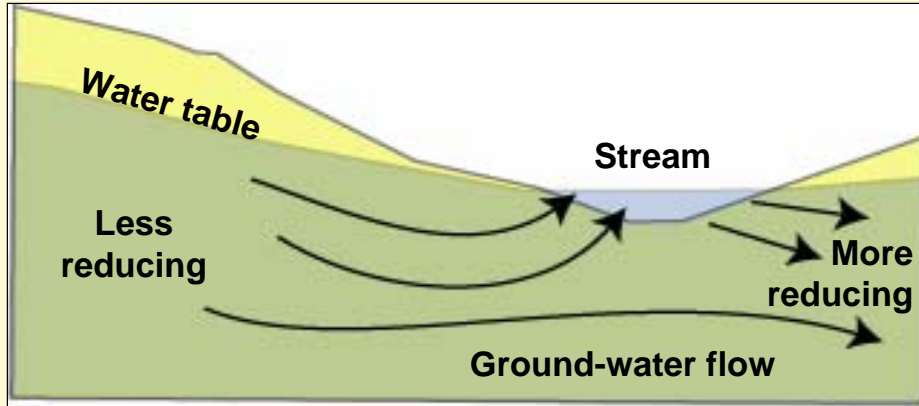
24

New Hampshire

Flow-through stream, Mirror Lake, NH

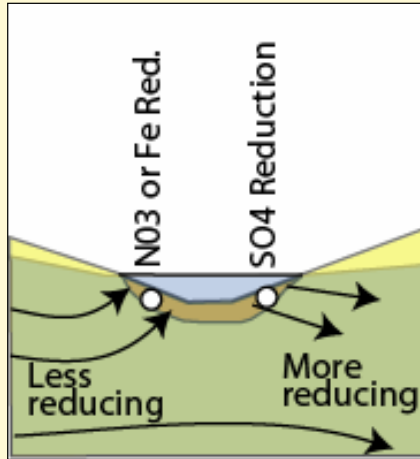


Flow-through stream, Mirror Lake, NH

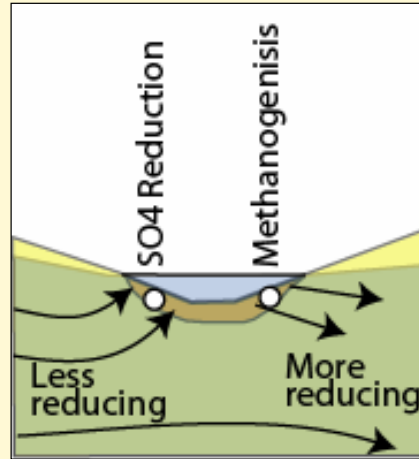


Fractured rock and saprolite, so little or no TOC

Data from streambed H_2 samplers
(Winter et al., in press)



Transect 2



Transect 3

27

27

SO_4 in the aquifer is 10-30 mg/L in most places, and is locally absent. Most places there is no nitrate, so the second transect probably is Fe reduction

SUMMARY



- ★ **Hydrogen is a useful parameter for examining solute fate at the GWSWI to better understand flux.**
- ★ **Diffusion samplers can be used as a simple tool to obtain high-resolution redox data on concentrations of solutes at the GWSWI.**
- ★ **Redox information is important because TEAPS can influence contaminant degradation rates and contaminant flux across the GWSW interface.**