Sea water. The precipitation of FeOOH (‘iron curtain’) at the sediment surface and in the sediments acts as a temporal trap for dissolved phosphate and the (temporal?) impact by the activity of iron-oxidizing bacteria is indicated. The results are further compared to the composition of groundwaters sampled from drinking and observation wells near the Baltic Sea coastline as well as the local isotopic meteoric water line established for Warnemünde.

METHODS

Water samples from the springs and the stream, underlying pore waters, as well as the water column of the Baltic Sea were taken and analyzed following established procedures (Kowalski et al. 2012; Winde et al. 2014). Water aliquots were immediately filtered (0.45 μm membrane filters) for further analyses by ICP-OES (Thermo iCAP 6300 Duo, Thermo Fisher Scientific) and a QuAAtro nutrient analyzer (SEAL Analytical). ICP-OES and SEM-EDX were used to analyze the composition of acidic sediment extracts and the microstructure of FeOOH precipitates, respectively. Measurements of tritium, helium isotopes and neon followed Sueltenfuß et al. (2009). Stable C and S isotopes were analyzed with a Thermo Finnigan MAT253 mass spectrometer attached to a Gasbench II or and Thermo elemental Flash analyzer. Stable water (H, O) isotope measurements were conducted by means of Picarro CRDS systems. All stable isotope results are given in the conventional δ-notation (equivalent to milli Urey) versus respective international standards. Hydrogeochemical results were additionally subjected to a thermodynamic analysis via PHREEQC.

Figure 1. Sketch showing the generation of ferruginous ground water springs and a the development of a subterrestrial mixing zone for SGD with Baltic Sea water at the shore line. Black: Fissured clayish layer.
RESULTS AND DISCUSSION

Spatial and seasonal dynamics of spring waters

Ferruginous fresh groundwaters springs occurring at the shore line of the southern Baltic Sea were investigated on a seasonal base for a period of more than 7 years. The geostationary springs emerge in small pits of up to about 70 cm diameter with up to 15 cm water depth. The shape of the pits and the stream beds, in particular closer to the Baltic Sea water line varied considerably due to regular sediment re-structuring driven by wind and wave activity. The outflowing ground waters are oxygen-free, but rich in dissolved iron, sulfate, phosphate and dissolved inorganic carbon (DIC; Fig.2). They showed constantly minor relative differences between springs through the years, with an exception for redox-sensitive elements like Fe$^{2+}$ that are further impacted by storm-related redistribution of surface sediments.

Figure 2. A-C Temporal dynamics of selected dissolved major and minor components and the stable isotope composition of DIC and SO$_4$ for three springs waters. D: In-situ measurements at spring Q1 during winter time.

Tritium-noble gas dating indicates ages between 25 and 35 years, with surprisingly high different mixing contributions from older tritium-free waters. This indicates a high complexity of the hydrogeology of the coastal aquifers with aquifers essentially build of glacial deposits. The observed differences in ground water composition reflect heterogeneous flow path conditions (including residence times) before reaching the Baltic Sea shore line, highlighting the importance of local and regional investigations in the evaluation of the impact SGD discharge on the transport of substances (DIC, nutrients, metals) into coastal ecosystems. The hydrogeochemical and stable isotope composition
indicates that the spring water composition is controlled by the dissolution of biogenic carbon dioxide in the unsaturated soil zone of the catchment area followed by the dissolution of marine carbonate and biogenic pyrite in the sediments building up the aquifers (e.g., Zhang et al. 2012; Donis et al. 2017).

**Processes impacting stream water composition in air contact**

Each springs leads to a surface run-off towards the Baltic Sea. After flowing for several meters in contact with the atmosphere, the fresh water is lost to underground drainage through the beach sands reaching a mixing zone with brackish Baltic Sea waters and finally ending as submarine ground water discharge (SGD). Surface flow is associated with the uptake of gaseous oxygen, the microbially promoted precipitation of iron oxi(hydroxi)des, adsorption of phosphate (Fig.3), the loss of isotopically light carbon dioxide into the atmosphere, and probably minor calcite precipitation. Spring waters are saturated with respect to calcite, but undersaturated with respect to other rock-forming minerals like dolomite and gypsum, turning into calcite supersaturated solutions along the surface flow-path. According to our present conceptional understanding (Fig.1) an essentially anaerobic flow path directs fresh ferruginous ground water into a mixing zone with aerobic Baltic Sea water. This leads to physico-chemical and geomicrobiological changes in the composition of the aqueous solution and the surrounding sediments. This process is superimposed by the spring waters that are modified by the precipitation of FeOOH and associated adsorption of phosphate and arsenic, before seeping away into the mixing zone. This iron curtain acts as a temporal sink for Fe and P in the coastal sediments that may be transported into the Baltic Sea ecosystem during storm events.

**Figure 3.** A and B: SEM-EDX analysis of a FeOOH sample from the surface sediments of the stream. C and D: Residual leftovers of Fe oxidizing bacteria (e.g., Leptothrix) in the stream bed.
Comparison with ground waters in the catchment and other SGD sites

The hydrogeochemical and stable isotopic composition of the ferruginous springs is close to those found in some ground waters of Mecklenburg-Western Pomerania. Coastal pore waters in front of the Hüttemoor area are impacted by subterrestrial freshening due to SGD originating from the rewetted peatland. The estimated composition of this fresh water component differs substantially from the springs found close to Kühlungsborn, likely due to a substantial overprint by early diagenetic reactions taking place in the marine sediments and a hydrological cycle in the peatland that may differ from the one in the catchment of the ferruginous springs.

ACKNOWLEDGEMENTS

This study was partly conducted within the framework of the Research Training Group 'Baltic TRANSCOAST' funded by the DFG (Deutsche Forschungsgemeinschaft) under grant number GRK 2000 (www.baltic-transcoast.uni-rostock.de). The research was further supported by BMBF within the BONUS project AMBER, and Leibniz IOW. Thanks are due to R. Bahlo, A. Köhler, and I. Scherff for technical support. This is Baltic TRANSCOAST publication no. GRK2000/0009.

REFERENCES


Contact Information: Michael E. Böttcher, Geochemistry & Isotope Biogeochemistry Group, Marine Geology Department, Leibniz IOW, D-18119 Warnemünde, FRG, email: michael.boettcher@io-warnemuende.de.