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

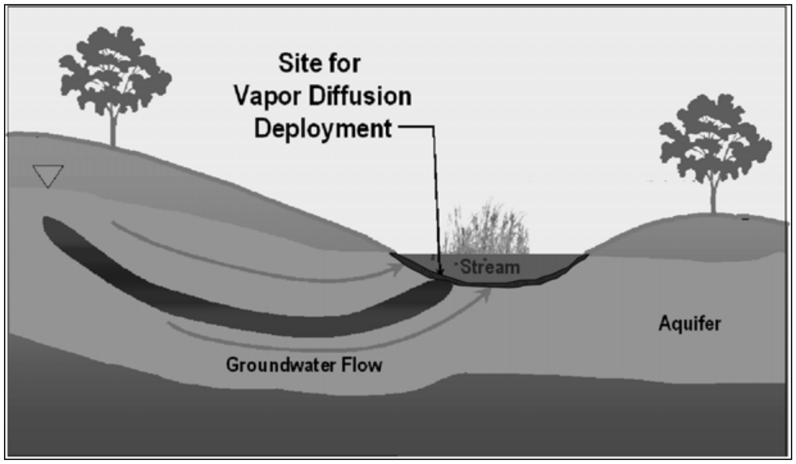
By Don A. Vroblesky
U.S. Geological Survey
Columbia, S.C.
(vroblesk@usgs.gov)

1 1

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



2

2

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.

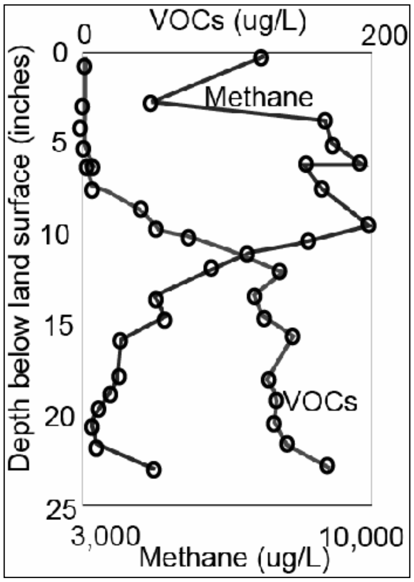
•Rigid body with openings that are typically hold about 1 to 20 mL of water.

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

3

3

CVOCs and methane in streambed peepers *(modified from Lorah et al., 1997)*



4

4

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.

5

Importance of Terminal Electron Accepting Processes (TEAPS)

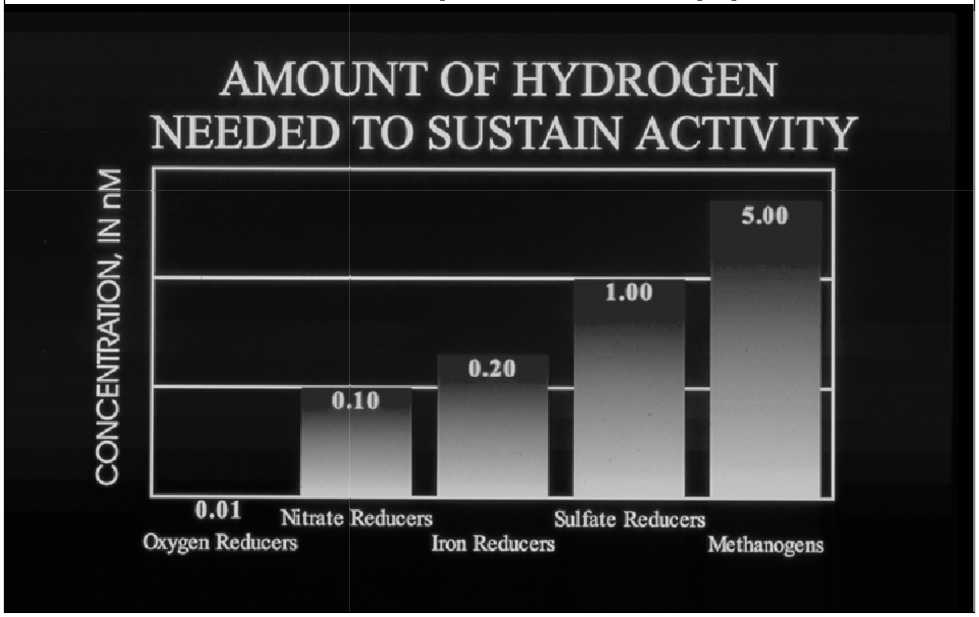
- TEAPS influence CVOC degradation rates
- TEAPS influence MTBE degradation rates: SO4, Fe(II), Mn(IV)<NO3<O2
- Nitrate concs. in a stream can be influenced by daily, storm-event, and seasonal variations in TEAP conditions (Grimaldi et al., 2004).
- TEAP zones can shift spatially and temporally depending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

6

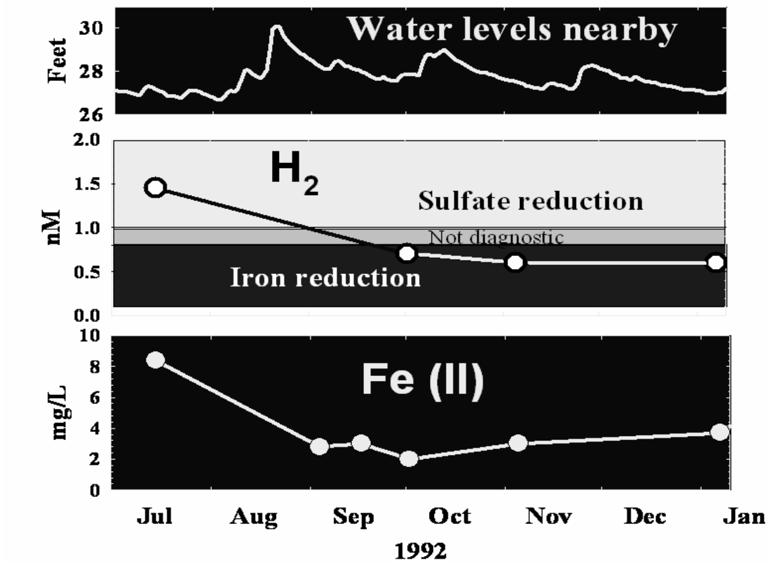
6

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

9

9

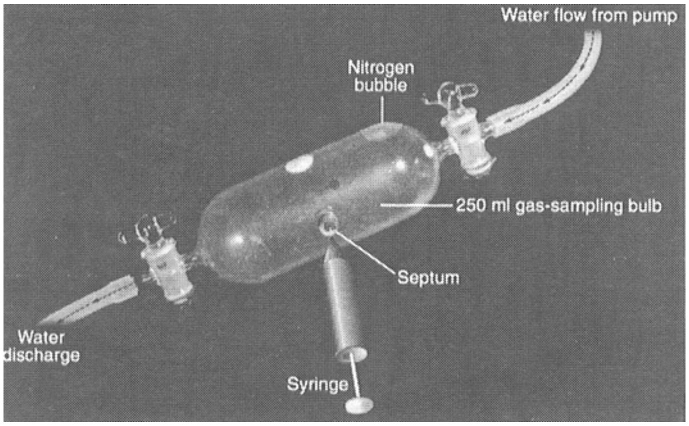
Dissolved hydrogen in pore water as an indicator of the terminal electron accepting process

Predominant TEAP	H_2 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

10

10

The commonly used bubble-strip method for H_2 is not usually appropriate for GWSWI



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

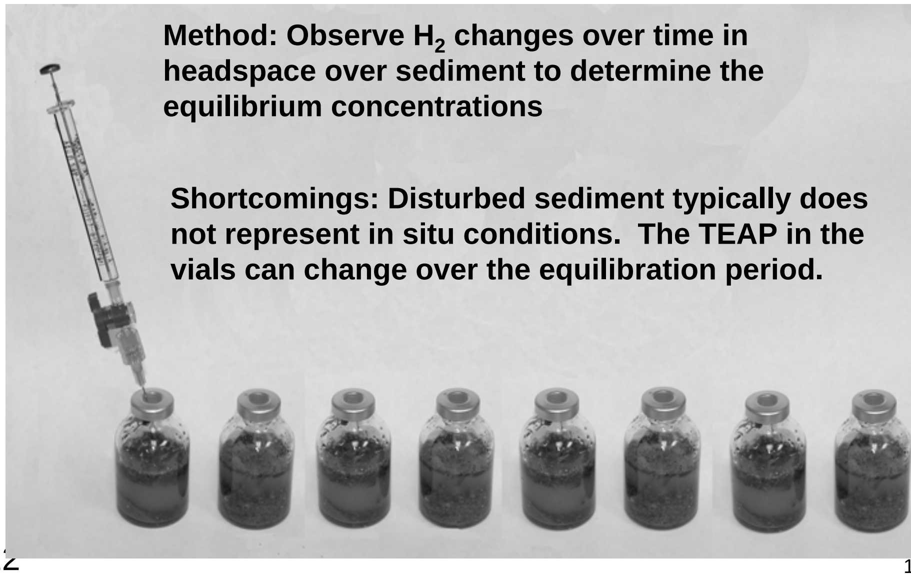
11

11

Typical determination of H_2 in stream sediment

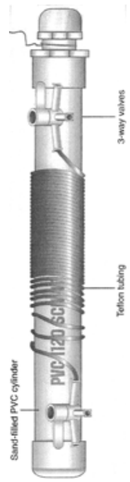
Method: Observe H_2 changes over time in headspace over sediment to determine the equilibrium concentrations

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



12

Previous H_2 Samplers



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

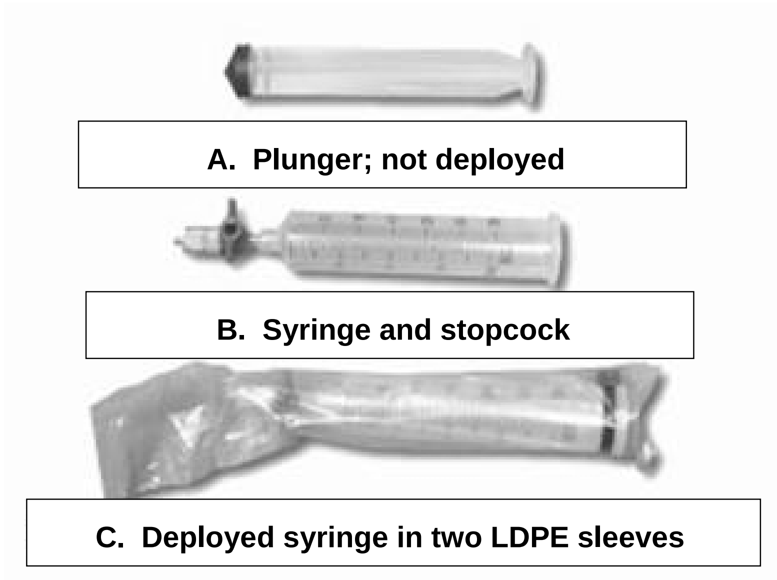
(Spalding and Watson, ES&T, 2006)

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

13 13

H_2 Syringe Sampler
(Vroblesky et al., in press, Ground Water)

USGS

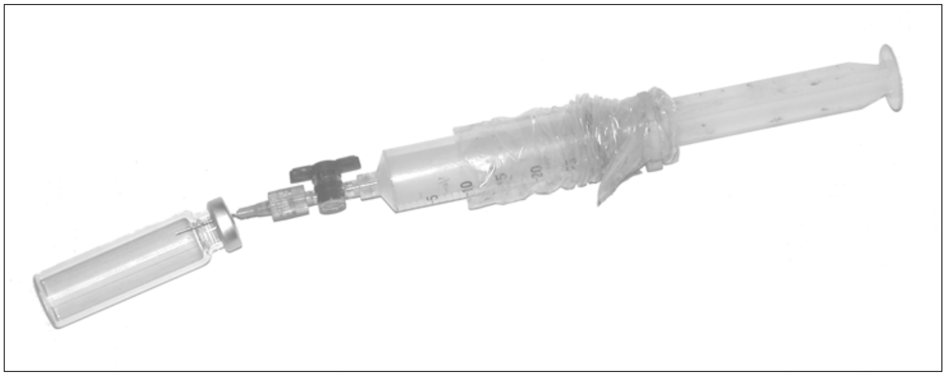


14

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

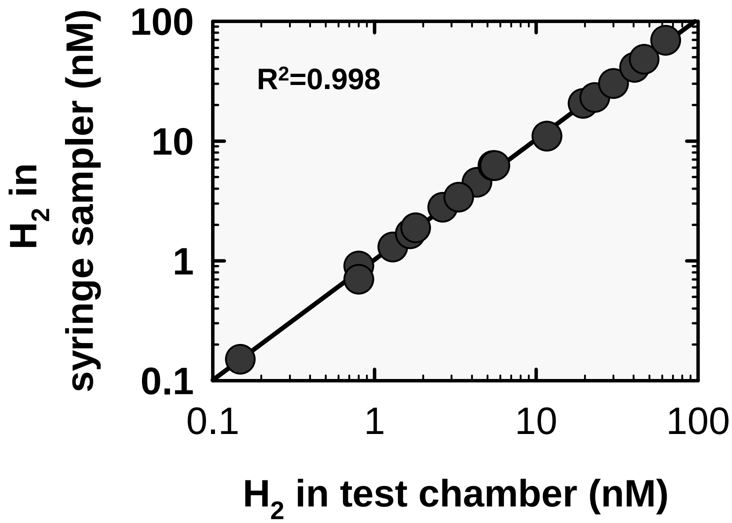


(Vroblesky et al., in press, Ground Water)

15

15

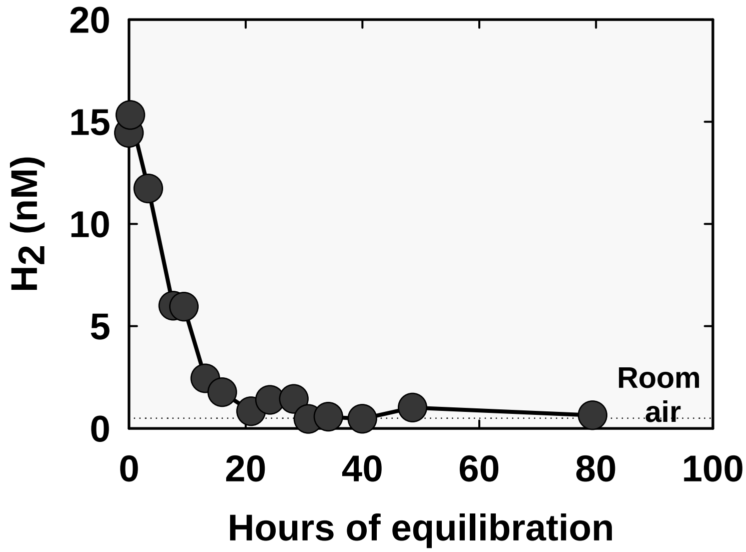
Comparison of passive H_2 samplers to ambient H_2



16

16

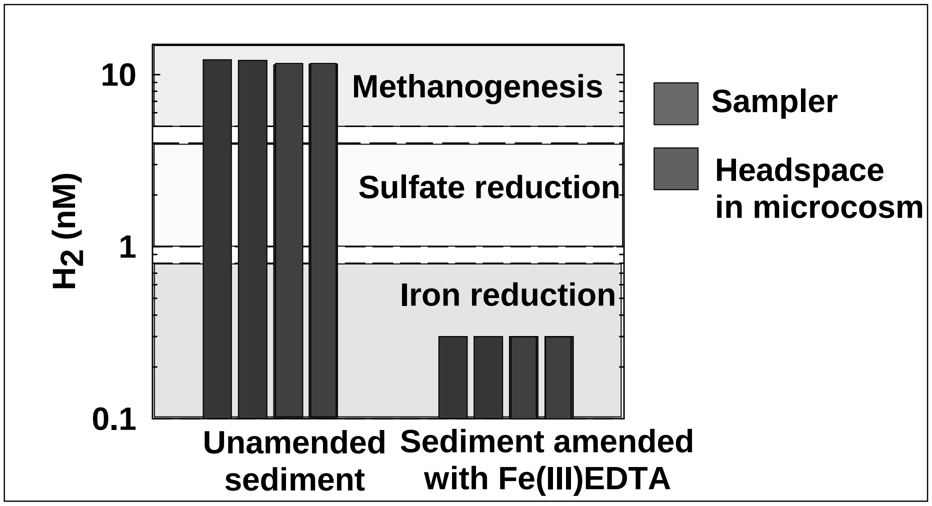
Equilibration of 20-mL H_2 syringe samplers



17

17

Comparison of H_2 in microcosms and passive samplers

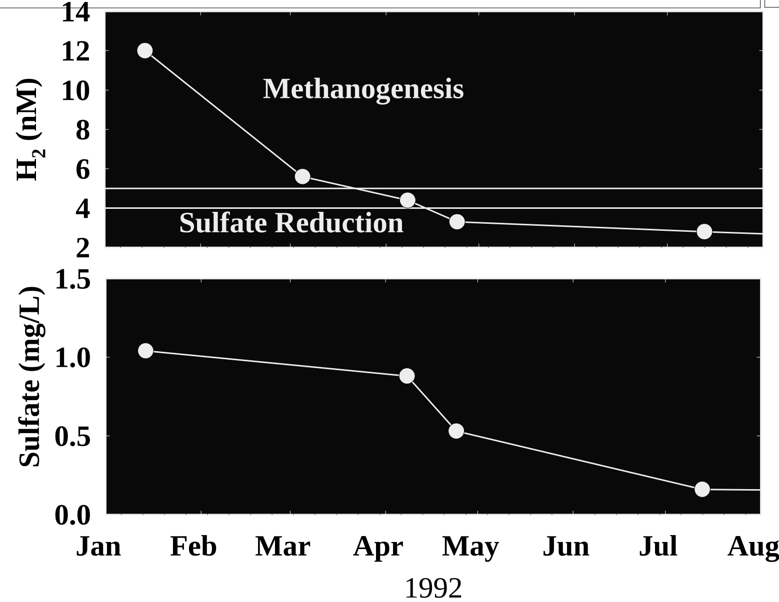


18

18

Shift from methanogenesis to sulfate reduction

(Vroblesky and Chapelle, Water Resour. Research, 1994)



19

19

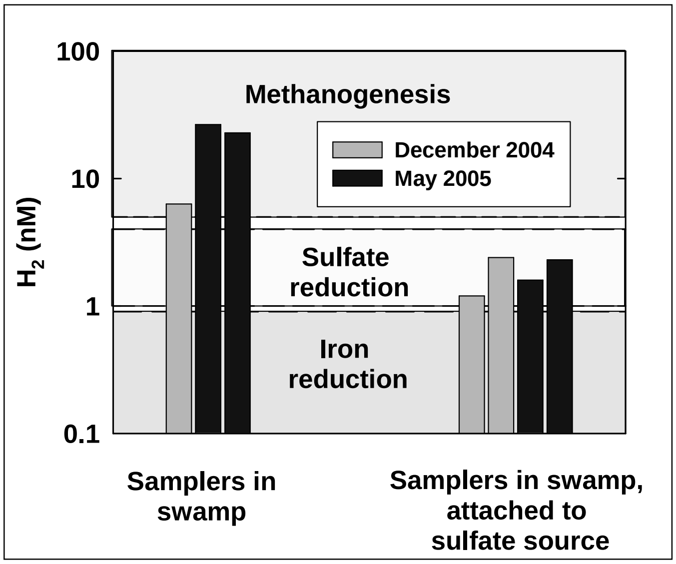
Field test of the diffusion sampler in a swamp took advantage of the fact that methanogens can be outcompeted by sulfate reducers when sulfate is present.

Syringe sampler attached to gypsum

20 20

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

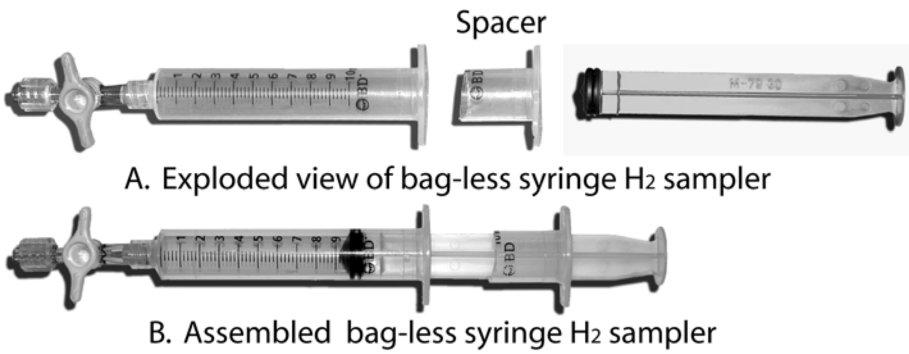
H2 in passive samplers deployed in swamp



21

21

Robust H_2 Diffusion Sampler for Deep Environments



22

22

Tested down to about 100 ft below water.

Comparison of syringe H_2 sample and bubble-strip sample

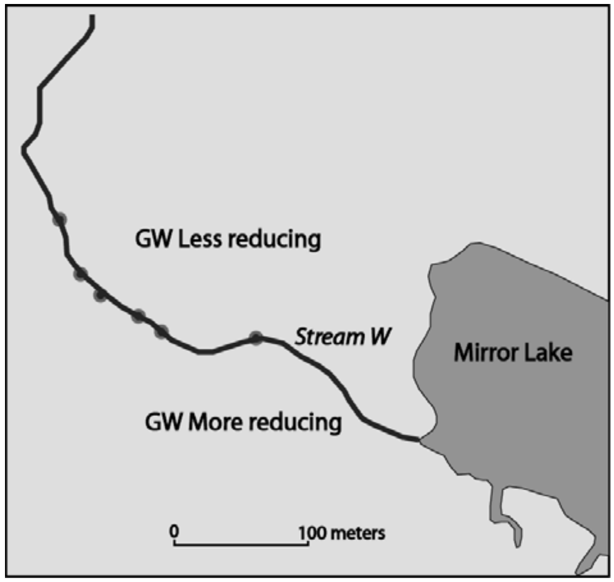
[m, meters; n*M*, nanomoles per liter; ns, not sampled]

Sampled Depth (m)	H_2 concentration (n*M*)	
	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

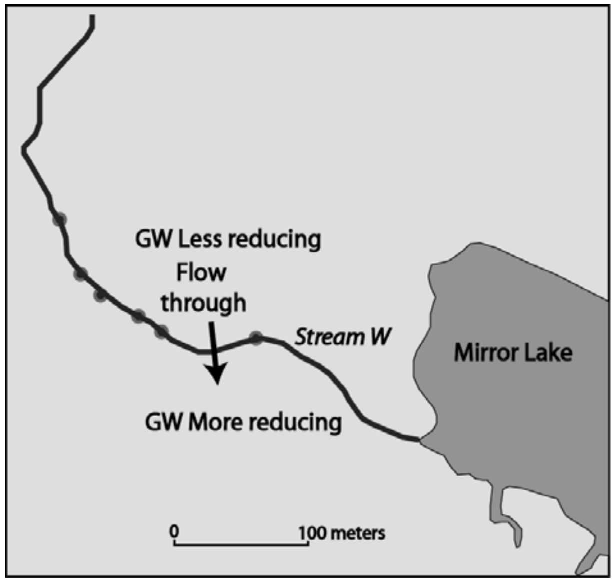


24

24

New Hampsire

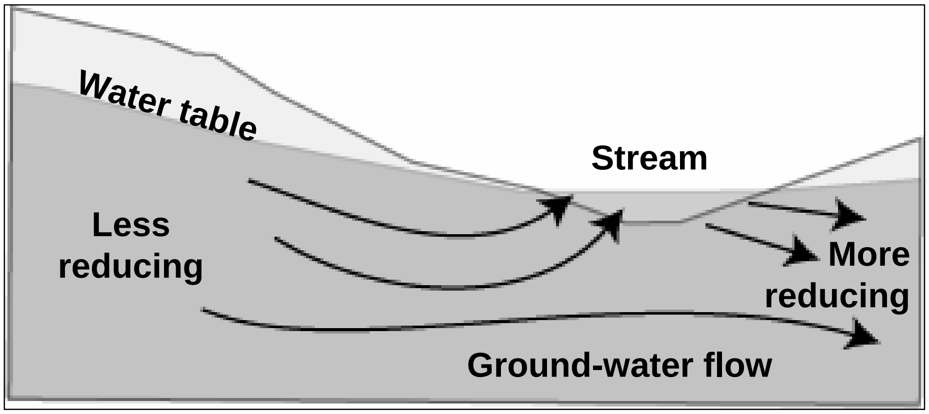
Flow-through stream, Mirror Lake, NH



25

25

Flow-through stream, Mirror Lake, NH



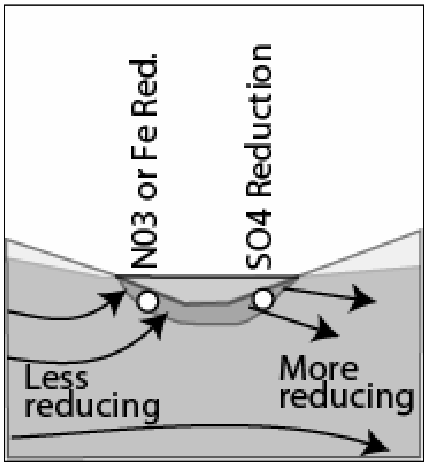
Fractured rock and saprolite, so little or no TOC

26

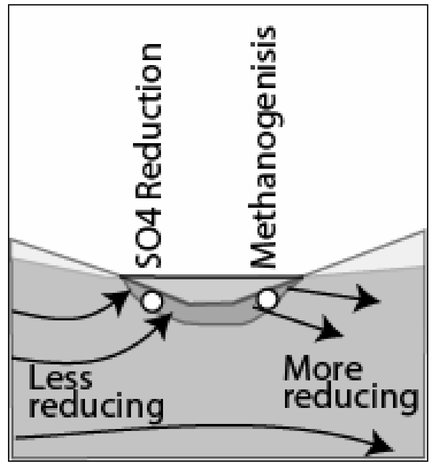
26

Data from streambed H2 samplers (Winter et al., in press)

USGS



Transect 2



Transect 3

27

27

SO4 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.

28

28