CARL VON OSSIETZKY universität OLDENBURG

ICBM

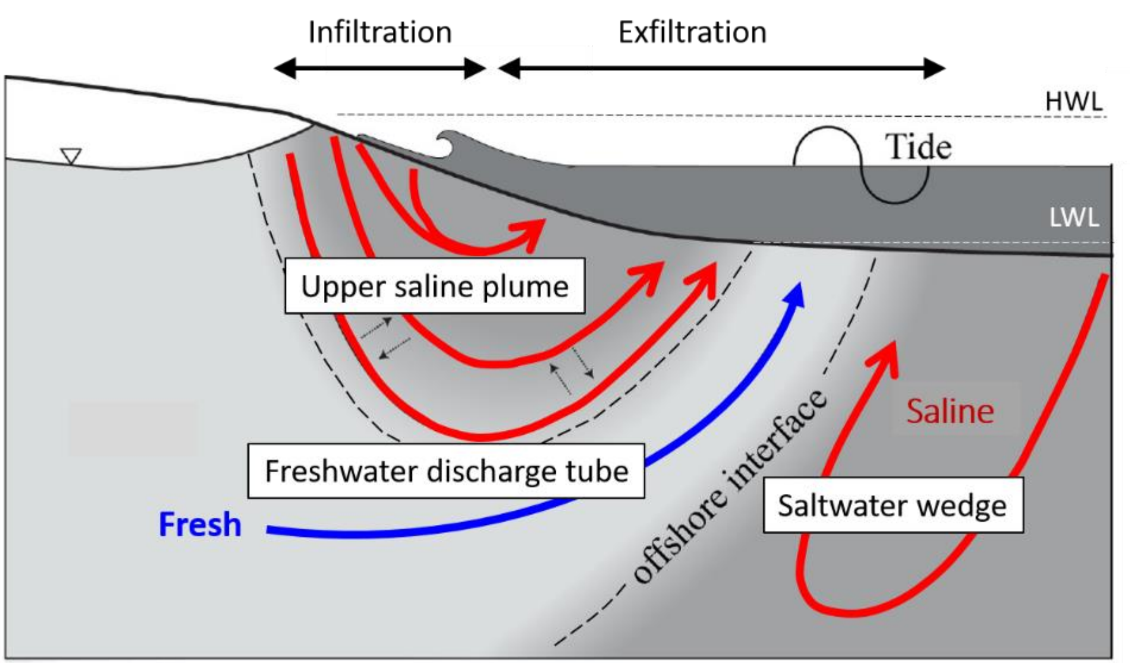
Molecular properties of dissolved organic matter (DOM) in the subterranean estuary of a high-energy beach: Finding proxies for reactive transport

Hannelore Waska[1]*, Heike Simon[1], Janis Ahrens[2], Melanie Beck[2], Kai Schwalfenberg[3], Stephan Seibert[4], Gudrun Massmann[4], Oliver Zielinski[3], Thorsten Dittmar[1]

[1]ICBM-MPI Bridging Group for Marine Geochemistry, Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg
*Email: hannelore.waska@uni-oldenburg.de
[2]Microbiogeochemistry Group, ICBM, University of Oldenburg
[3]Marine Sensor Systems Group, ICBM, University of Oldenburg
[4]Hydrogeology Group, IBU, University of Oldenburg

The beach subterranean estuary

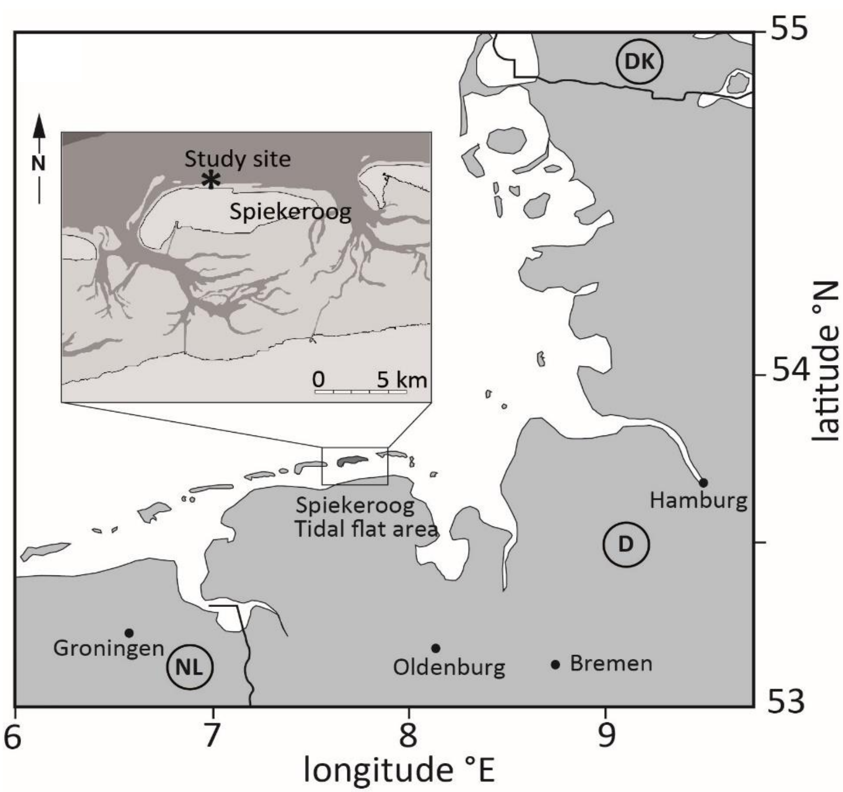
- Beaches are permeable land-ocean interfaces which allow **discharge of meteoric groundwater** from land to the ocean.
- Tidal pumping and wave action cause **infiltration of seawater** into beaches.
- The mixing zone between groundwater and percolating seawater is called a **subterranean estuary.**
- In contrast to surface estuaries, the subterranean estuary has **longer water residence times**, closer **water-sediment-interactions**, and complex **redox zonations**.

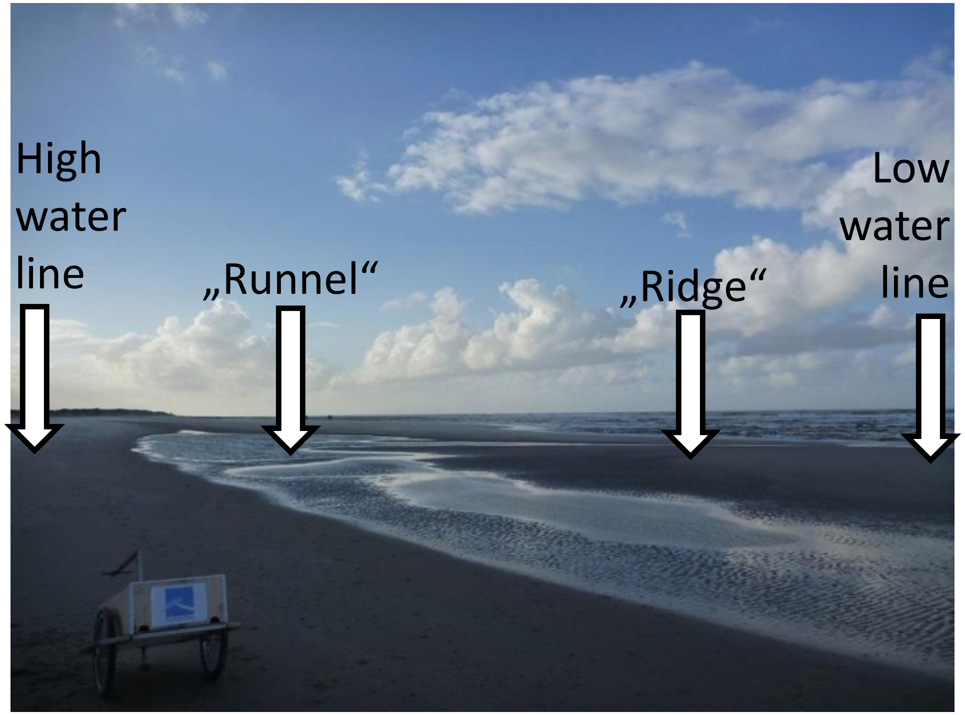


Grünenbaum et al. (2020) J Hydrol 587, 124948

Study site: Spiekeroog Beach

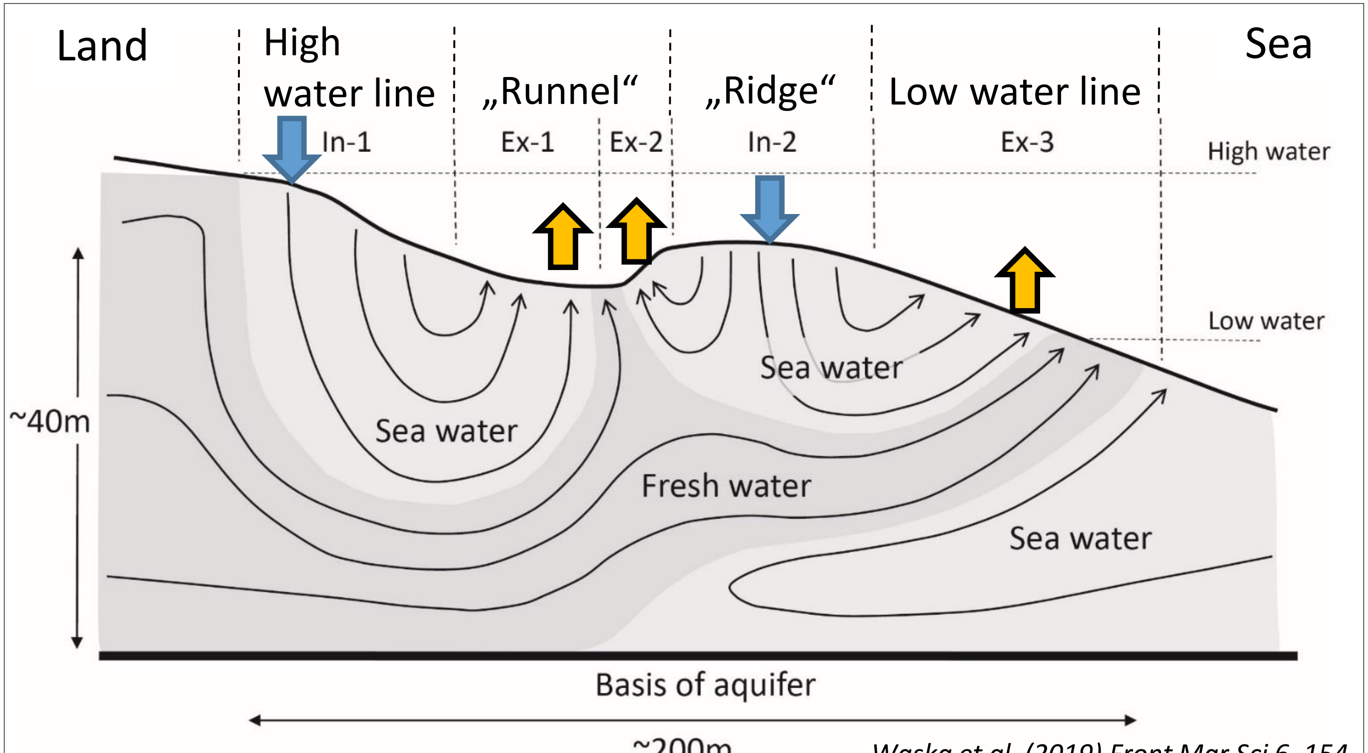
- Spiekeroog is a Barrier island in the Southern North Sea, with **mesotidal range** (2.7 m).
- The northern shore has a dynamic topography and is exposed to **high-energy waves**.
- The topography impacts the advective water flow paths through the sediments: elevated ridges cause **seawater infiltration**, runnels induce **exfiltration of porewater**.





STE flow paths

- The beach STE of the study site contains two seawater circulation cells:
  - Infiltration zone 1 (**In-1**) is at the high water line and porewater exfiltrates into a runnel (**Ex-1**), together with a small contribution of fresh groundwater.
  - Infiltration zone 2 (**In-2**) is located on a shore-parallel ridge and porewater exfiltrates into the runnel (**Ex-2**) as well as at the low water line (**Ex-3**), together with elevated contributions of fresh groundwater.



Waska et al. (2019) Front Mar Sci 6, 154

Rationale and aims

Research gaps

- Mesotidal high-energy beach STEs are common worldwide, but rarely studied
- Dynamic changes in topography and flow paths produce high biogeochemical complexity. Disentanglement of mixing and degradation is often difficult.
- It is not known whether high-energy beach STEs are net sources or sinks of organic carbon to the coastal ocean.

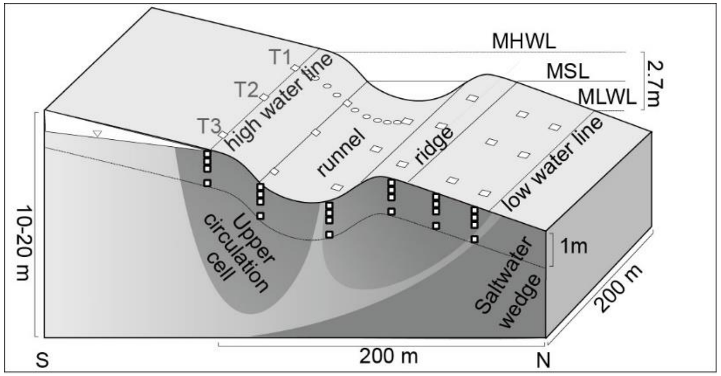
Hypotheses

- Beach topography influences distribution of inorganic and organic porewater constituents.
- Dissolved organic carbon is efficiently degraded along flow paths.
- Mixing and degradation result in distinct traits of DOM.

Strategy

Sampling:

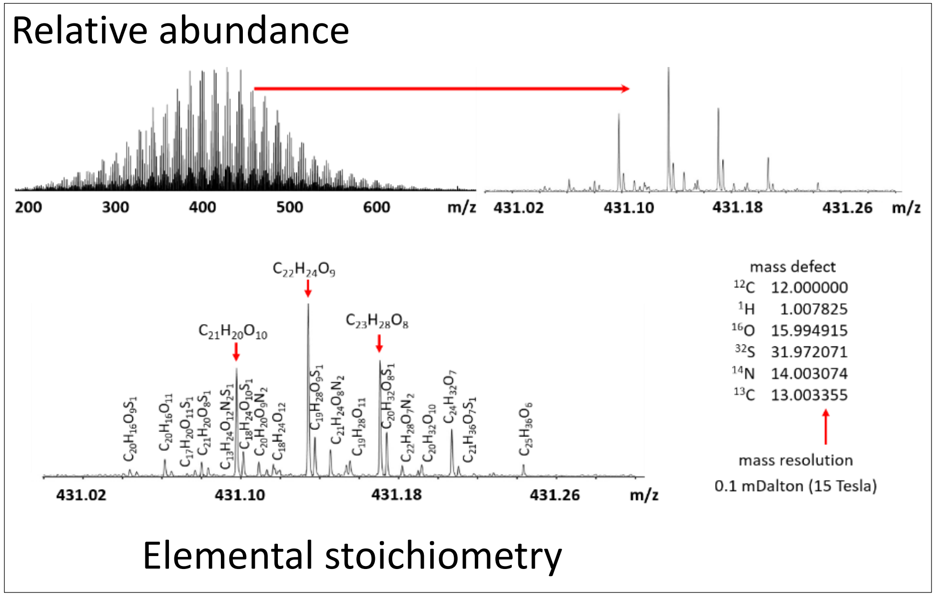
- Seawater collection from nearshore water column
- Porewater collection along shore-perpendicular transects



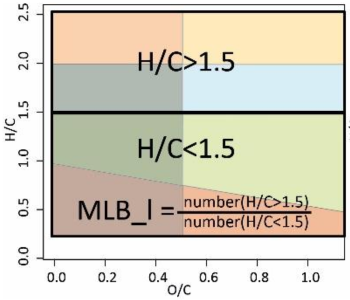
Ahrens et al. (2020) JGR Biogeosciences, 125

Analyses:

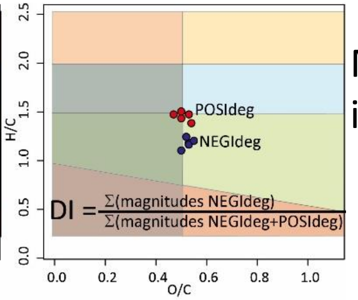
- In situ fluorescence („humic-like“ FDOM)
- Dissolved organic carbon (DOC) concentrations
- Molecular composition via FT-ICR-MS:



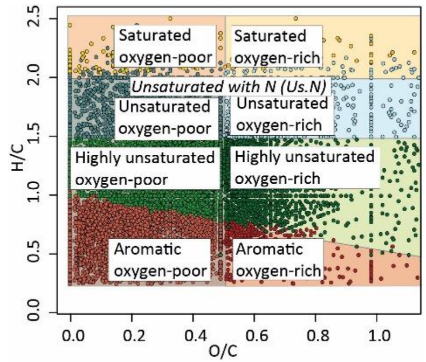
D'Andrilli et al. (2015) RCMS.29



Flerus et al. (2012) Biogeosci.9



Molecular indices

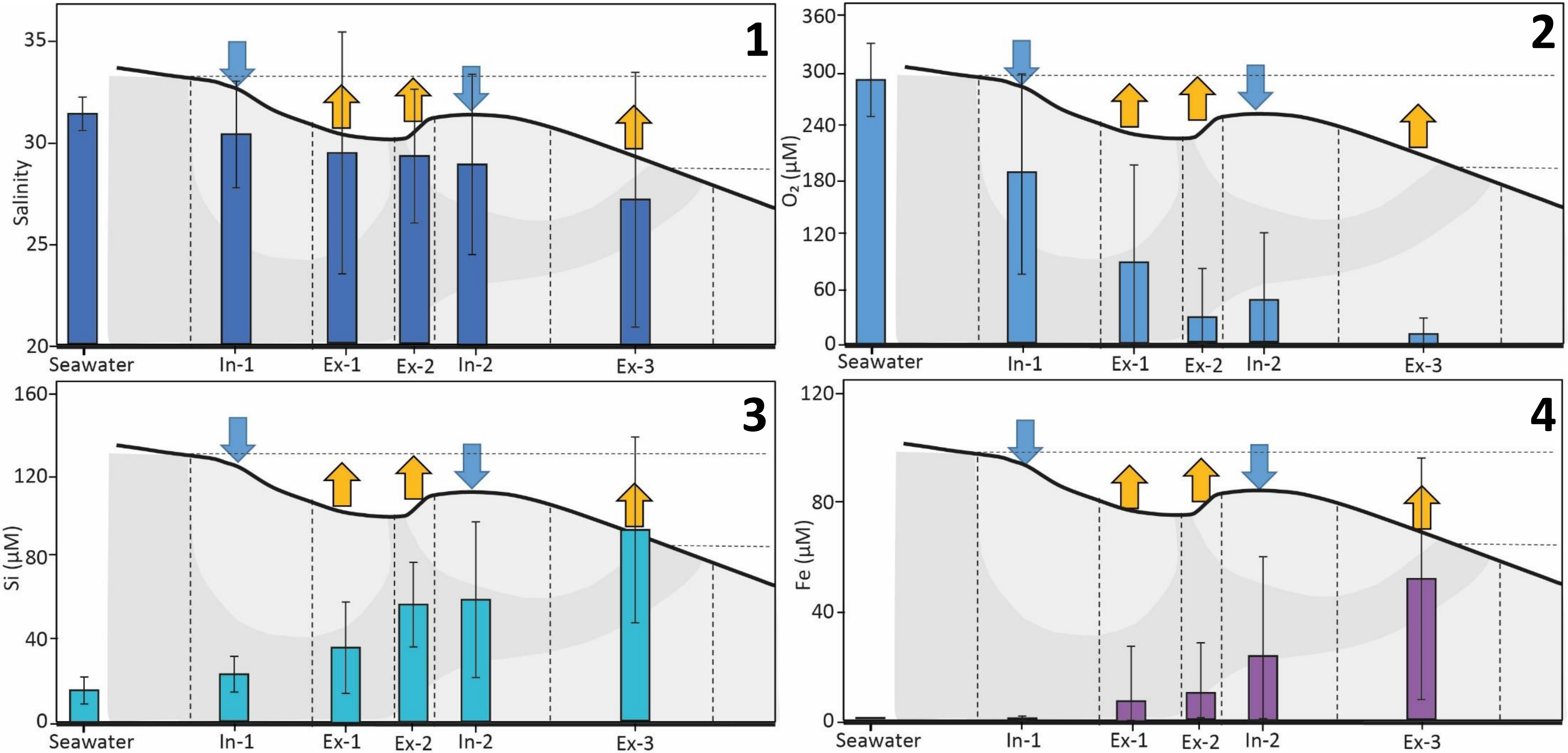


Merder et al. (2020) Anal. Chem.

Structural information

Porewater chemistry

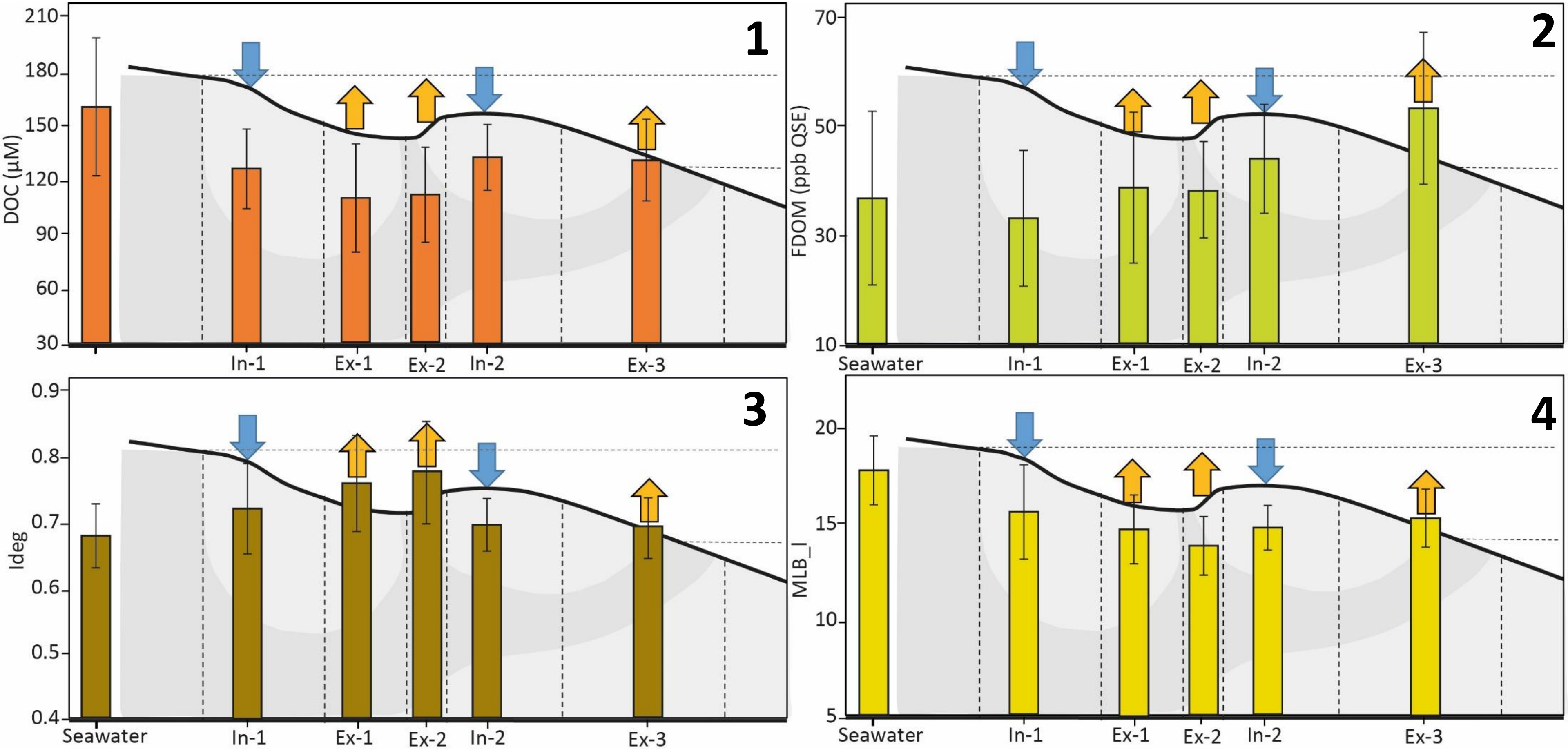
1. Porewater salinity decreases along the flow path.
2. O_2 concentrations decrease along the flow path, increase slightly again at In-2.



3. Si concentrations increase along the flow path.
4. Fe concentrations increase along the flow path, starting from Ex-1.

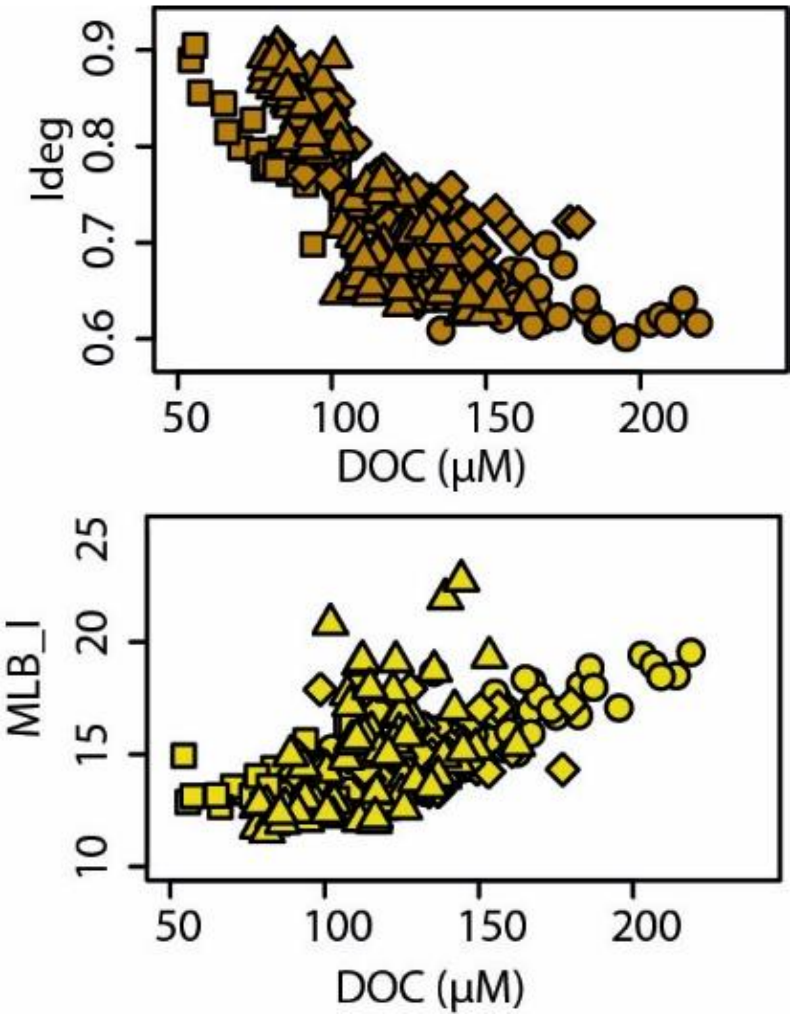
DOM chemistry

1. DOC concentrations decrease along the flow path, increase slightly again at In-2.
2. FDOM concentrations increase continuously along the flow path.



3. Molecular degradation index Ideg increases along the flow path, decreases at In-2.
4. Molecular lability index MLB_l decreases along the flow path, increases at In-2.

DOC vs. DOM



Ideg:

- Negative correlation with DOC
- Molecular degradation together with DOC utilization

MLB_l:

- Positive correlation with DOC
- High lability with high DOC indicates „new"production

Summary

- Beach topography influences distribution of inorganic and organic porewater constituents :
  - Formation of ridges induces „resetting“ through seawater infiltration
  - Formation of runnels induces „aging“ through exfiltration of porewater

- Dissolved organic carbon is efficiently degraded along flow paths:
  - DOC utilization is particularly effective in upper seawater circulation cell
  - Even with meteoric groundwater influence, DOC output is lower than input

- Mixing and degradation result in distinct traits of DOM:
  - FDOM (and Si) originate mainly from increasing fresh groundwater source
  - DOM degradation along the flow paths is revealed by two contrasting molecular indices

Acknowledgements: The BIME Team, Ina Ulber, Matze Friebe, Katrin Klaproth, Joachim Ihnken, Swaantje Fock, Gregor Scheiffarth.

Funding: MWK Niedersachsen ZN3184

Niedersächsisches Ministerium für Wissenschaft und Kultur