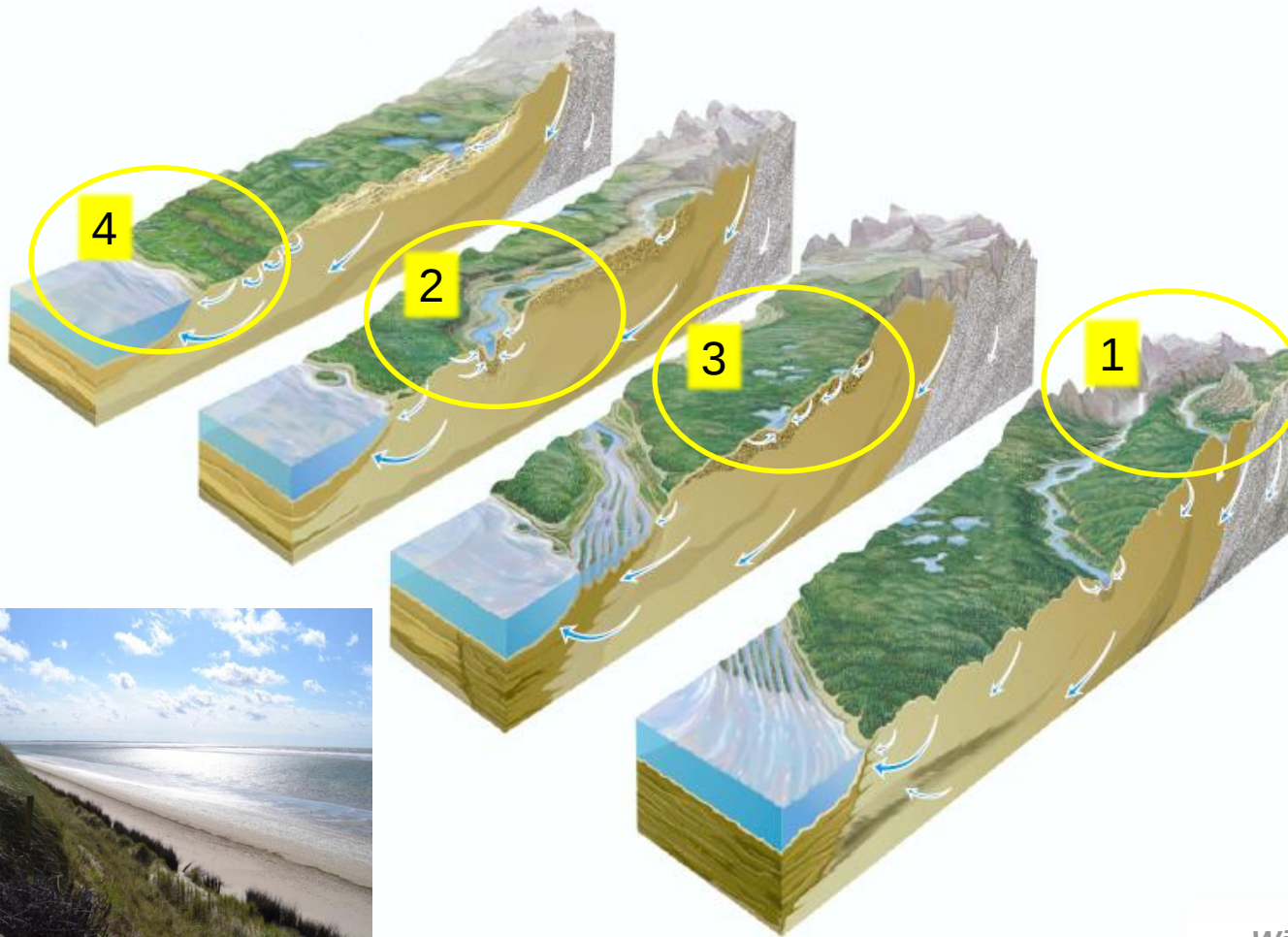


Dynamic interfaces and their influence on groundwater biogeochemistry

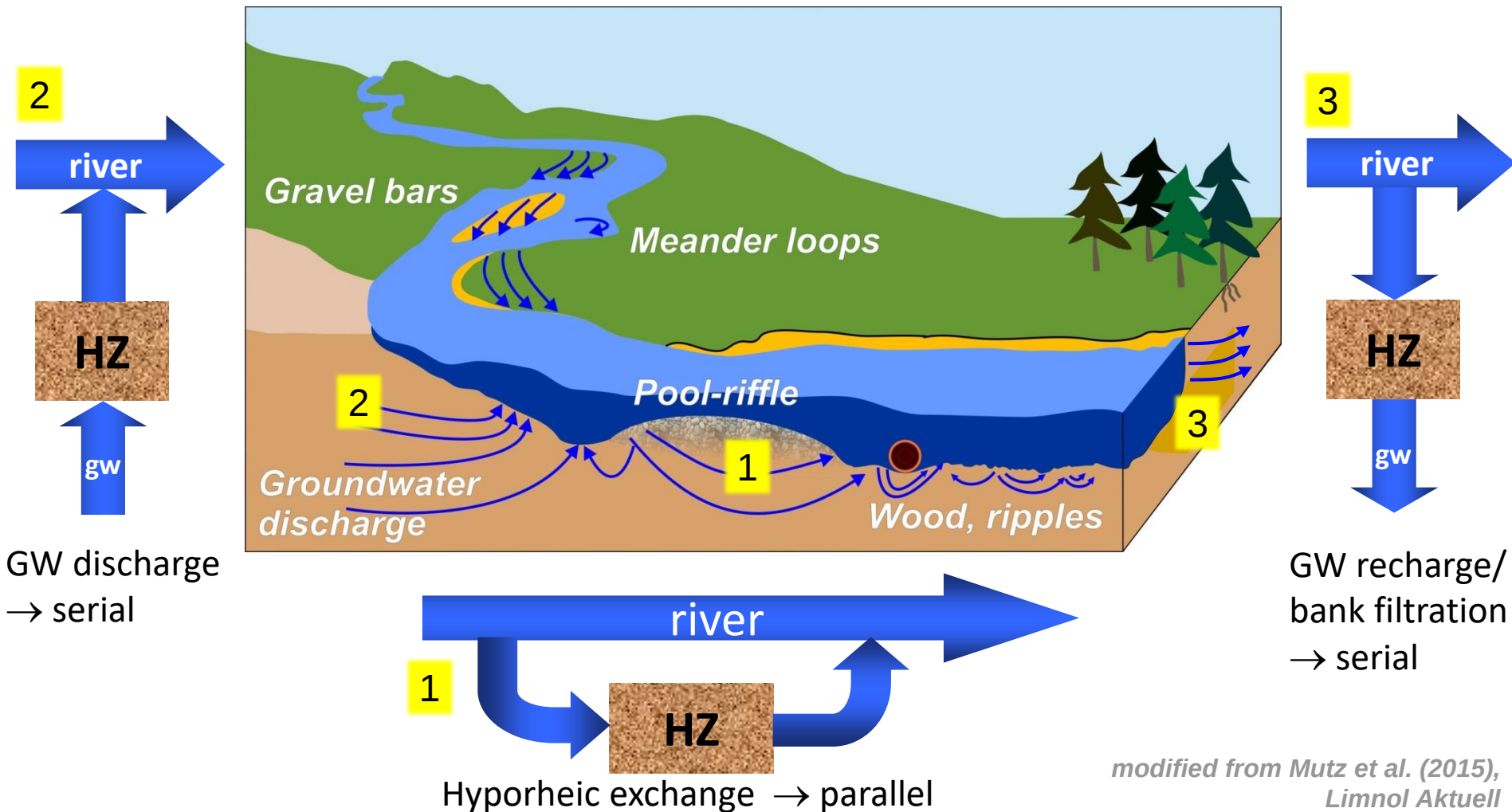


Gudrun Massmann & Janek Greskowiak
Hydrogeology & Landscape Hydrology

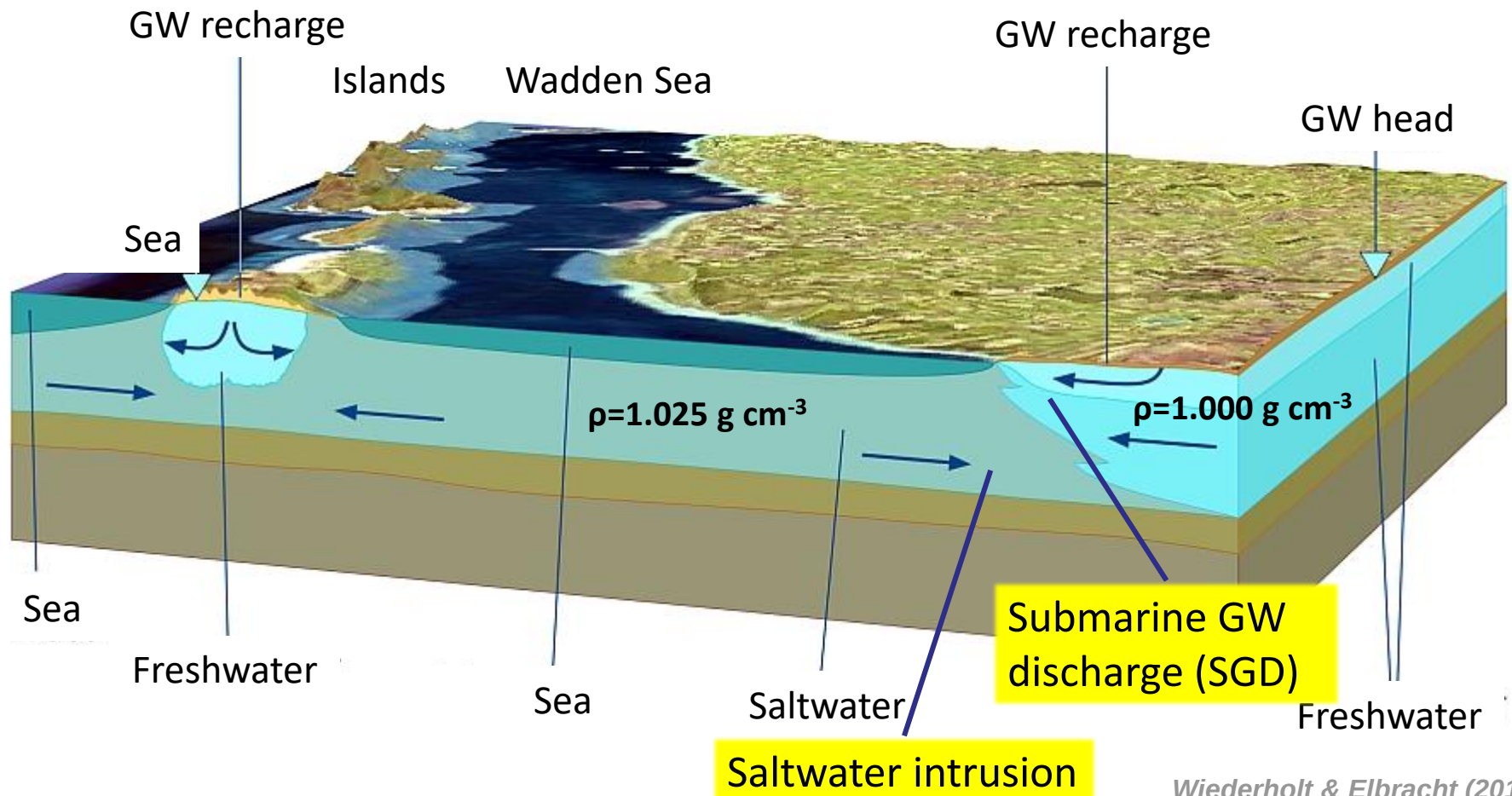
Surface water – groundwater exchange



Hyporheic exchange versus serial exchange



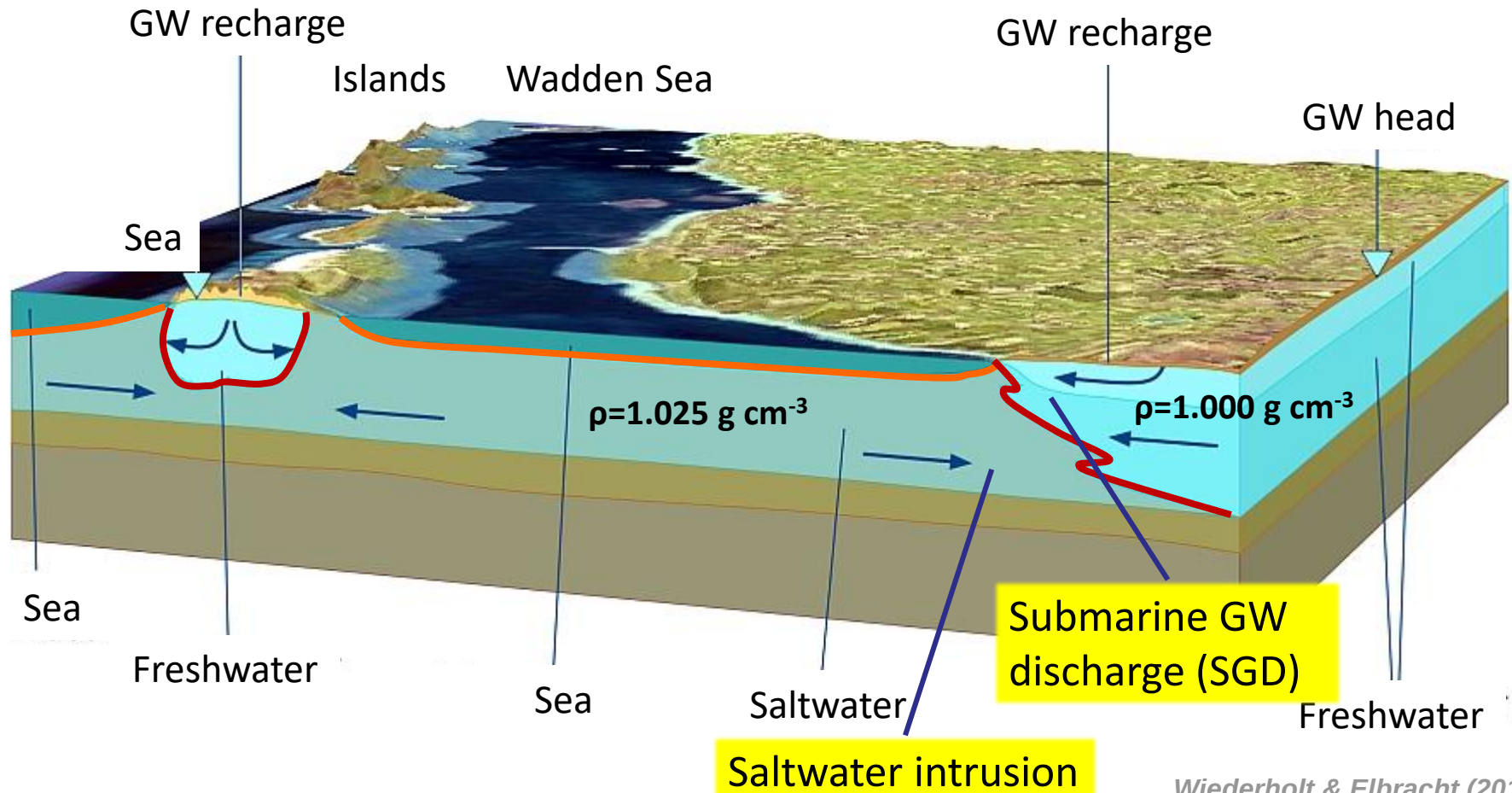
SW-GW exchange at the coast



Different “interfaces”

SW–GW interface

Interface between chemically different water bodies



Characteristics of the SW-GW exchange zone

- Mixing zone of waters with distinctly different water chemistry
- Strong gradients (hydraulics, temperatures, density, biogeochemistry)
- High microbial activity
- (Variable) input of organic matter and electron acceptors
- Often very dynamic (hydraulics, temperatures, biogeochemistry)

→ **Effective bioreactors**

Objectives

- To give two distinctly different examples for dynamic SW-GW exchange and its effect on groundwater quality:
 1. Effect of transient pumping and SW temperatures on redox conditions (and trace organic compounds) during bank filtration in Berlin (urban environment)
 2. Effect of tides, morphodynamics and storm floods on geochemical patterns below a (pristine) high-energy beach

Bank filtration in Berlin

- **Natural and Artificial Systems for Recharge and Infiltration** (NASRI, 2002-2005)
- Redox sensitivity and long-term persistence of organic trace pollutants in groundwater: Wastewater-bound compounds (DFG project, 2010-2014)
- Development of operating strategies for an improved removal of organic micropollutants during the process of bank filtration (2015-2016)
- Operation strategies and technologies for water reuse to support drinking water supply in urban areas (TrinkWave, 2016-2020)



Bundesministerium
für Bildung
und Forschung

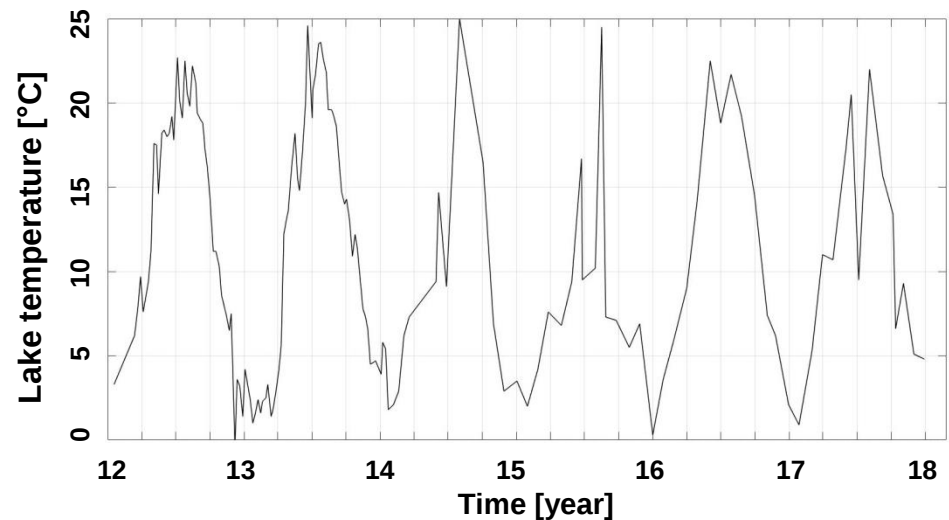
Objective and motivation

- To elucidate behaviour of trace organic compounds (TOrcs) during bank filtration in a partially-closed urban water cycle
- Motivated by the fact that managed aquifer recharge (MAR) can help ease water stress and improve water quality (and provides drinking water for Berlin)

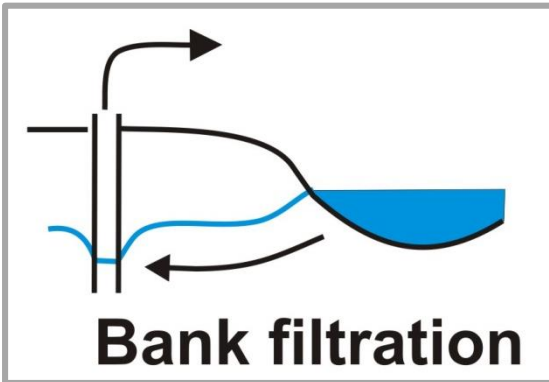
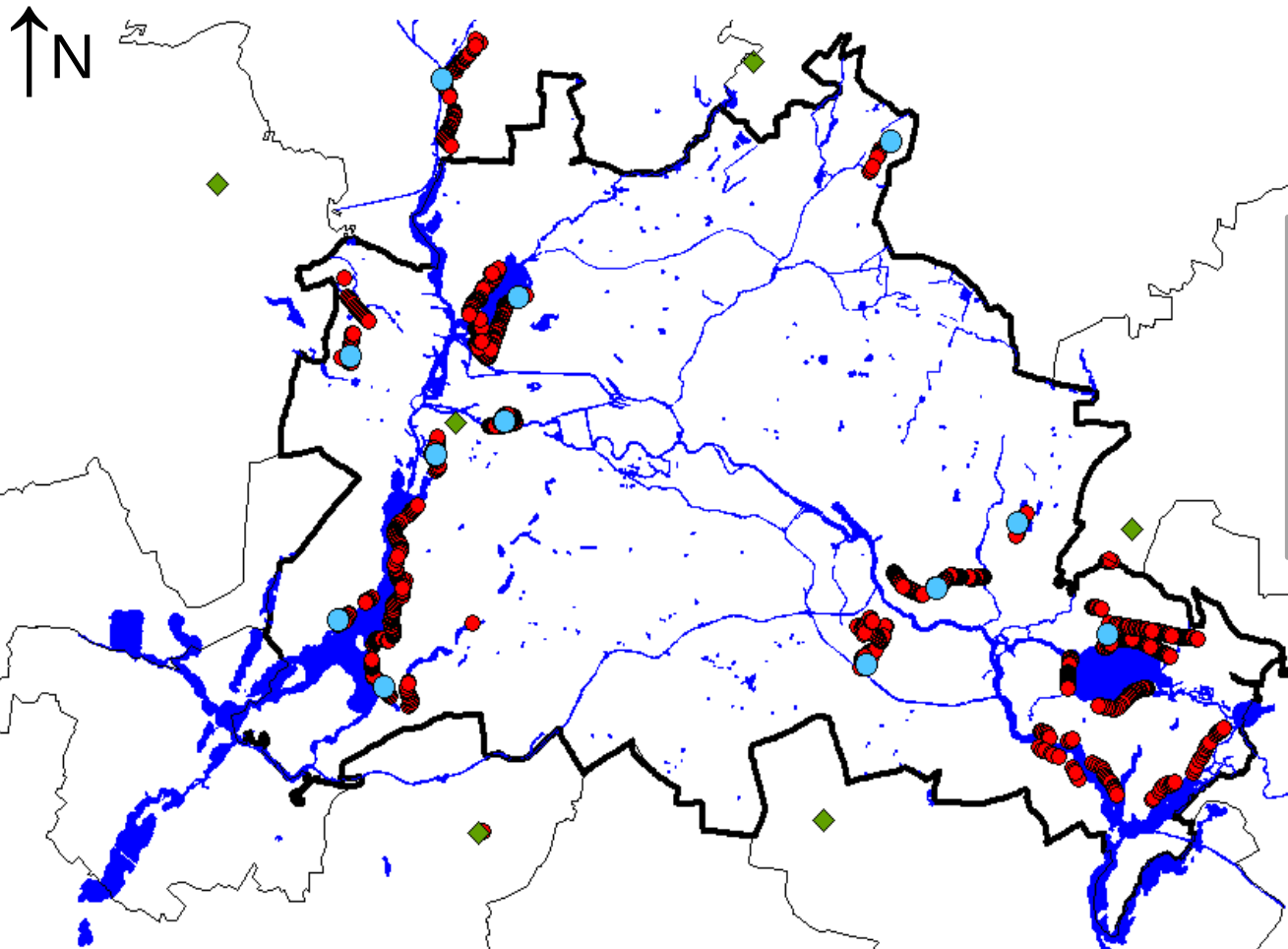
Study site Berlin



- “Lakes” with strong seasonal temperature fluctuations
- Locally high proportion of treated WW → TOrCs

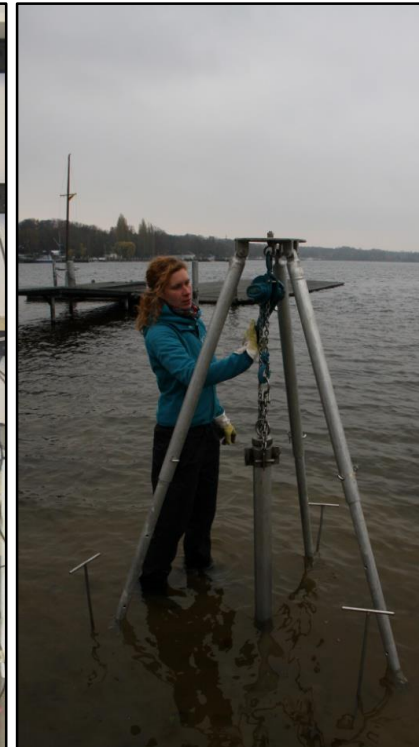
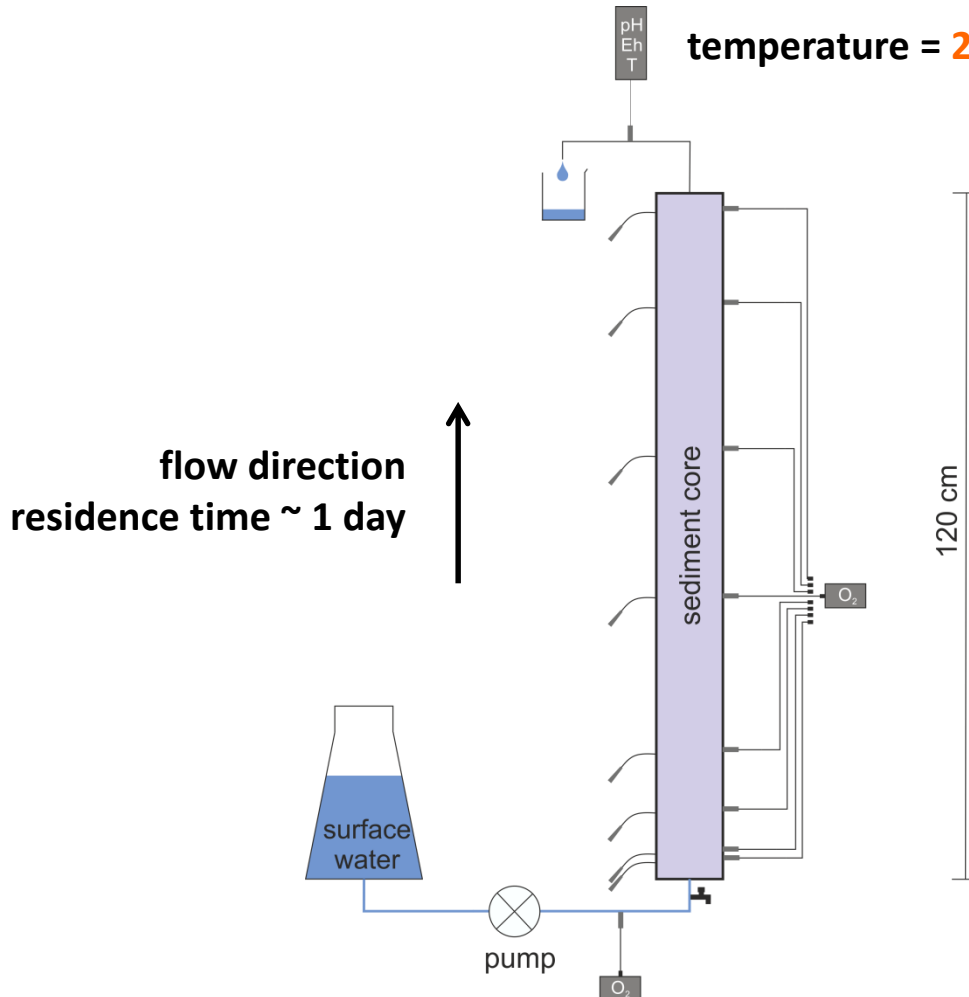


Partially closed water-cycle



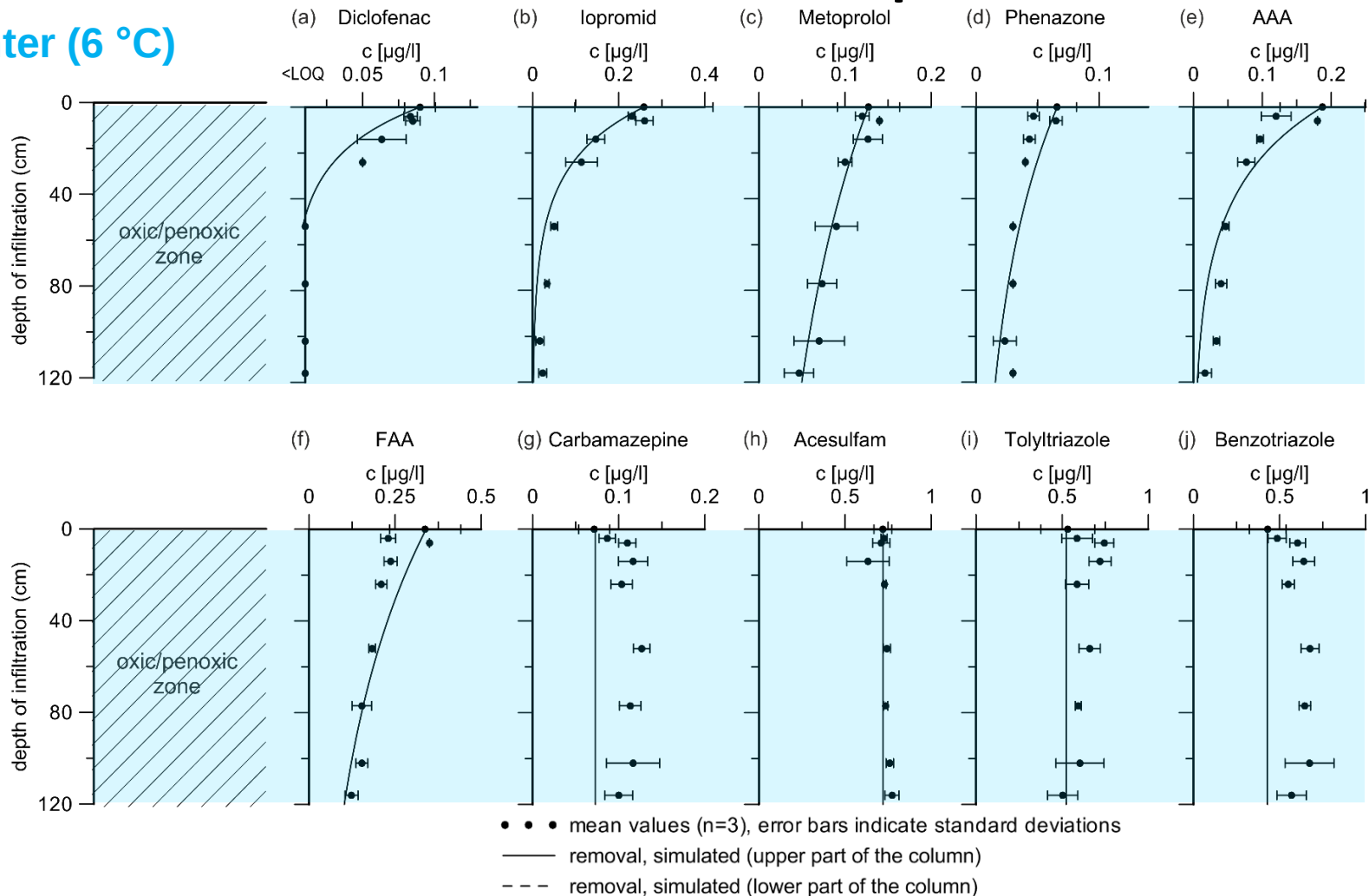
- ◆ Sewage treatment plants
- Drinking water treatment plants
- Production wells

Column experiments on seasonal TOrC attenuation



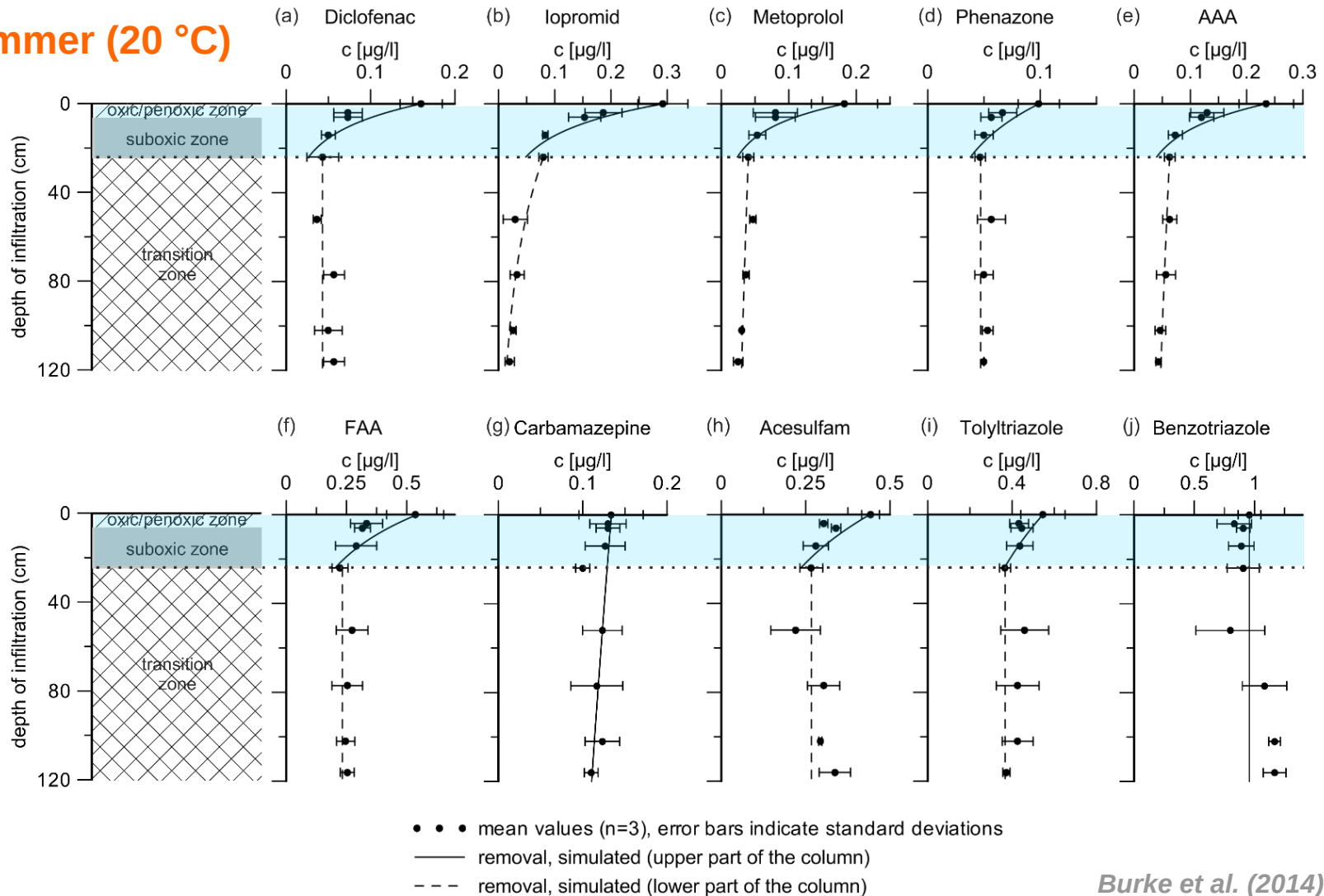
TOrC attenuation is function of temp. & redox conditions

Winter (6 °C)

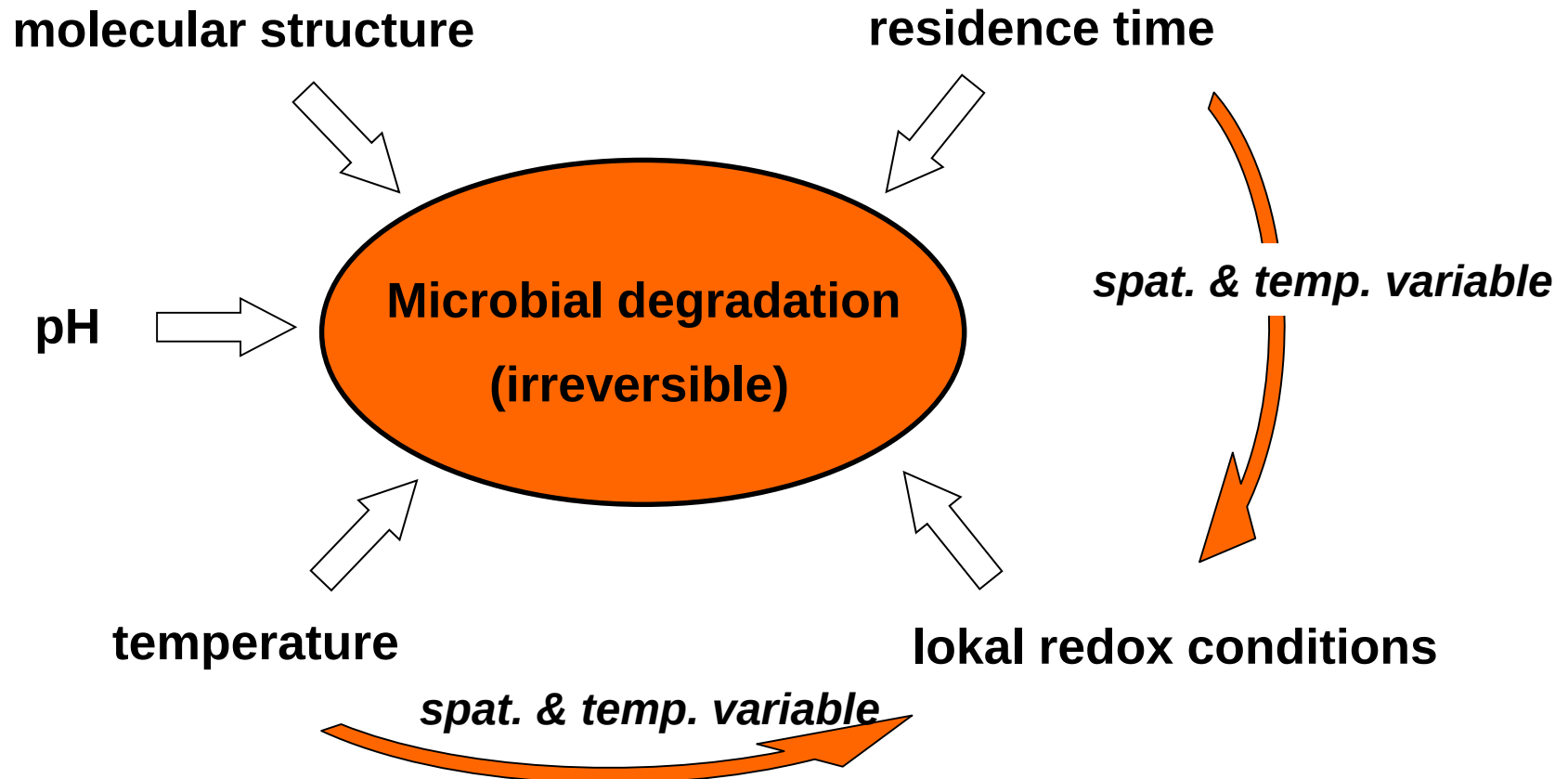


TOrC attenuation is function of temp. & redox conditions

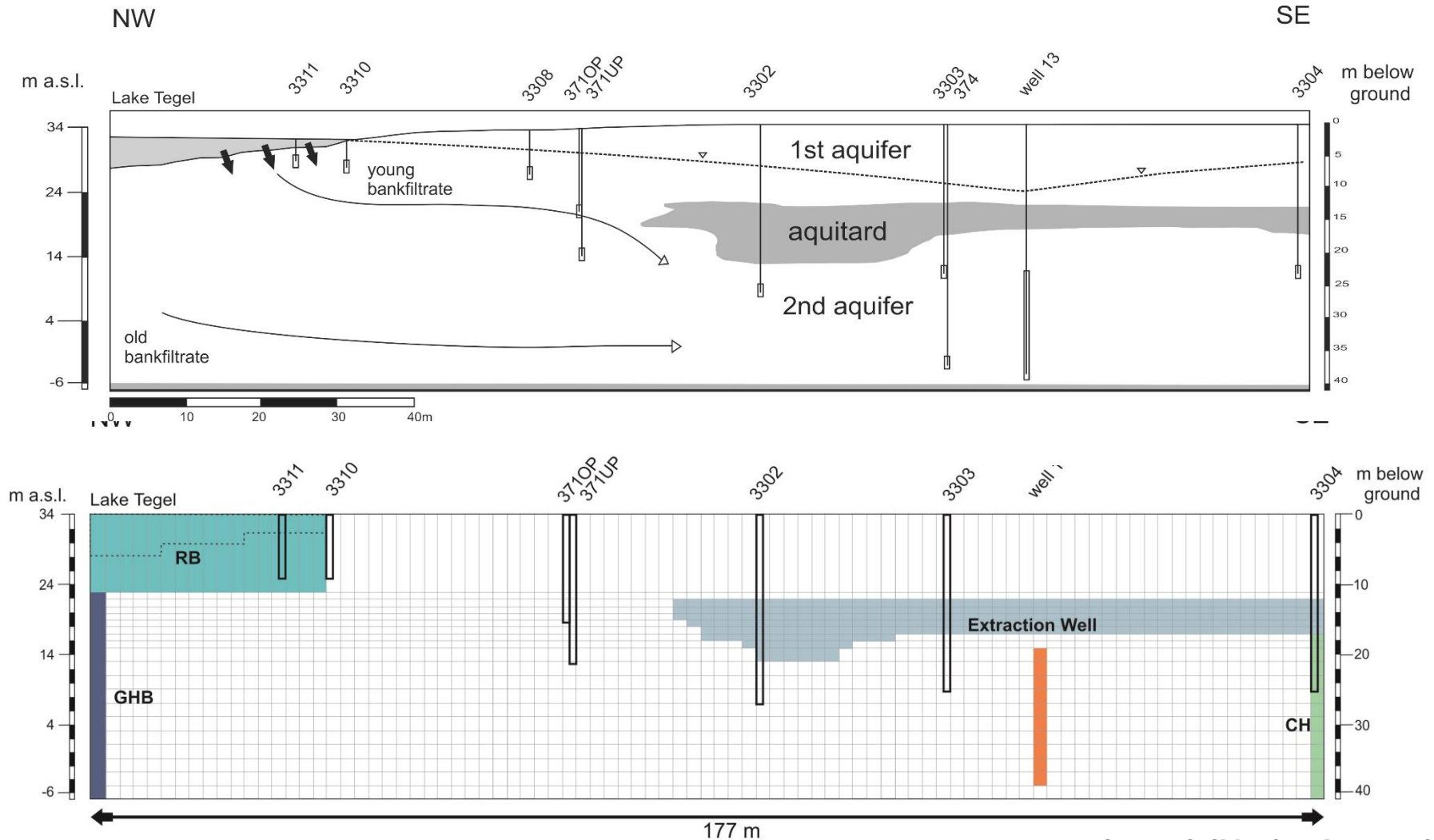
Summer (20 °C)



Factors influencing primary degradation



Research transect and numerical reactive transport model



Temperature dependent reaction kinetics

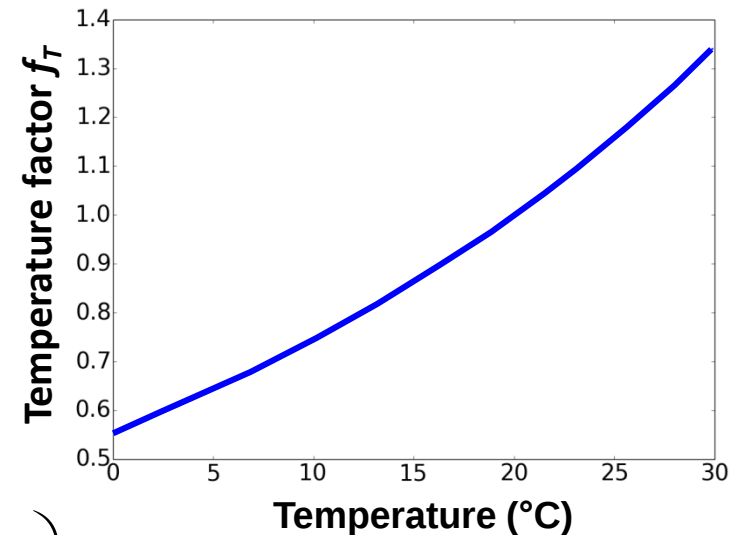
Oxygen reduction

$$r_{ox} = f_T k_{ox} \left(\frac{C_{ox}}{K_{ox} + C_{ox}} \right)$$

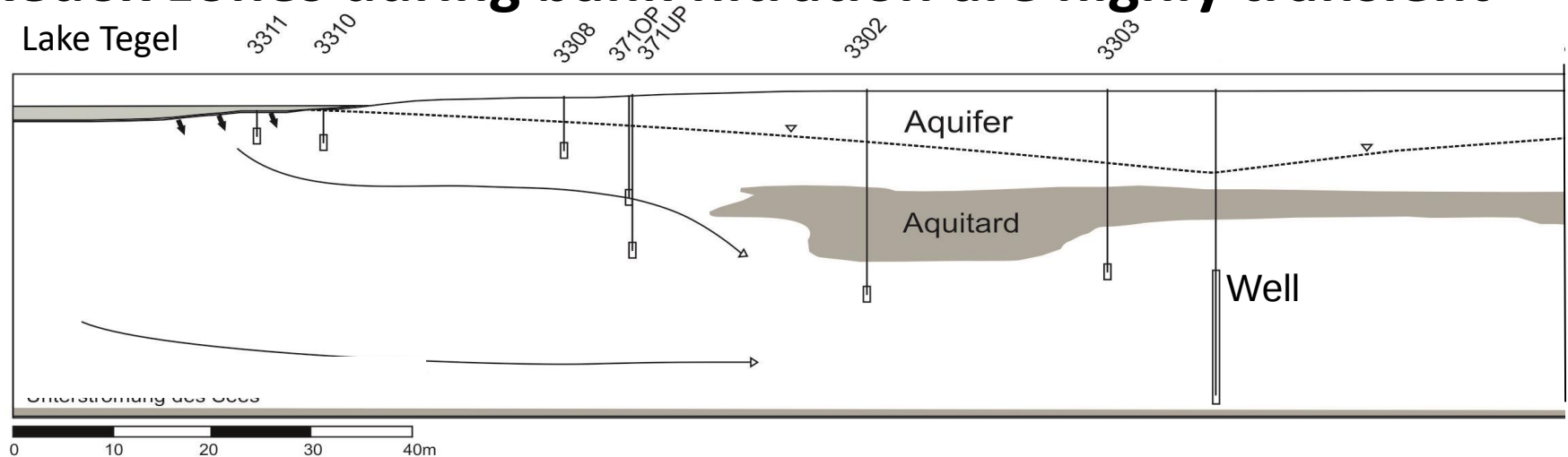
Nitrate reduction

$$r_{nitr} = f_T k_{nitr} \left(\frac{C_{nitr}}{K_{nitr} + C_{nitr}} \right) \left(\frac{K_{ox_inh}}{K_{ox_inh} + C_{ox}} \right)$$

$$f_T = e^{\left(\alpha + \beta T \left(1 - 0.5 \frac{T}{T_{opt}} \right) \right)}$$

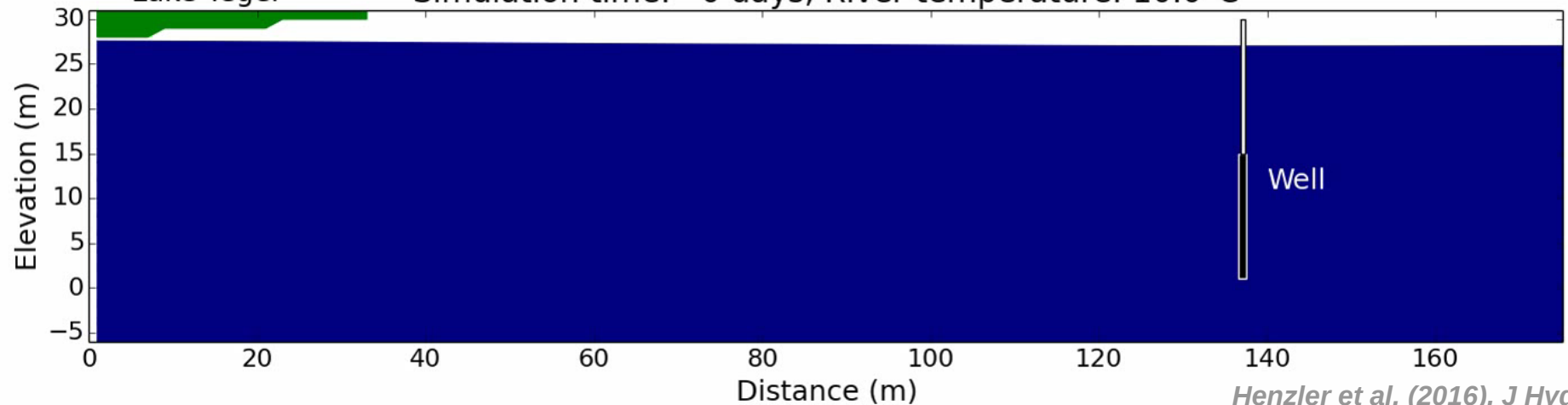


Redox zones during bank filtration are highly transient



■ Oxidic
 ■ Nitrate-reducing
 ■ Mn-/Fe-reducing

Lake Tegel Simulation time: 0 days, River temperature: 10.0°C



SW-GW exchange in the subterranean estuary

- Formation, Characterization and Groundwater Flow Patterns of a Barrier Island Freshwater Lens (Spiekeroog, Northwest Germany)
(Dissertation project Tania Röper 2014)
- Assessment of ground- and porewater-derived nutrient fluxes into the German North Sea – Is there a „Barrier Island Mass Effect“?
(BIME 2016-2020)



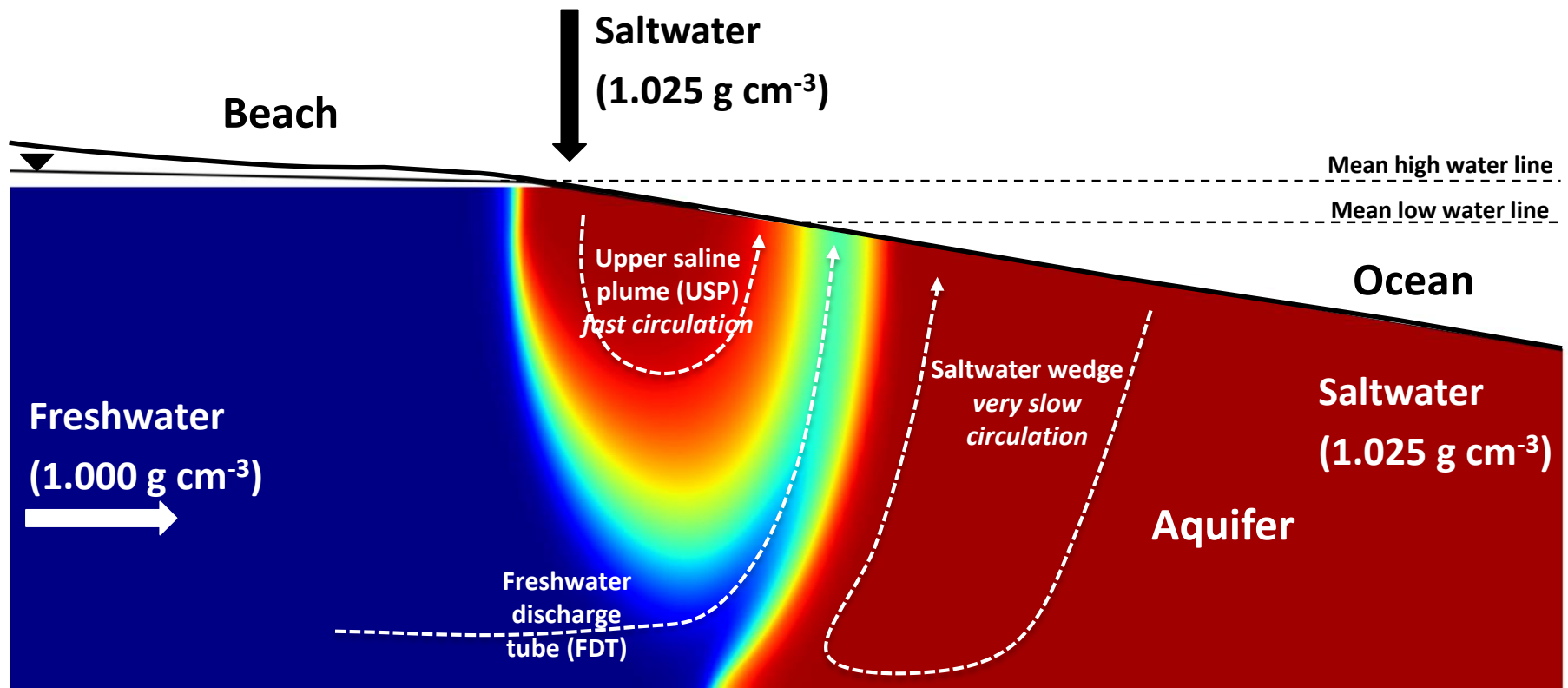
Niedersächsisches Ministerium
für Wissenschaft und Kultur



Objectives and motivation

- To elucidate coupled flow and biogeochemical processes in the subterranean estuary to understand its role with regard to elemental fluxes to the sea
- Motivated by the fact that SGD fluxes affect coastal ecosystems

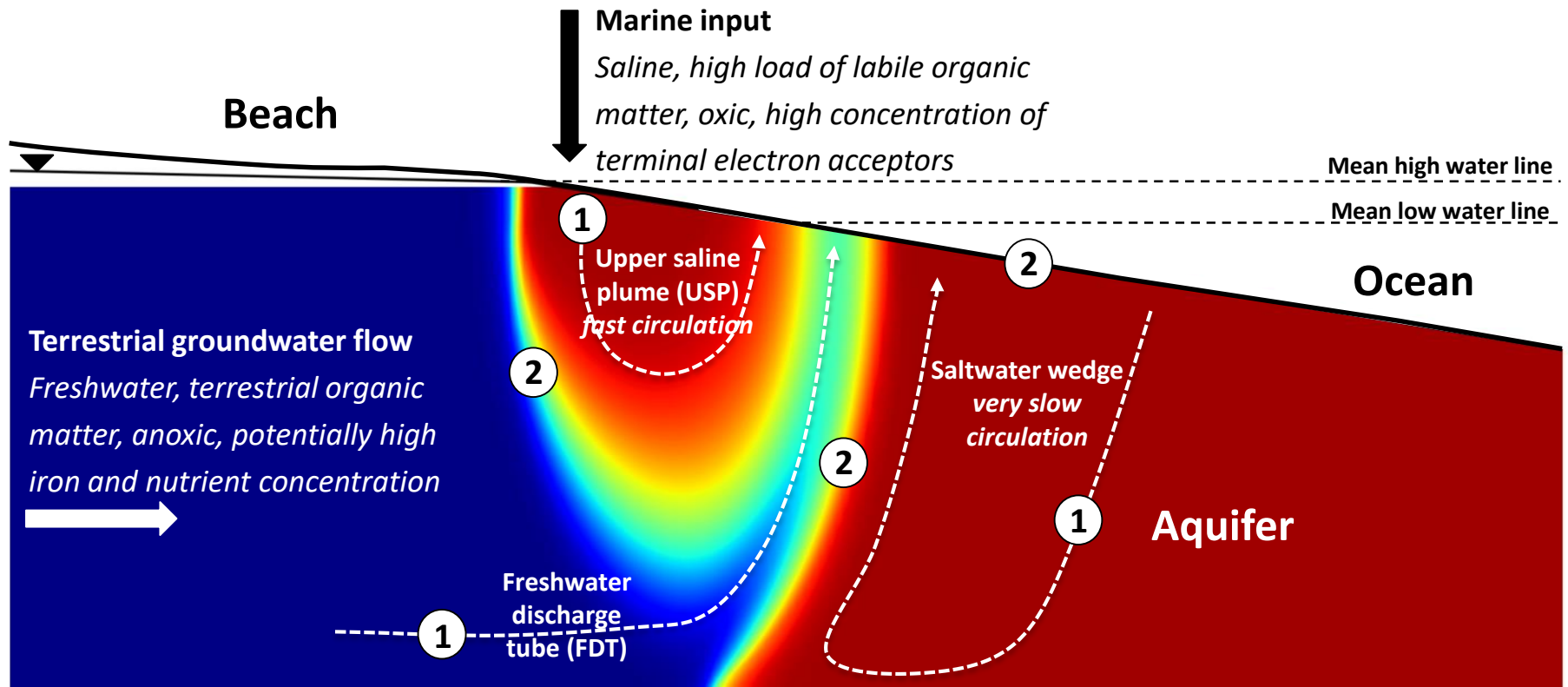
The subterranean estuary under tidal influence



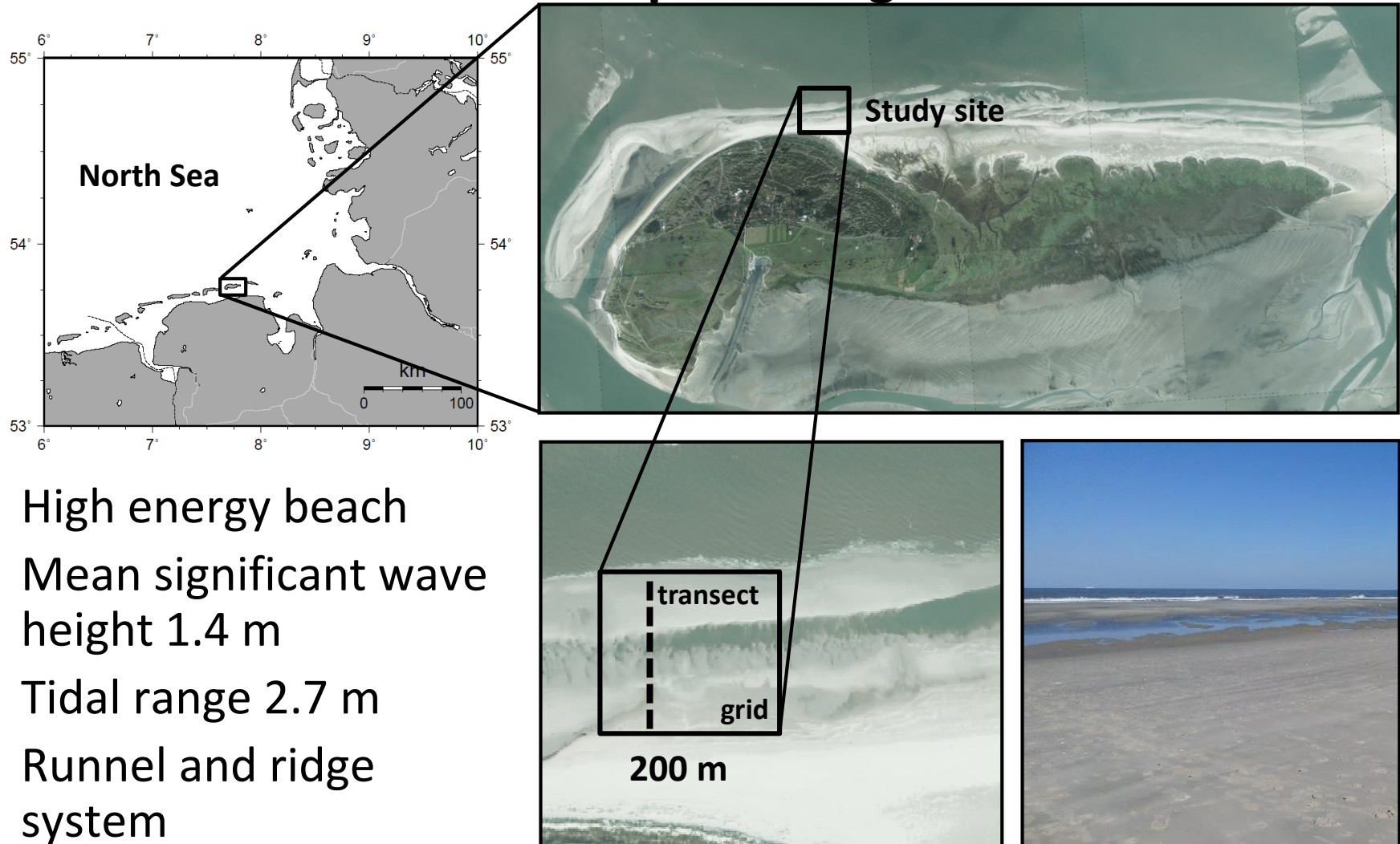
The subterranean estuary under tidal influence

- ① Biogeochemical processes along flow paths

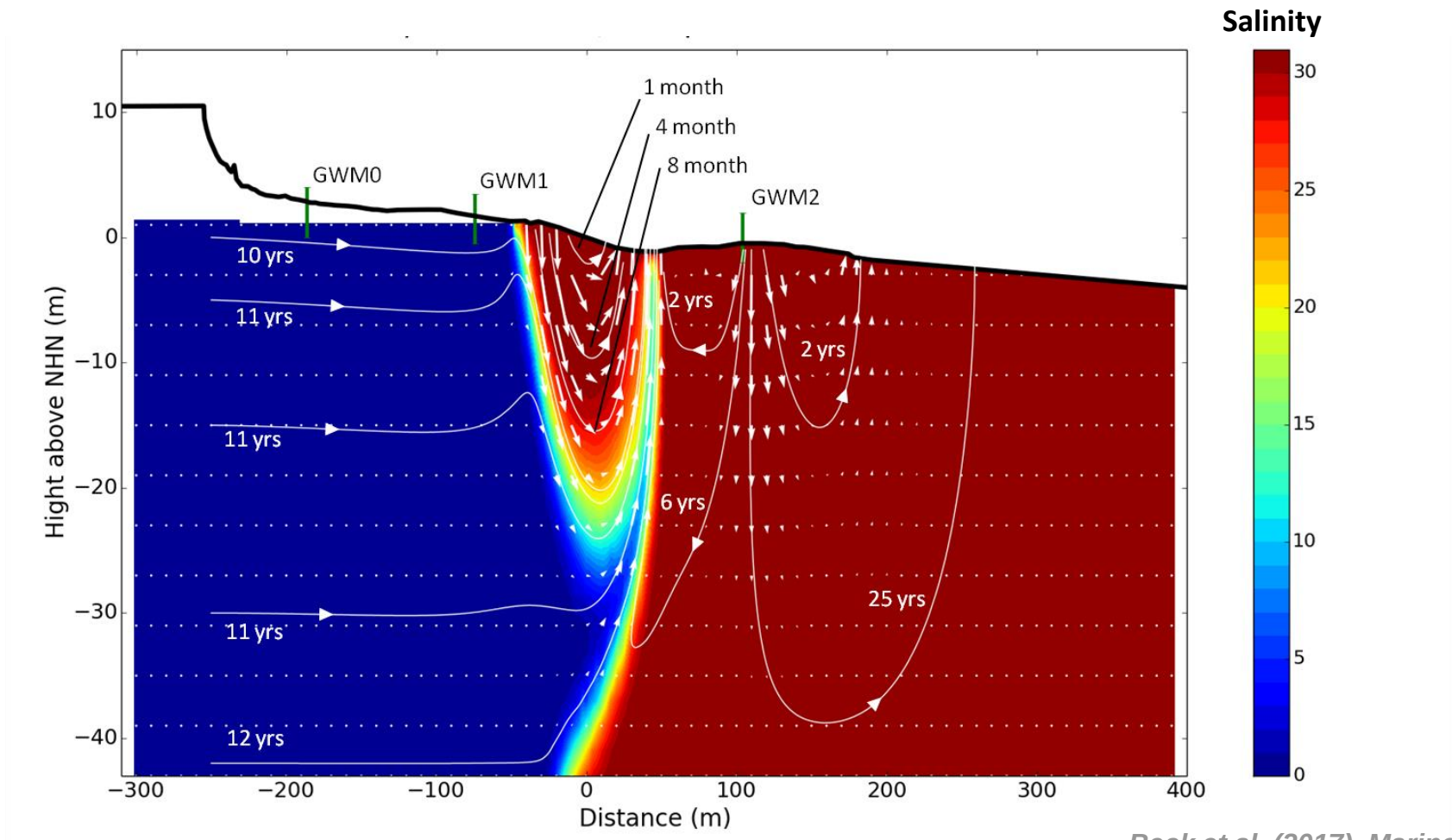
- ② Mixing and biogeochemical reactions across interfaces



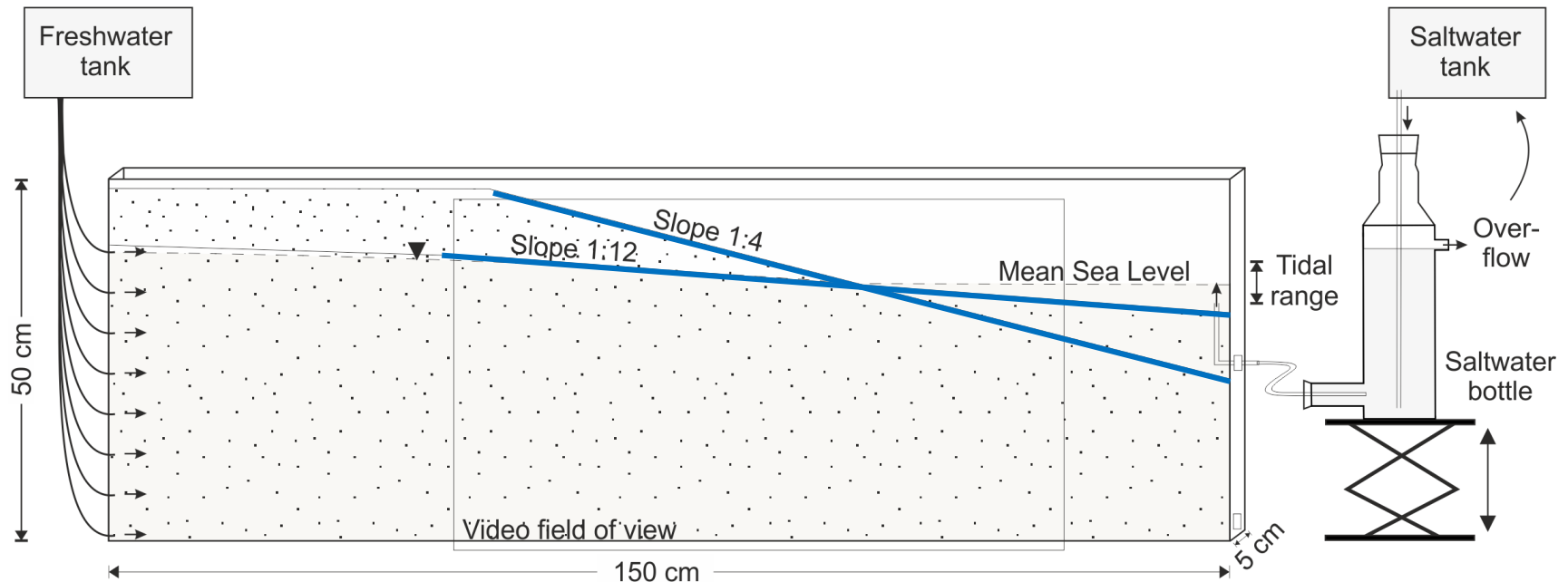
Field site on barrier island Spiekeroog



First model confirms “classic” salinity distribution



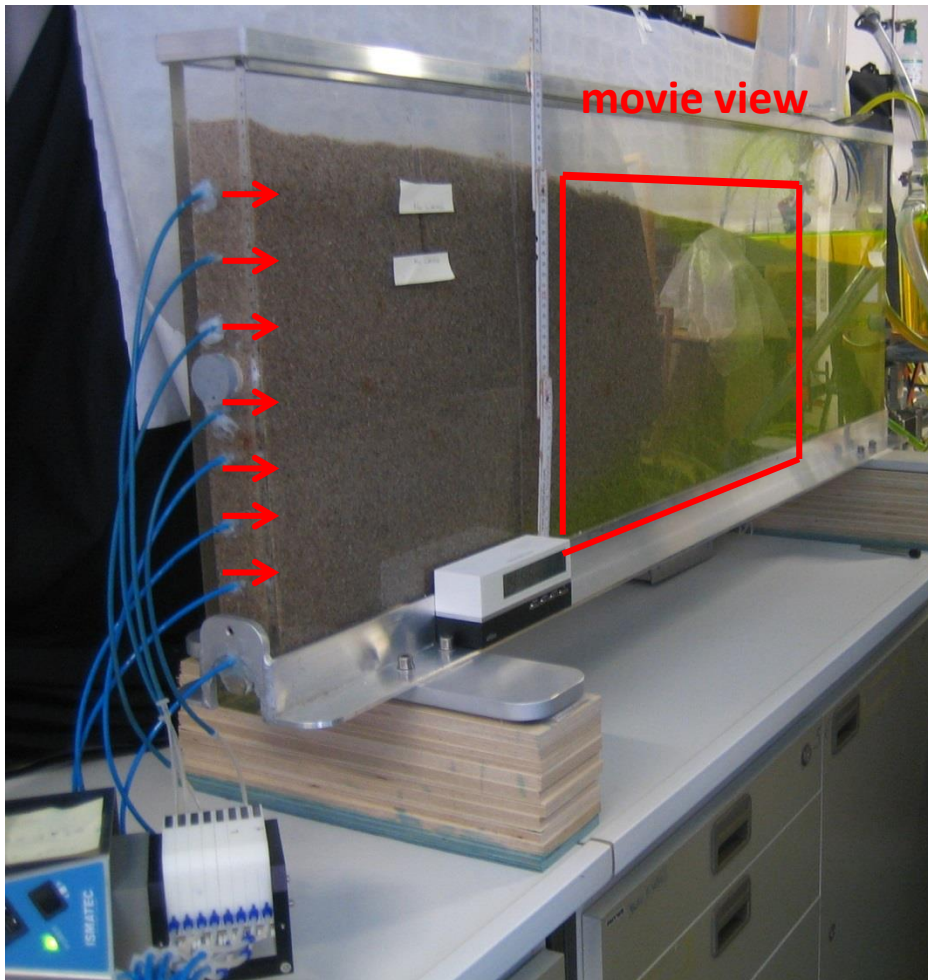
Tank experiments on flow stability



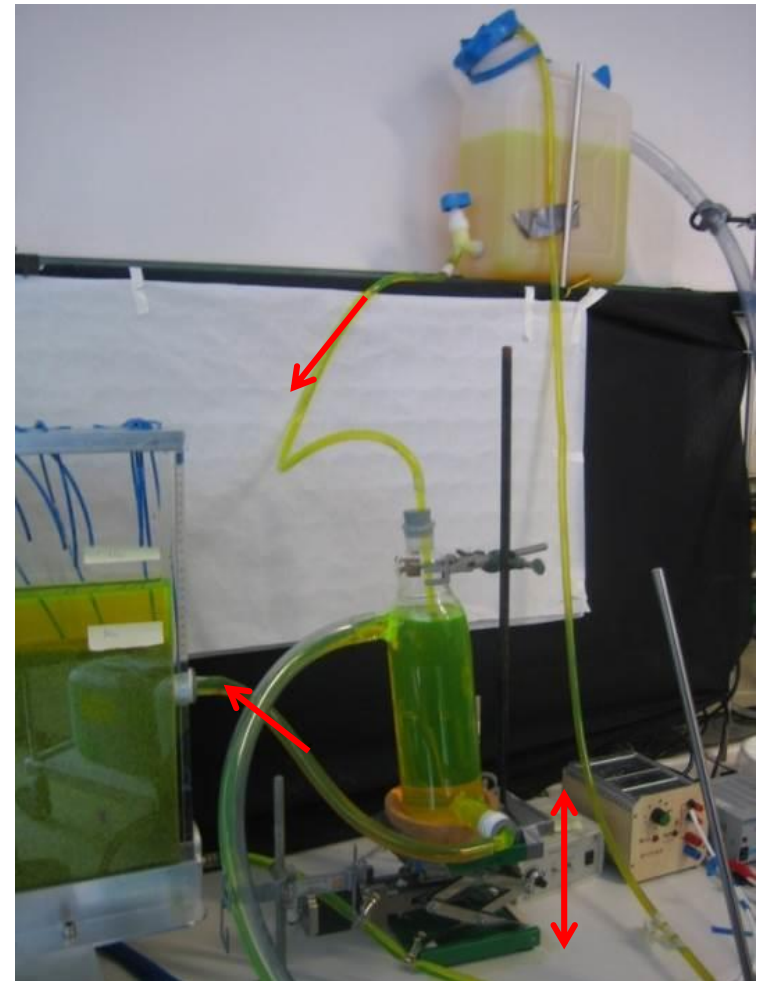
- grain size sand: 0,71–1,4 mm
- hydraulic conductivity (m/s):
 - $8,5 \cdot 10^{-3}$ (sieving)
 - $1,38 \cdot 10^{-2}$ (numerical model)
- SGD rate: 1,2 l/h

- tidal amplitude: 5 cm
- period length: 2 min
- saltwater density: 35 g/l
- Tracer uranine: 1 g/l

Tank experiments on flow stability



Freshwater inflow



Saltwater inflow

Tidal amplitude

Instabilities appear at flat slopes (1:12)

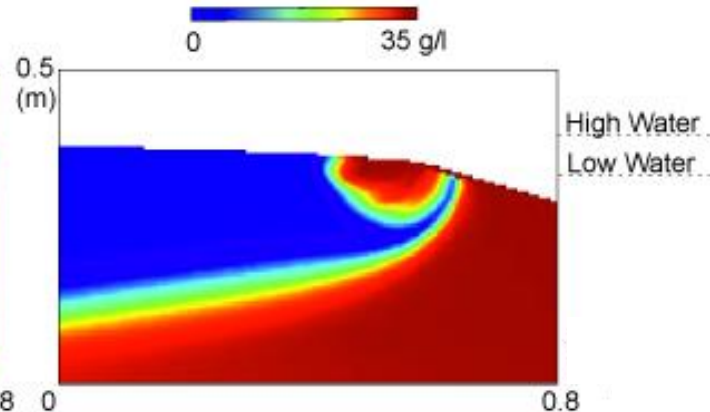
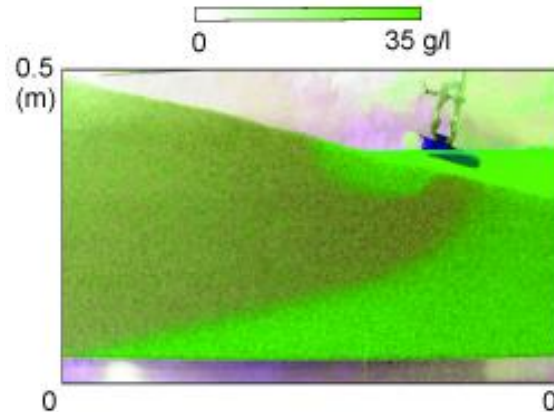


Stable versus instable flow as function of beach slope

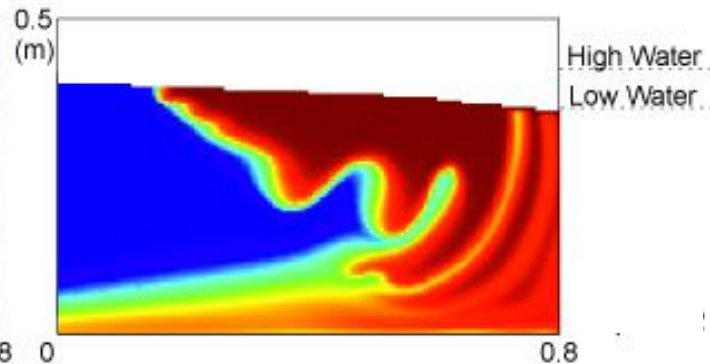
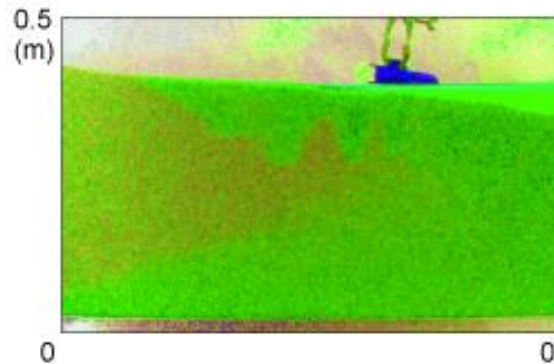
Physical model

Numerical model

Slope 1:4

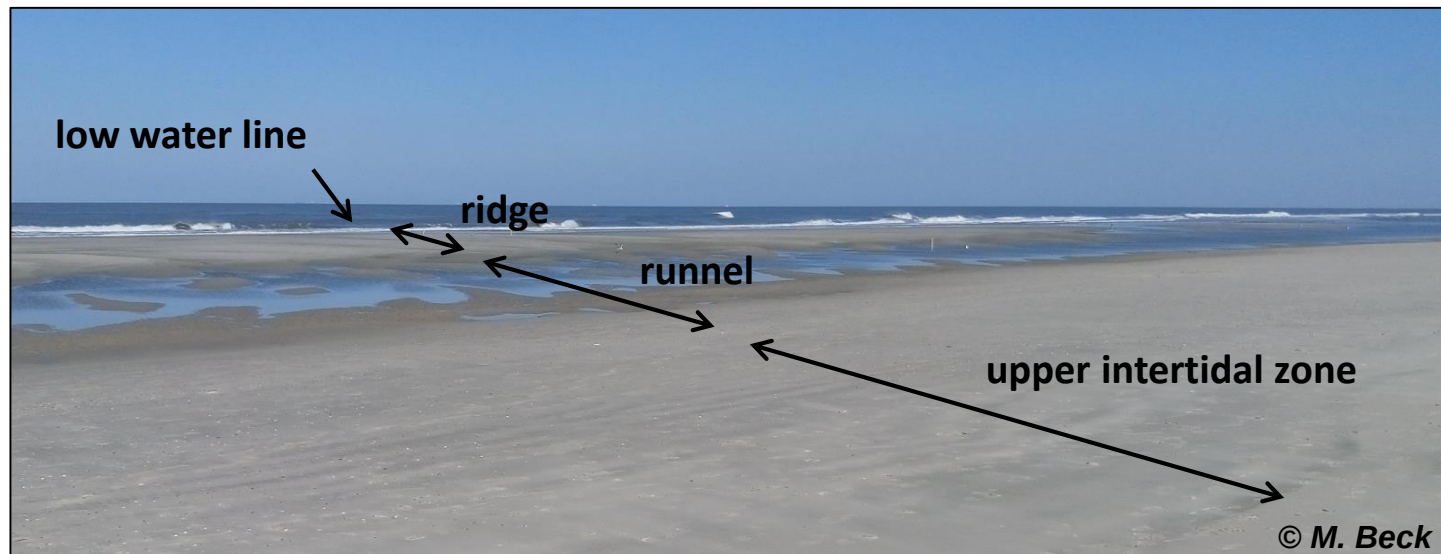
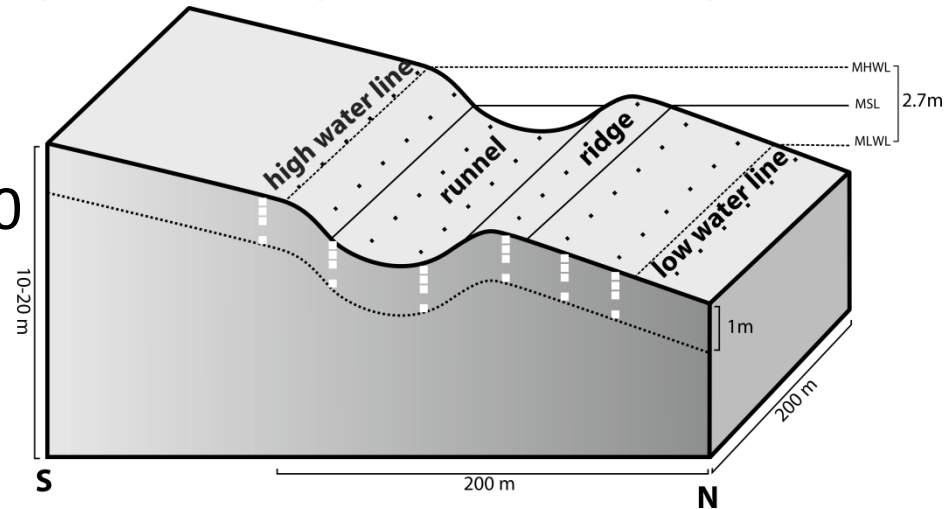


Slope 1:12



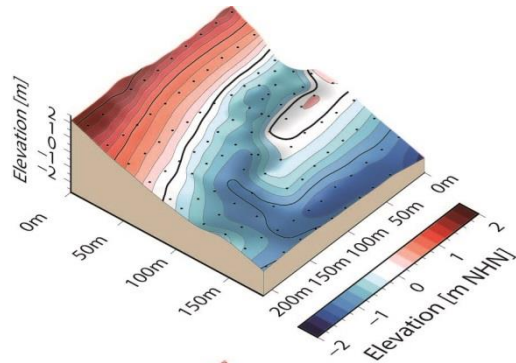
Field data from grid sampling campaign (BIME project)

- Seasonal near-surface porewater sampling (50 & 100 cm depth) of the intertidal zone (200*200m grid)

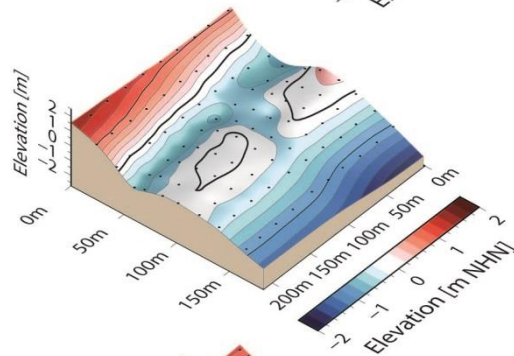


Subsurface flow is function of (highly variable) topography

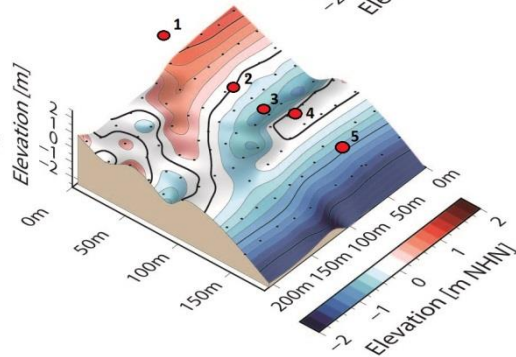
October
2016



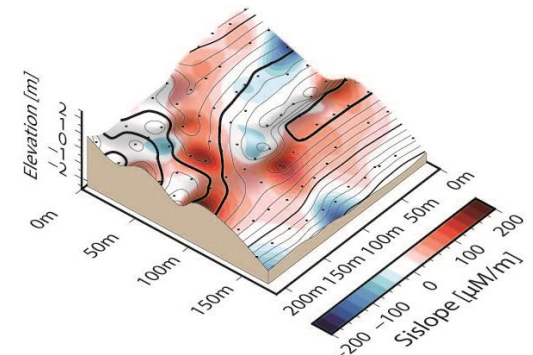
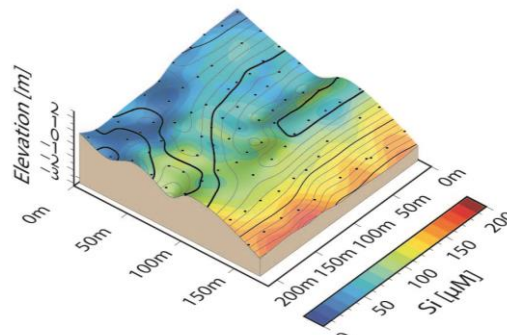
March
2017



August
2017

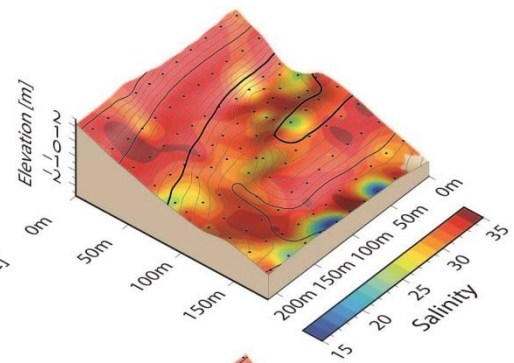
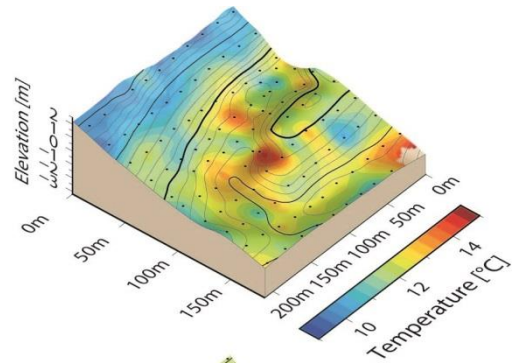
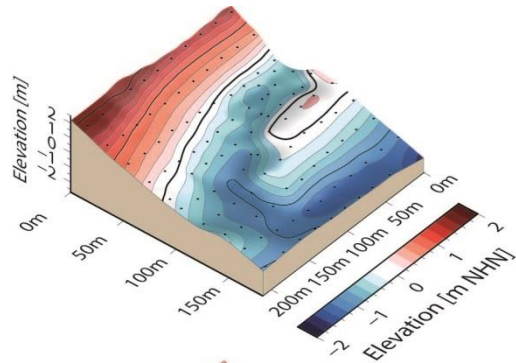


- Si concentrations increase with residence time → elevated at discharge locations
- Si gradients ($\text{conc}_{100\text{cm}} - \text{conc}_{50\text{cm}}$) reveal recharge (red) and discharge (blue) locations following topography

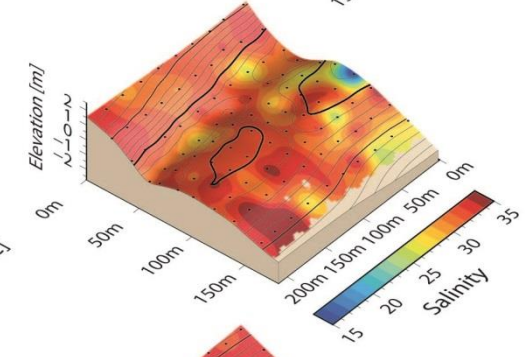
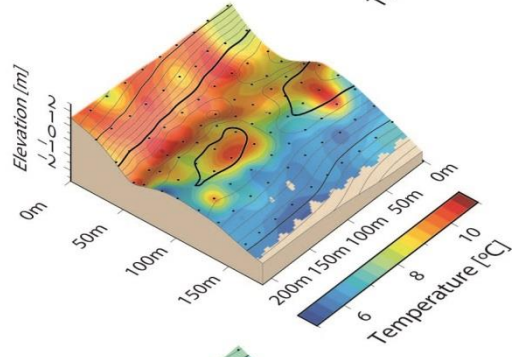
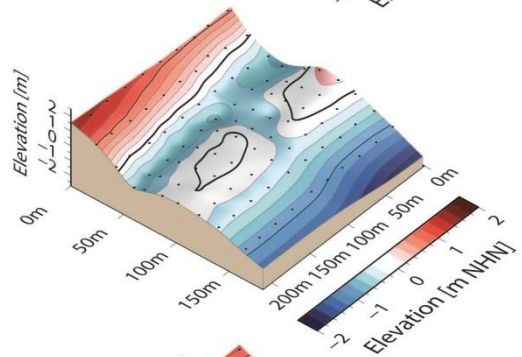


Topography, porewater temperatures & salinities vary

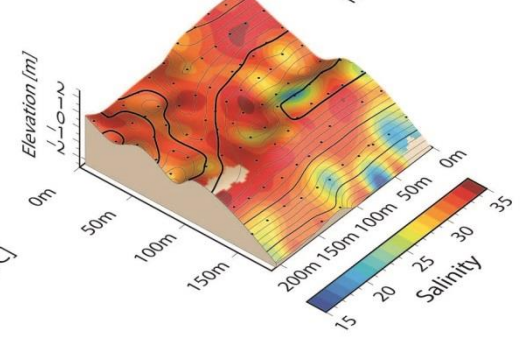
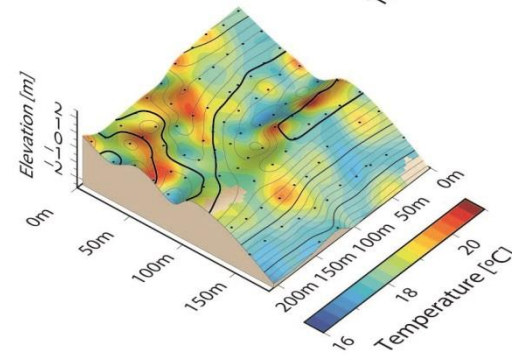
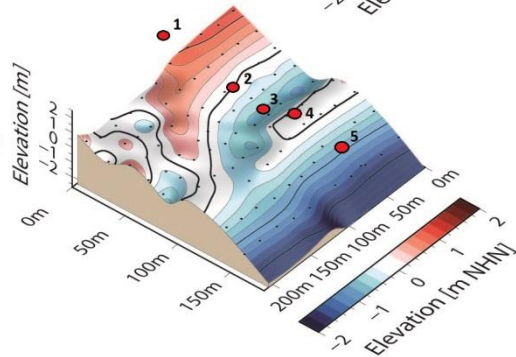
October
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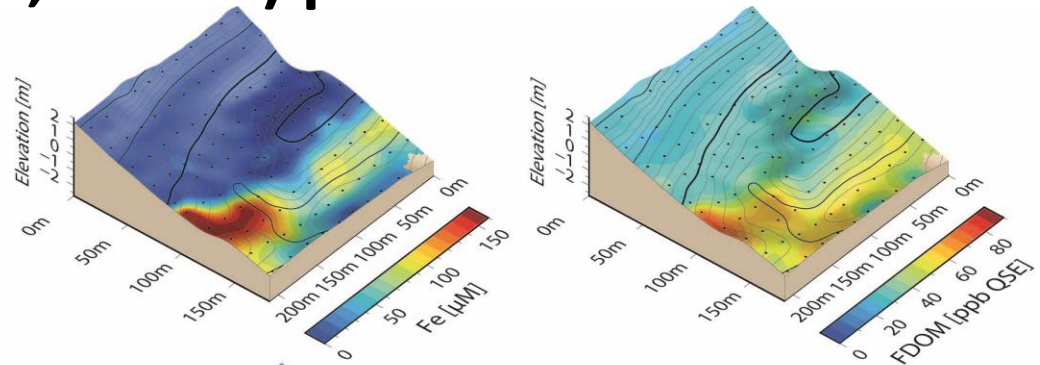


August
2017

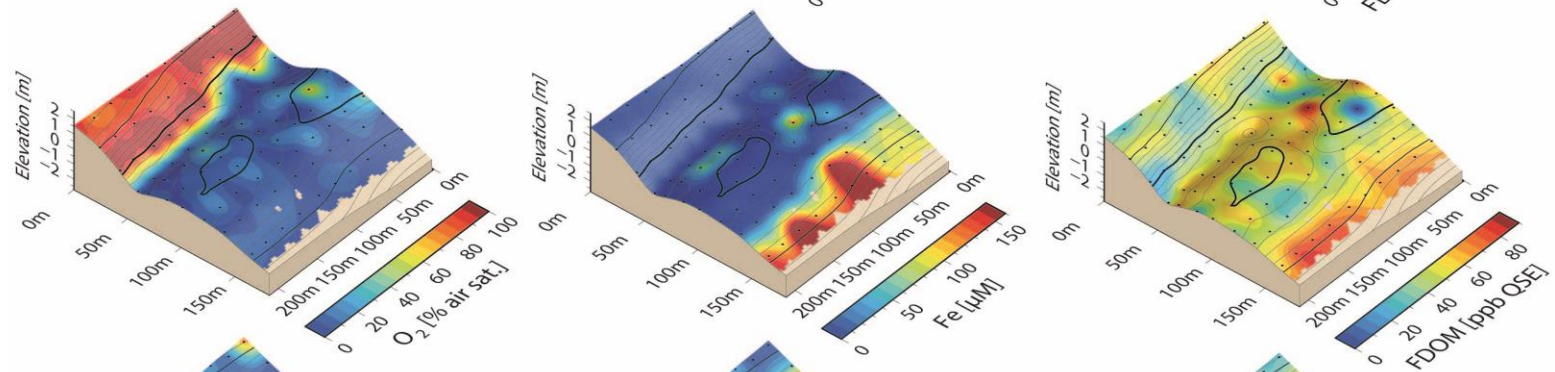


Geochemical (O_2 , Fe, FDOM) patterns are transient

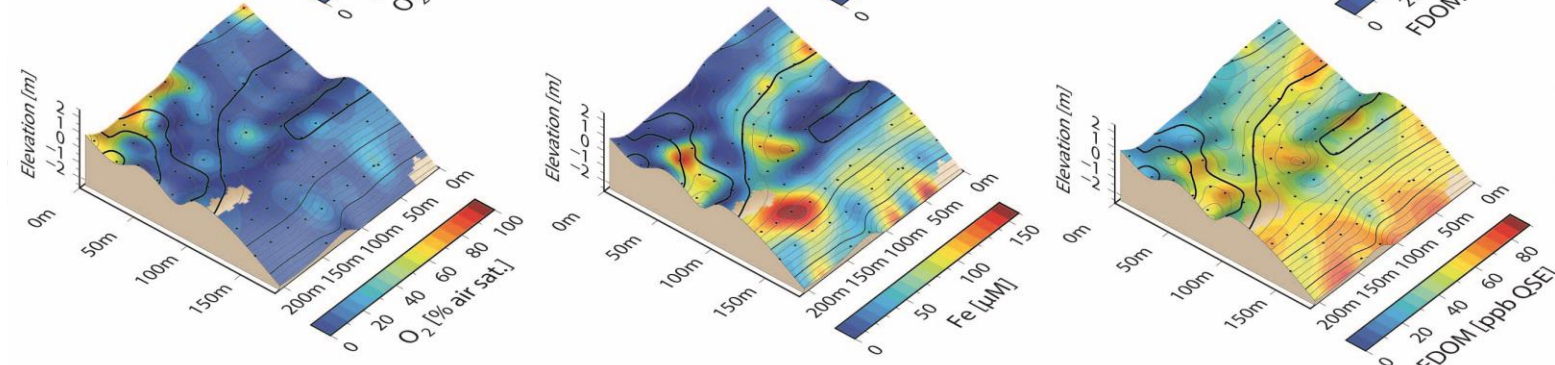
October
2016



March
2017

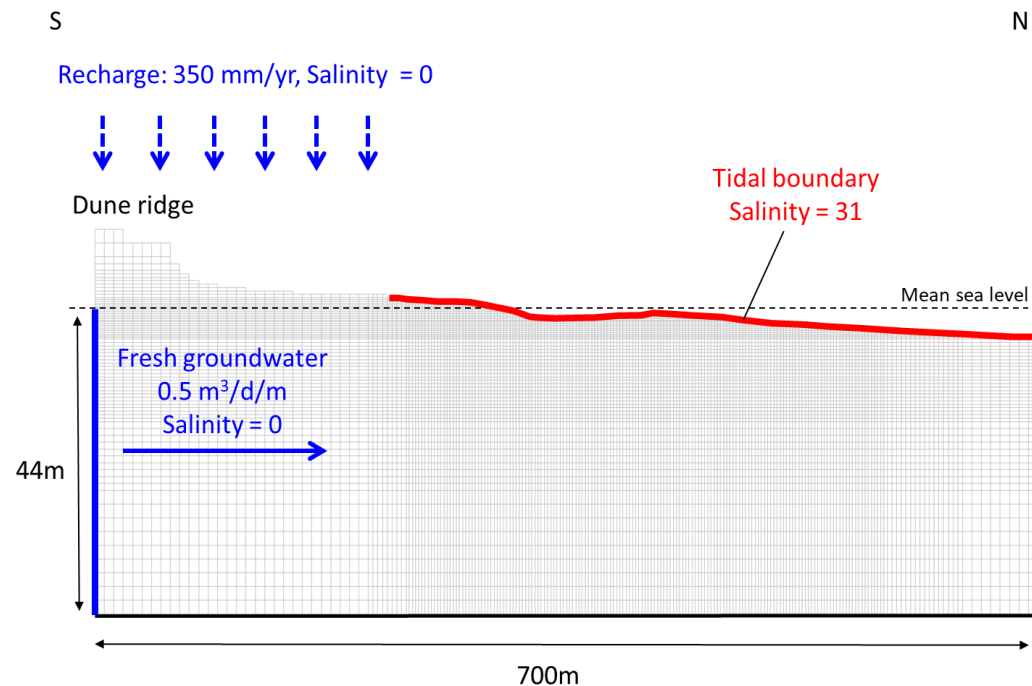


August
2017

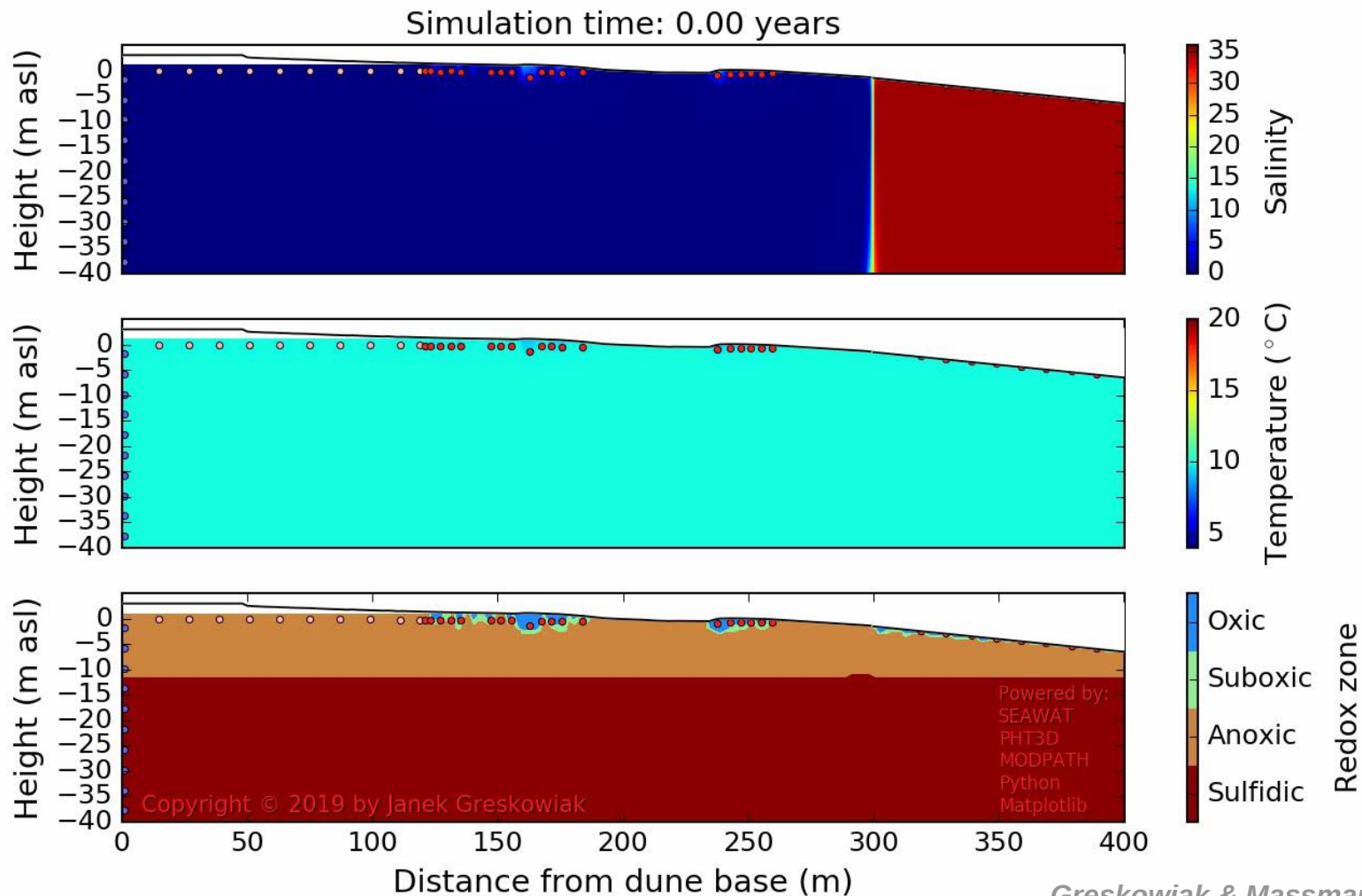


Semi-generic reactive transport model

- SEAWAT/PHT3D model resembling Spiekeroog beach
- Time-variant 3rd type flow boundary at top to (indirectly) account for variable topography
- Three storm-floods per year
- Temperature dependent kinetic redox reactions
- Seasonal oxygen and nitrate input
- No calibration with field data



Salinities, temperatures & redox zones highly dynamic



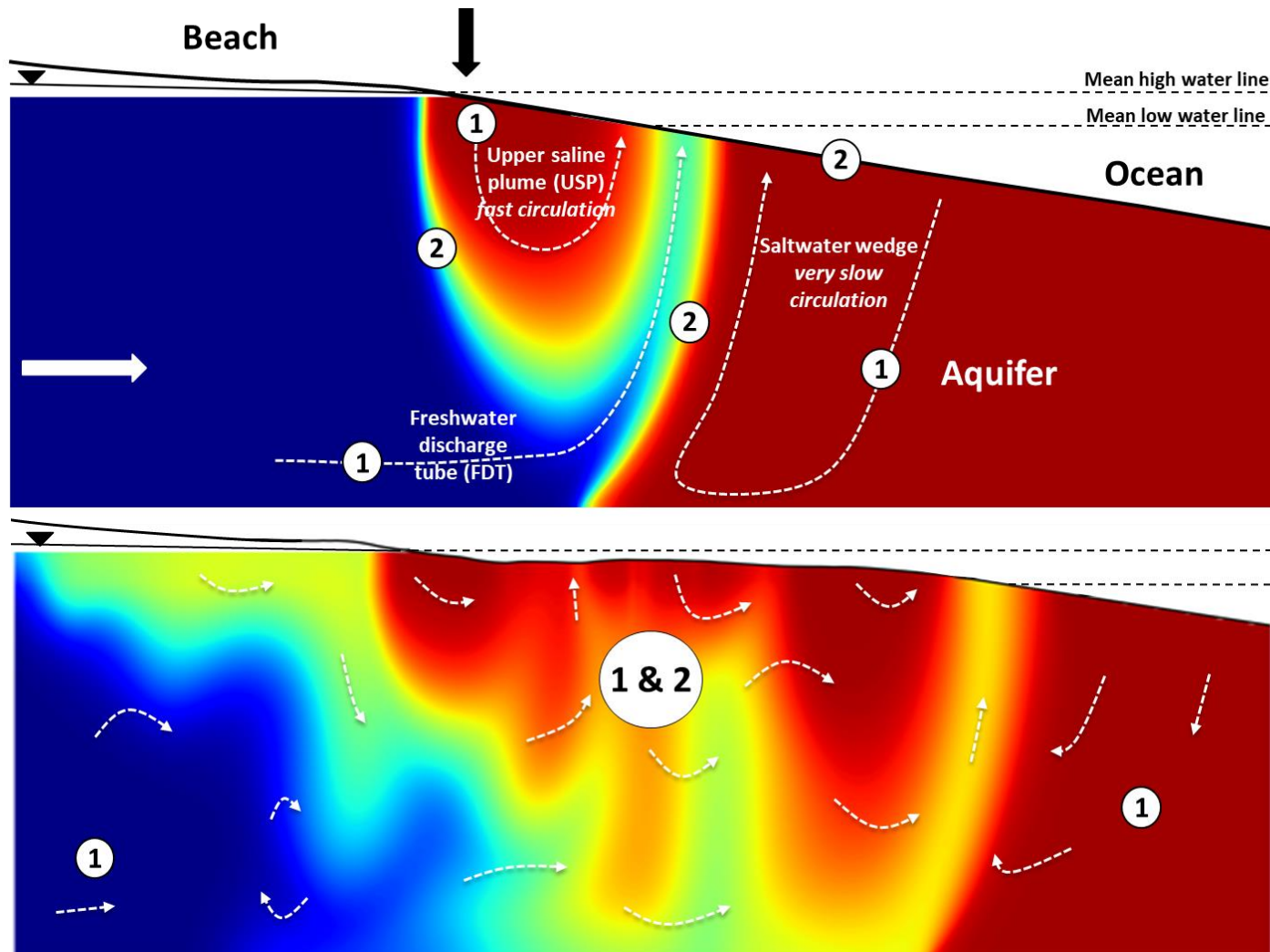
Summary & conclusions

- Seasonal SW temperatures (electron acceptors & DOC input, pumping) cause highly transient subsurface redox conditions during bank filtration → TOrCs affected
- Flow conditions below high-energy beaches most likely highly dynamic, as are geochemical patterns and fluxes
- More high-resolution sampling (time and space) needed to resolve SW-GW exchange processes
- Reactive transport models necessary as transience and interdependencies between morphodynamics, densities, temperatures, redox conditions, attenuation of pollutants cause complex (often non-intuitive) patterns

Thank you to all co-authors of studies cited

- **Berlin:** T. Asmuß, V. Burke, R. Bremermann, U. Dünnbier, J. Greskowiak, A. Sperlich, T. Taute
- **Spiekeroog:** J. Ahrens, Ahmerkamp, M. Beck, T. Birner (Röper), S. P. Böning, H. J. Brumsack, J. Degenhardt, T. Dittmar, C. Ehlert, B. Engelen, J. Greskowiak, N. Grünenbaum, M. Holtappels, K. Pahnke, H. K. Marchant, D. Meier, B. Schnetger, K. Schwalfenberg, H. Simon, V. Vandieken, H. Waska, O. Zielinski
- ... and many more

Transient interfaces throughout subterranean estuary



O₂ reduction (oxic)

$$r_{ox} = -k_{ox} \left(\frac{C_{ox}}{K_{ox} + C_{ox}} \right) f_T$$

Nitrate reduction (suboxic)

$$r_{nitr} = -k_{nitr} \left(\frac{C_{nitr}}{K_{nitr} + C_{nitr}} \right) \left(\frac{K_{ox_inh}}{K_{ox_inh} + C_{ox}} \right) f_T$$

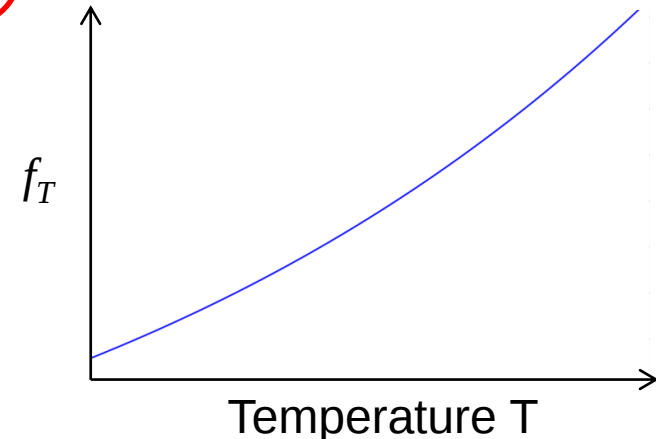
Iron/Sulfate reduction (anoxic/sulfidic) if O₂ and Nitrate are gone

$$r_{fe} = k_{fe} f_T \quad r_{HS} = -r_{SO_4} = k_{SO_4} f_T$$

If $C_{HS} > 10 \mu\text{mol/L} \rightarrow$ sulfidic conditions

$$f_T = e^{\left(\alpha + \beta T \left(1 - 0.5 \frac{T}{T_{opt}} \right) \right)}$$

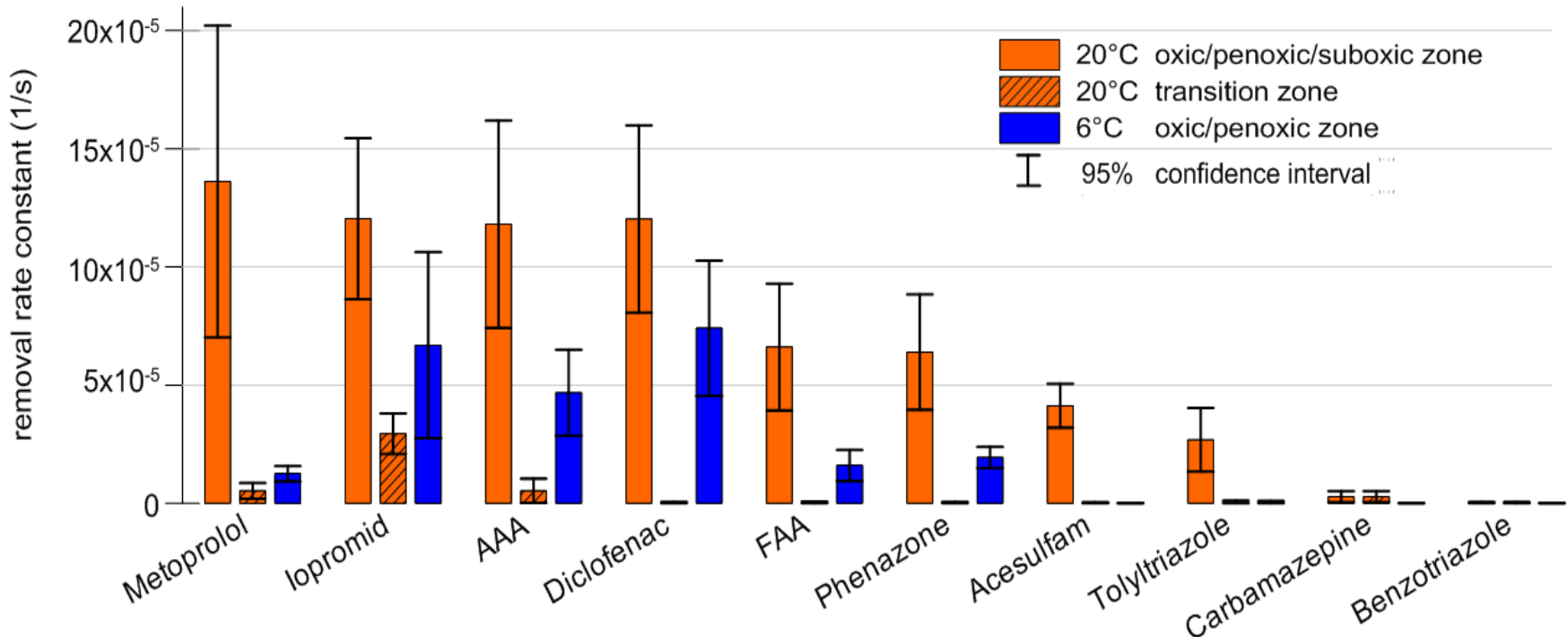
(O' Connell, 1990)



TOrC attenuation is function of temp. & redox conditions

$$c = c_o * e^{-\lambda t}$$

$$t_{1/2} = \ln(2)/\lambda$$

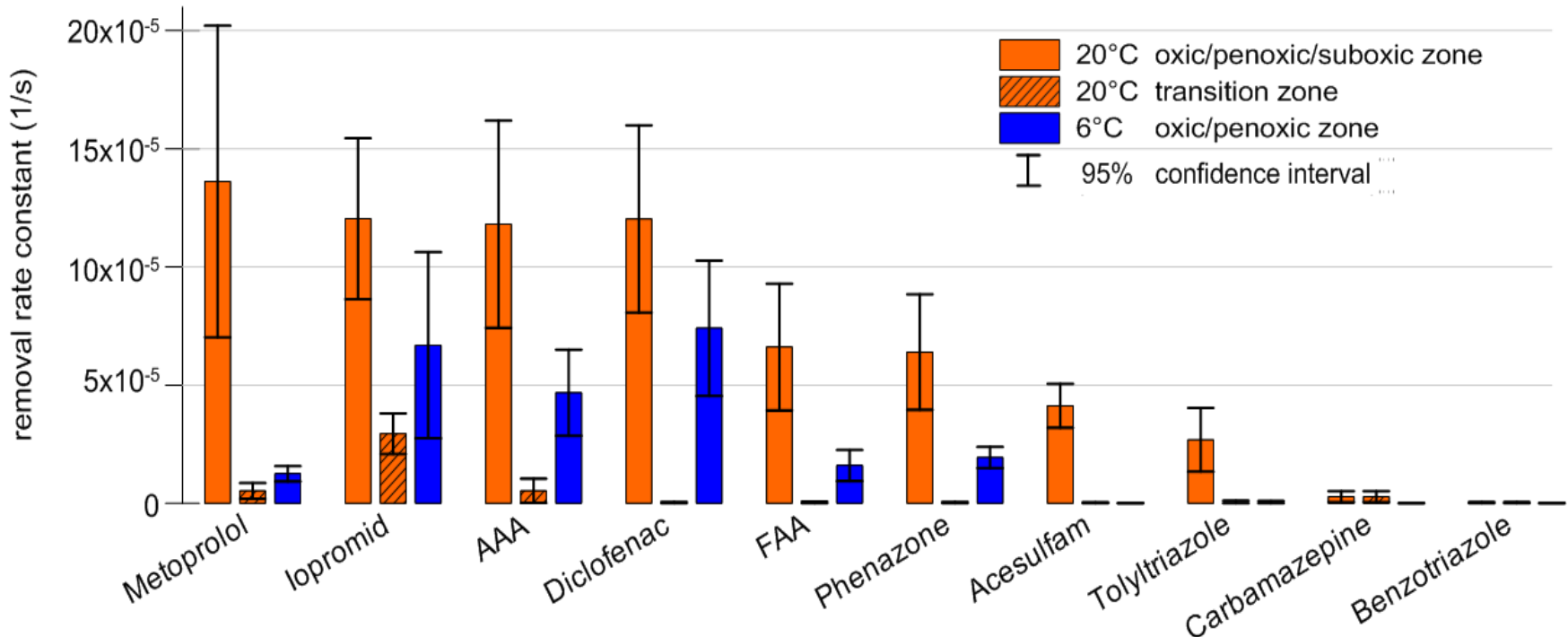


→ warm/oxic > cold/oxic > warm/transition zone (=Mn-reducing)

TOrC attenuation is function of temp. & redox conditions

$$c = c_o * e^{-\lambda t}$$

$$t_{1/2} = \ln(2)/\lambda$$



→ warm/oxic > cold/oxic > warm/transition zone (=Mn-reducing)