Impact of submarine groundwater discharge on biogeochemical processes and benthic fluxes in coastal sands

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Area of study
Low-salinity groundwater escapes at the coast line of Hel Peninsula through seeps within permeable sandy near shore sediments.
- What is the fate of solutes supplied by SGD in the surface sediments?
- How does the presence of SGD impact aerobic benthic processes?
Map of the main seepage areas obtained by high resolution survey (10 cm b.s.f.) with a conductivity sensor.
August 2011

Map of the main seepage areas obtained by high resolution survey (10 cm b.s.f.) with a conductivity sensor

<table>
<thead>
<tr>
<th>Water column parameter</th>
<th>Seep / Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>270-320 µmol L-1</td>
</tr>
<tr>
<td>Temperature</td>
<td>18-20 °C</td>
</tr>
<tr>
<td>Salinity</td>
<td>7 PSU</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sediment parameter</th>
<th>Seep</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (20 cm) %</td>
<td>0.14 (0.15-2cm)</td>
<td>0.11(0.17-2cm)</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>388</td>
<td>312</td>
</tr>
<tr>
<td>Permeability (x10^{-11} m²)</td>
<td>1.95</td>
<td>2.32</td>
</tr>
</tbody>
</table>
In situ incubations (benthic chambers)
21 hours (day/night at seep and reference site)
(DIC $\delta^{13}$C$_{DIC}$ Fe$^{2+}$ Mn$^{2+}$ Na$^{2+}$ SO$_4^{2-}$ PO$_4^{3-}$ + SGD rates, O$_2$ benthic flux)

Porewater profiles
Samples from 5 depths (1-18 cm b.s.f. at seep and ref.) extracted in situ with a porewater lance and ex situ with rhizons
(DIC $\delta^{13}$C$_{DIC}$ Fe$^{2+}$ Mn$^{2+}$ Na$^{2+}$ SO$_4^{2-}$ PO$_4^{3-}$ )
Pore water profiles

- Seep site
- Reference site

Salinity (PSU)

cm b.s.f.
Pore water profiles: seep site two-layer structure
Pore water profiles: seep site two-layer structure

- Seep site
- Reference site

- Intense advective transport
- No exchange with bottom water
Groundwater characteristics

<table>
<thead>
<tr>
<th></th>
<th>Sal. (PSU)</th>
<th>O₂  μmol L⁻¹</th>
<th>DIC mmol L⁻¹</th>
<th>δ¹³C DIC  ‰</th>
<th>Fe²⁺ μmol L⁻¹</th>
<th>Mn²⁺ μmol L⁻¹</th>
<th>Ca²⁺ μmol L⁻¹</th>
<th>Mg²⁺ μmol L⁻¹</th>
<th>SO₄²⁻ mmol L⁻¹</th>
<th>PO₄³⁻ μmol L⁻¹</th>
<th>HS⁻ μmol L⁻¹</th>
<th>CH₄ μmol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom water</td>
<td>7</td>
<td>300</td>
<td>1.7</td>
<td>0.3</td>
<td>0.07</td>
<td>0.04</td>
<td>2.5</td>
<td>8.5</td>
<td>4.6</td>
<td>0.6</td>
<td>0.03</td>
<td>60</td>
</tr>
<tr>
<td>Ground-water (18 cm b.s.f.)</td>
<td>0</td>
<td>0</td>
<td>6.4</td>
<td>-13.6</td>
<td>1</td>
<td>5.4</td>
<td>1</td>
<td>0.6</td>
<td>0.03</td>
<td>60</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

- Fresh, anoxic, DOC (up to 7 mg L⁻¹)
- Enriched in
  - DIC (δ¹³C DIC signature -13.6 ‰)
  - Methane (300 μmol L⁻¹)
  - Sulfides (300 μmol L⁻¹)
  - Phosphates and Silicates (60, 600 μmol L⁻¹)
Seepage meters-benthic chambers

Vol = 5 L
Seepage meters-benthic chambers

Vol = 5 L

Seepage rates

Seep site

Reference site

L m$^{-2}$ d$^{-1}$
Seepage meters-benthic chambers

Oxygen

Vol = 5 L

15 cm

20 cm
100% Salinity (7 PSU)

0% Salinity = 0 PSU

Reference

Seep

% Salinity

21:00  1:00  5:00  9:00  13:00  17:00

0% Salinity = 0 PSU
Temporal and spatial solute concentration gradients- Conservative behavior

SO$_2^-$

Time

DIC

SO$_2^-$ (mmol L$^{-1}$)

DIC (mmol L$^{-1}$)

Depth cm

SO$_4^{2-}$ (mmol L$^{-1}$)

DIC (mmol L$^{-1}$)
Temporal and spatial solute concentration gradients - Non conservative behavior

**PO\textsuperscript{3-4}**, **Fe\textsuperscript{2+}**, **Mn\textsuperscript{2+}**

![Graphs showing concentration over time and depth for PO\textsuperscript{3-4}, Fe\textsuperscript{2+}, and Mn\textsuperscript{2+}](image)
Temporal oxygen concentration gradients

![Temporal oxygen concentration gradients graph](image-url)
Benthic oxygen flux

= based on slope of linear regressions of solute concentration time series (optode readings) for dark and light periods.
Temporal oxygen concentration gradients

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*Measured oxygen flux* = all processes of oxygen removal and release.
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SGD-related apparent flux = due to the replacement of oxic chamber water with anoxic ground water.
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Net oxygen flux = corrected for SGD-related apparent flux
Temporal oxygen concentration gradients

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Net oxygen flux = corrected for SGD-related apparent flux
Benthic oxygen flux

Reference

Night

Day

Seep

mmol O₂ m⁻² d⁻¹

Measured flux

Apparent flux (SGD)

Flux corrected for SGD

Night

Day

Seep
Benthic oxygen flux

- Measured flux
- Apparent flux (SGD)
- CH₄ and H₂S oxidation
- Flux corrected for SGD

Reference

Night

Day

Seep

mmol O₂ m⁻² d⁻¹
- Oxygen may be fully used to oxidize H\textsubscript{2}S and CH\textsubscript{4}.

\[\text{HS}^* + \text{O}_2 \rightarrow \text{HO}^* + \text{SO}^*\]

\[\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}\]
- Oxygen may be fully used to oxidize H$_2$S and CH$_4$

- If so, no oxygen would be left for OM mineralization...

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\[ \text{OM mineralization} \]

\[ HS^- + O_2 \rightarrow HO^- + SO^- \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]
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\begin{align*}
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Open questions

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\text{OM mineralization}
\]

\[
\text{How much sulfide is removed?}
\]

\[
\text{How much oxidized?}
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Open questions

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\end{align*}
\]

OM mineralization

How much sulfide is removed?
How much oxidized?

How (and when) is the oxidized iron pool replenished?
- Oxygen may be fully used to oxidize H$_2$S and CH$_4$.

- If so, no oxygen would be left for OM mineralization.

..but we do not see OM accumulation

Open questions

\[
\begin{align*}
    \text{OM mineralization} \\
    \text{How much sulfide is removed?} \\
    \text{How much oxidized?} \\
\end{align*}
\]

Which methane oxidation pathway?

How (and when) is the oxidized iron pool replenished?

\[
\begin{align*}
    HS^* + O_2 &\rightarrow H^*O + SO^* \\
    CH_4 + 2O_2 &\rightarrow CO_2 + 2H_2O
\end{align*}
\]
Conclusions

Combining porewater sampling and flux measurements with “seepage meter-benthic chambers” seem to be a trustworthy approach to tackle accumulation or removal of groundwater constituents along its flowpath and the effect on benthic coastal systems.
Both sites show similar bulk oxygen fluxes and are net autotrophic.

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- Both sites show similar bulk oxygen fluxes and are net autotrophic.
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- At the seep site seepage of anoxic waters significantly contributes to oxygen uptake and anaerobic mineralization pathways may play a more prominent role.
Acknowledgments

7th framework program, ITN-SENSEnet project

Amber project, BONUS+

Patrick Meyer (MPI, Bremen, Germany)
Susan Volger (IOW, Warnemünde, Germany)
Lech Kotwicki, Beata Szymczycha (Institute of Oceanology, Warsaw, Poland)

HGF-MPG Group for Deep Sea Ecology and Technology, MPI, Bremen, Germany

Sea-tech and electronic workshop TAs at MPI (Bremen) and Hel Marine Station.