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The hydrogeochemical evolution of a barrier island freshwater reservoir: Conceptual understanding and identification of key processes

Stephan Seibert (1), Tobias Holt (1), Janek Greskowiak (1), Holger Freund (2), Michael E. Böttcher (3), and Gudrun Massmann (1)

(1) Institute for Biology and Environmental Sciences, Carl von Ossietzky-University, D-26129 Oldenburg, Germany (stephan.seibert@uni-oldenburg.de), (2) Institute for Chemistry and Biology of the Marine Environment, Carl von Ossietzky-University, D-26382 Wilhelmshaven, Germany, (3) Geochemistry & Isotope Biogeochemistry, Institute for Baltic Sea Research (IOW), D-18119 Warnemünde, Germany

Coastal aquifers play an important role in satisfying the water demands for many people in the world. However, exposition to storm surges, climate change and extensive abstraction pose a threat to current and future use of these valuable water resources in many cases. To mitigate water quality constraints and ensure safe water supply applications, an in-depth understanding of relevant process that determine the water quality is required.

We investigated two freshwater reservoirs below the barrier island Spiekeroog, Germany. The main freshwater reservoir is located at the western part of the island, ∼350 years old and has a vertical extension of ∼45m. The other investigated freshwater reservoir is located at the east of Spiekeroog, only a few decades old and has a vertical extension <7m. The ultimate goal of our work is to identify, quantify and model the processes governing the water quality evolution of freshwater reservoirs below barrier islands. During sampling campaigns in 2011, 2014 and 2016, field parameters were measured and samples for major cation and anion analysis were taken from 16 freshwater wells. Additional samples were taken in 2011 (^{3}H-^{3}He, δ^{18}O, δD), 2014 (DOC, HS^-, NH_4^+, phosphate) and 2016 (DOC, HS^-, NH_4^+, phosphate, ^{3}H-^{3}He, δ^{18}O, δD, δ^{13}C-DIC). Based on the collected data, we conceptualized some important hydrogeochemical processes that are potentially relevant at Spiekeroog. This includes cation exchange, calcite dissolution and redox reactions.

The expected freshening time of the main aquifer was estimated by means of the retardation formula for sharp fronts and corresponds to ∼880 years. A 1D PHREEQC simulation showed, however, that the effects of ongoing freshening on the present water quality (after ∼350 years) are negligible. Calculated decalcification rates amount to ∼4.4 mm/year which corresponds to ∼1.5 m downward movement of the decalcification front within the last 350 years. pH values ranging between 7.5-8.5 confirm that groundwater at Spiekeroog is in equilibrium with calcite and underline that calcite dissolution is an important process. With respect to the redox system, the data indicates oxygen and nitrate reduction within the first meters of the saturated zone but Mn-Oxide and Fe-Oxide reduction rates seem to be low in the aquifer based on measured dissolved Mn(2+) and Fe(2+) concentrations. The absence of dissolved Fe(2+) could be explained by the formation of iron sulfide minerals which is in agreement with observed sulfate reduction at greater depth indicated by elevated H_2S concentrations and PHREEQC speciation calculations.