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

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


- 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)*

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<tbody>
<tr>
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<td>No</td>
<td>Fair</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
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<td>DCE</td>
<td>Poor</td>
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<td>VC</td>
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<td>Poor</td>
<td>Fair</td>
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<table>
<thead>
<tr>
<th>Oxidation</th>
<th>O2 Red.</th>
<th>Mn(IV) Red.</th>
<th>Fe(III) Red.</th>
<th>SO4 Red.</th>
<th>Methanogenesis</th>
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<tr>
<td>TCE</td>
<td>A CoM</td>
<td>No</td>
<td>No</td>
<td>No</td>
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<td>DCE</td>
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<tr>
<td>VC</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
<td>H. acid red.</td>
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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

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

<table>
<thead>
<tr>
<th>Predominant TEAP</th>
<th>H\textsubscript{2} concentration (nM)</th>
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<tbody>
<tr>
<td>Nitrate reduction</td>
<td>&lt;0.1</td>
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<tr>
<td>Mn reduction</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>1-4</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>5-30</td>
</tr>
</tbody>
</table>
The commonly used bubble-strip method for $H_2$ is not usually appropriate for GWSWI

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.
Previous $H_2$ Samplers

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

(Spalding and Watson, ES&T, 2006)

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

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 $H_2$

Comparison of passive $H_2$ samplers to ambient $H_2$.

$$R^2 = 0.998$$
Equilibration of 20-mL \( H_2 \) syringe samplers

![Equilibration graph]

- \( H_2 \) (nM) vs. Hours of equilibration

Room air
Comparison of $H_2$ in microcosms and passive samplers

- Methanogenesis
- Sulfate reduction
- Iron reduction

Unamended sediment vs. Sediment amended with Fe(III)EDTA

$H_2$ (nM)
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.
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

![Diagram showing H2 (nM) levels for different processes and sampling periods: December 2004, May 2005.]
Robust $H_2$ Diffusion Sampler for Deep Environments

Tested down to about 100 ft below water.
Comparison of syringe $H_2$ sample and bubble-strip sample

<table>
<thead>
<tr>
<th>Sampled Depth (m)</th>
<th>$H_2$ concentration (nM)</th>
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<tbody>
<tr>
<td></td>
<td>Syringe Sampler</td>
</tr>
<tr>
<td>15.5 (unpacked)</td>
<td>0.86±0.27</td>
</tr>
<tr>
<td>18 (packed interval)</td>
<td>1.0±0.45</td>
</tr>
<tr>
<td>21 (packed interval)</td>
<td>0.70±0.25</td>
</tr>
<tr>
<td>24 (packed interval)</td>
<td>0.93±0.12</td>
</tr>
<tr>
<td>46.6 (packed interval)</td>
<td>ns</td>
</tr>
</tbody>
</table>

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

These are results for the unbagged syringe sampler
Flow-through stream, Mirror Lake, NH

New Hampshire
Flow-through stream, Mirror Lake, NH

GW Less reducing Flow through
GW More reducing

Stream W

Mirror Lake

0 100 meters
Flow-through stream, Mirror Lake, NH

Fractured rock and saprolite, so little or no TOC
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.