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Anoxic groundwaters as a source of CO_2 and PO4 for the coastal southern Baltic Sea: The role of an iron curtain

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Submarine ground water discharge (SGD) into coastal ecosystems is perceived as an important source of fresh water and solutes (nutrients, metabolites, trace elements) in marine biogeochemical cycles. Less is known about its significance for the German coastal zone. We present here the results of hydrogeochemical and stable isotope geochemical studies in an area that is affected by SGD into the southern Baltic Sea.

Anoxic groundwaters emerging as springs at the shore zone of the southern Baltic Sea are windows into the composition of subterrestrial ground water composition. They were investigated on a seasonal base for about five years. Water samples were analyzed for the concentrations of major and trace elements, pH, and the stable isotope ratios of water, DIC and sulfate. Newly formed precipitates in the stream bed were characterized via SEM-EDX and the stable isotope composition, as well as chemically extracted for the determination of the solid composition.

The springs emerge in small pits yielding discharges of about 10 l/min each. Surrounding sediments are sandy with gravels found at depth and corresponding high permeabilities. The positions of different springs on the shore zone were geostationary during the investigation period while their shape varied due to wind- and wave action. The 2H and 18O contents of the spring waters indicate the ground water to originate from relatively young mixed meteoric waters. Dating by means of tritium and noble gases (3H, 3He, 4He, Ne) yields an age of the spring waters of about 25-32 years, with different mixing proportions of tritium-free waters.
The springs are hydrogeochemically characterized by dissolved Ca, Mg, Na, bicarbonate, and sulfate, mainly reflecting the water-rock interaction with aquifer material in the recharge area. The isotope signature of DIC indicates the uptake of biogenic CO_2 in the soil zone followed by the dissolution of carbonate minerals in the soil/ aquifer system.
The oxygen-free ground water is rich in dissolved iron (Fe) and phosphorous (P). Iron(oxyhydr)oxide precipitates in the stream beds acting as a sink for dissolved PO4 and minor Ca. The investigation reveals that the surface precipitation on the beach leads to the formation of submarine groundwater discharge essentially free of dissolved Fe and PO4. The formation of Fe-phases in the subterranean estuary is supposed at depth influencing the release of nutrients and metals into the coastal ecosystem.
Before the water passes to underground drainage into a subterranean mixing zone with brackish Baltic Sea waters, the above ground draining streams degas carbon dioxide and take up oxygen in contact with the atmosphere. Iron(oxyhydr)oxide precipitates in the stream beds acting as a sink for dissolved phosphate. Residues of Fe-oxidizing bacteria were found in the stream bed rust indicating an involvement of microbes to catalyze the dissolved Fe removal. The investigation reveals that the surface precipitation on the beach leads to the formation of submarine groundwater discharge essentially free of dissolved iron and phosphate. The formation of Fe-phases in the subterranean estuary is also supposed to take place at depth thereby influencing the release of nutrients and metals into the Baltic Sea coastal ecosystem.

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