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The hydro- and multi-isotope geochemistry of iron-rich ground waters emerging at the southern Baltic Sea coast line

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Iron-rich groundwater springs emerging at the shore zone of the southern Baltic Sea (BS; Site Meschendorf) were examined on a seasonal base for a period of about two years. Besides major, minor, and trace elements, stable isotopes of water (H-2, O-18), dissolved inorganic carbon (DIC; C-13), and sulfate (S-34) were analyzed. The stream bed sediment was extracted for the geochemistry of the newly formed precipitates and further characterized via SEM-EDAX. Subsequently, the hydrogeochemical results were subjected to a thermodynamic analysis via the PHREEQC speciation model.

The springs emerge from small pits (about 60 cm diameter; up to 15cm depth). Surrounding sediments are sandy with gravels found at depth and corresponding high permeabilities. The positions of different springs on the shore zone were stable during the investigation period while the shape of the pits and the stream beds may vary due to wind- and wave-driven forces. Selected measurements of spring yield discharges close to 10 L/min. The H-2 and O-18 contents of the spring waters indicate the ground water to originate from relatively young mixed meteoric waters. The hydrochemistry of the springs was similar and showed some variability in between which indicates that the genetic processes for the ground water before reaching the surface may slightly differ. The springs are characterized by dissolved Ca, Mg, Na, DIC and sulfate, mainly reflecting the interaction with soils and bedrocks in the recharge area that is dominated by marly till. The oxygen-free ground water is rich in Fe, P, and DIC. Iron and dissolved sulfate originate from the oxidation of pyrite, as further confirmed by the 34-S signature of sulfate. The carbon isotope signature of DIC indicates a mixture of biogenic CO_2 from the soil zone with some water-rock interaction with carbonate minerals. The streams flow towards the BS and, in contact with the atmosphere, outgas carbon dioxide and takes up oxygen. Upon CO_2-degassing, C-12 is preferentially desorbed from the aqueous solution. The changes in the stream composition lead to the formation of iron(oxyhyr)oxide precipitates in the stream bed before the waters pass to underground drainage into a subterranean mixing zone with brackish BS waters. These ochrous precipitates act as a sink for dissolved phosphate and minor calcium. P : Fe ratios and Ca : Fe ratios are about 0.08 and 0.2, respectively, which are caused by P adsorption and a mixture with minor $CaCO_3$ and/or Ca-phosphate.

The investigation reveals that the surface precipitation on the beach leads to the formation of SGD essentially free of dissolved iron and strongly depleted in phosphate. Similar iron phases may also be an important part of the subterranean estuary supposed at that coast line, where retention of nutrients and heavy metals by iron(oxyhydr)oxides could influence the release of nutrients into the coastal ecosystem. Fe- and P-rich surface precipitates, however, are transported in suspension into the Baltic Sea during wind-driven flood events.

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