

# **Scientific Report of AMBER subproject WP B.5**

## **Geochemical Composition of Groundwater Seepage**

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The major aim of subproject WP B.5 was the hydrogeochemical and isotopic characterization of submarine ground water discharge (SGD). Major research area was the Puck Bay, southern Baltic Sea (Hel peninsula, north Poland, Fig.1). In addition, sampling campaigns were carried out at a site of ground water efflux in the German part of the southern Baltic Sea, close to Meschendorf (Fig.1). In cooperation with the WP B.3, on one occasion investigations were also carried in the Oder lagoon. Field sampling was conducted between years 2009 and 2011 at Hel (7 sampling campaigns), in the Oder lagoon in 2010 (1 sampling campaign), and at Meschendorf in 2011 (3 sampling campaigns). Pore water profiles were taken with pore-water lances and the SGD composition extrapolated based on vertical covariations of geochemical parameters with salinity. In addition results from the time-dependent applications of benthic chambers were used to estimate the composition of SGD. In year 2009, a cruise with the RV Professor A. Penck was carried out to investigate vertical profiles through the water column in the Puck Bay and to retrieve short sediment cores from the central part of the Bay for pore water analyses and further geochemical characterization of SGD. In collaboration with colleagues from Helmholtz UFZ, Halle (S. Weise), a preliminary  $^3\text{H}$  dating of SGD at Hel peninsula was carried out. A more detailed continuation is planned on a final sampling campaign in fall 2011. Sediments affected by SGD were geochemically characterized to derive an estimate for possible compositional changes of the SGD composition due to water-solid interactions and the microbially catalyzed degradation of organic matter. Finally, different possible SGD sources in northern Poland, e.g. ground waters from major aquifers

(Quaternary, Tertiary, and Cretaceous units) accessible via drinking water wells on Hel peninsula and the Polish mainland (Fig.2) were sampled and analyzed for essentially the same set of hydrogeochemical (Sal, pH, Na, Ca, Mg, K, SO<sub>4</sub>, TA, DOC, CH<sub>4</sub>, H<sub>2</sub>S, NO<sub>3</sub>, NH<sub>4</sub>, Si, P, Sr, Ba, Mn, Fe, Mo, Li, Cr, Co, Ni, Cu) and isotopic (<sup>13</sup>C-DIC, <sup>18</sup>O-H<sub>2</sub>O, <sup>2</sup>H-H<sub>2</sub>O, <sup>34</sup>S-SO<sub>4</sub>, <sup>34</sup>S-H<sub>2</sub>S) parameters that were applied to the SGD sites. <sup>18</sup>O-H<sub>2</sub>O and <sup>2</sup>H-H<sub>2</sub>O measurements were carried out at the Museum of Naturkunde, Berlin (U. Struck), and <sup>15</sup>N-NH<sub>4</sub> measurements at IOW by colleagues from WP B.3.

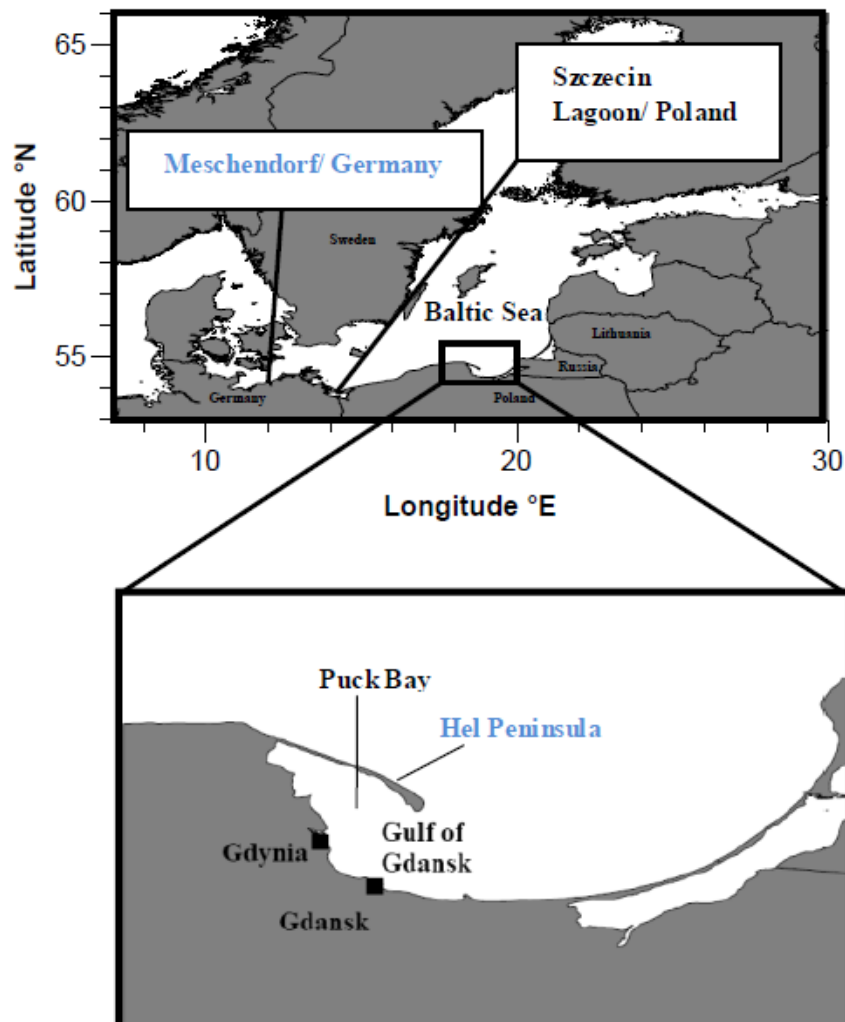


Figure 1: Map with positions of the main study area investigated for WP B.5 in the western Bay of Gdansk and the sampling areas at Meschendorf and the Oder lagoon, all located in the southern Baltic Sea area.

During the field campaigns in the years 2009 and 2010, it was found that low-salinity groundwater escapes at the coast line of Hel Peninsula through seeps within permeable sandy near shore sediments into the Puck Bay. Salinity decreased in shallow pore waters down to 0.5 PSU along with distinctly increasing loads of metabolites. Mixing calculations indicated that the groundwater was anoxic, containing methane (about 0.7 mM), sometimes minor dissolved sulphide or iron. The ground water contained Ca (~ 2 mM), Mg (~ 0.8 mM), and K (~ 0.3 mM). Compared to the brackish bottom water in the Bay, the ground water contained no nitrate, is depleted in Mo, but is enriched in alkalinity, protons, PO<sub>4</sub> (up to 130 μM), Si, DOC (up to 7 mg/L), NH<sub>4</sub>, and Mn. Mixing with brackish bottom waters in the surface sediments led to conservative as well as non-conservative behaviour depending on the specific element. The δ<sup>34</sup>S values of dissolved sulphur species in the pore waters indicated that sulphate in the top sediments was derived from seawater and dissolved sulphide in the essentially sulphate-free groundwater was isotopically heavy. Stable O and H isotopes and <sup>3</sup>H activity were measured in the water column, pore waters and selected well waters for further source and age characterization. δ<sup>18</sup>O and δ<sup>2</sup>H values of Hel pore waters were positioned on a regional meteoric water line and the isotopic composition for the ground water was close to isotope results found in the Cretaceous aquifer sampled from a well on Hel Peninsula. Furthermore, <sup>3</sup>H measurements indicated that the ascending groundwater contained only a small fraction of post 1950s water. This is consistent with a model that groundwater from the Cretaceous aquifer is probably migrating upwards, partially mixing with waters from the Quaternary aquifer where also mineralization of organic matter may take place.

Muddy surface sediments in the central part of Puck Bay are also shown to be affected by SGD. The dilution of the pore water by ascending ground water was only too limited to allow an extrapolation to the original ground water composition.

Ground water found at the Meschendorf coastline was highly enriched in dissolved iron (~ 100  $\mu\text{M}$ ) leading to the precipitation of iron oxides in contact with air or mixing with brackish bottom waters. This led to an effective adsorption of P before and/or when the fresh water mixes with brackish coastal waters.



Figure 2: Map with positions of river sampling stations and drinking water wells that were sampled and analyzed for WP B.5 to analyze a number of hydrogeochemical and isotopic parameters for the comparison with the ground water that was found to discharge through the sediments of the Puck Bay. Yellow squares denote river sites and red circles denote drinking water wells. Basic map taken from Google Earth with modifications.

Results from the WP B.5 have already been presented on the BONUS conferences and several international conferences (e.g., Vogler et al., 2010, 2011). Two manuscripts are in preparation that will be submitted to international scientific journals in late 2011.

All meta data sets from the sampling campaigns are published on the AMBER project homepage.

## References:

- Vogler S., Szymczycha B., Gentz T., Dellwig O., Kotwiczki L., Endler R., Pempkowiak J., Weslawski J.M., Schlüter M. & Böttcher M.E. (2010) The impact of submarine ground water discharge on a coastal ecosystem of the southern Baltic Sea: Results from the BONUS<sup>+</sup> project AMBER. *Geophys. Res. Abs.* 12, #2974
- Vogler S., Dellwig O., Escher P., Struck U., Weise S.M., Szymczycha B., Kotwiczki L., Gentz T., Mörth C.-M., Böttcher, M.E. & Schlüter M. (2011) A multi-isotope (C, O, S, H) and trace metal study in coastal permeable sands affected by submarine groundwater discharge. *Geophys. Res. Abs.* 13, #8757