

Geochemical Processes at a Freshwater/Seawater Interface in a Shallow Sandy Aquifer, Skansehage Denmark

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ABSTRACT

Chemical processes in a natural fresh-/seawater mixing zone were studied in a shallow sandy aquifer. The dominant redox-processes are sulfate reduction and methanogenesis. Methanogenesis produces CO₂, which causes calcite dissolution. The produced calcium induces ion exchange with sodium. The final result of these interactions between different types of geochemical processes is an anoxic groundwater enriched in bicarbonate and sodium.

INTRODUCTION

Of the geochemical processes related to the sea-/freshwater interface ion exchange has been studied most extensively. In contrast redox-processes have received much less attention. And rarely have the combined effects of ion exchange, redox-processes and calcite equilibrium been investigated in the field. In this study an attempt is made to explain changes in groundwater composition as a result of interconnected effects of the above geochemical processes.

The study was carried out in a shallow phreatic aquifer, 9 m thick and consisting of Holocene sand and gravel deposits of marine origin, containing thin lenses of peat. A thicker low-permeable peat layer constitutes the hydraulic lower boundary of the aquifer (Fig. 1). Water composition was monitored in 100 piezometers along a 120 m transect perpendicular to the coastline (Fig. 1).

The enrichment or depletion of different species relative to a conservative mixture of sea- and freshwater was calculated to delineate the geochemical processes in the aquifer. The fraction of seawater is calculated using chloride as conservative component and the expected mix-concentration is calculated for a given species *i*. The mix-concentration is subtracted from the observed groundwater concentration and the enrichment or depletion Δm_i is obtained. Positive Δm_i indicates the groundwater sample to be enriched for species *i*, a negative Δm_i indicates depletion.

RESULTS AND DISCUSSION

The 50 % seawater contour (thick 125 mM chloride contour in figure 1) was found at about 4 m depth at the coastline, and reaches the bottom of the aquifer at 9 m depth 40 m further inland. The fresh-/seawater mixing zone, from 100 % to 10 % seawater, is 4-5 m thick and extending up to 90 meters inland.

Redox-processes

Generally the aquifer is anoxic and dominated by sulfate reduction and methanogenesis. Groundwater in the mixing zone is depleted of sulfate and enriched

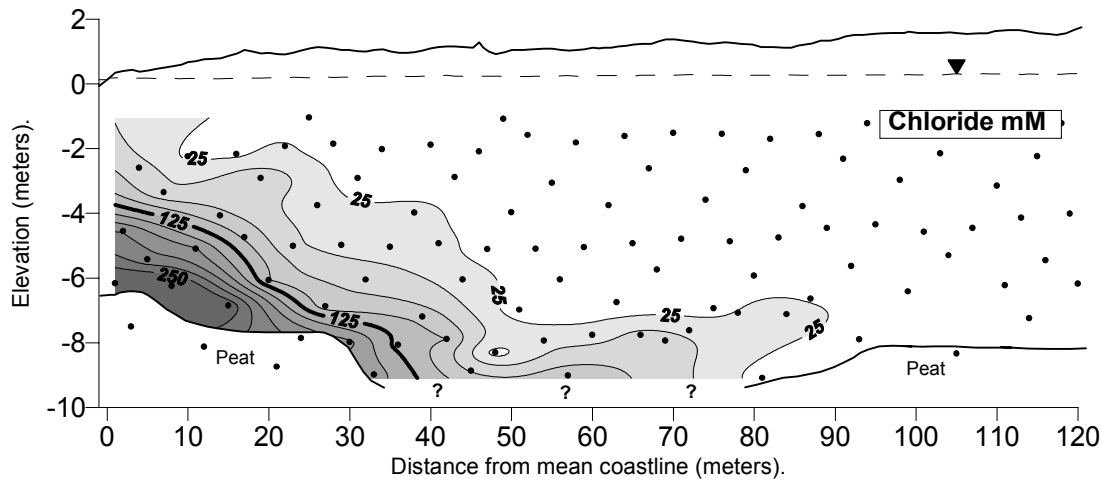


Figure 1: Chloride concentrations (mM) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater). Vertical exaggeration is 4.

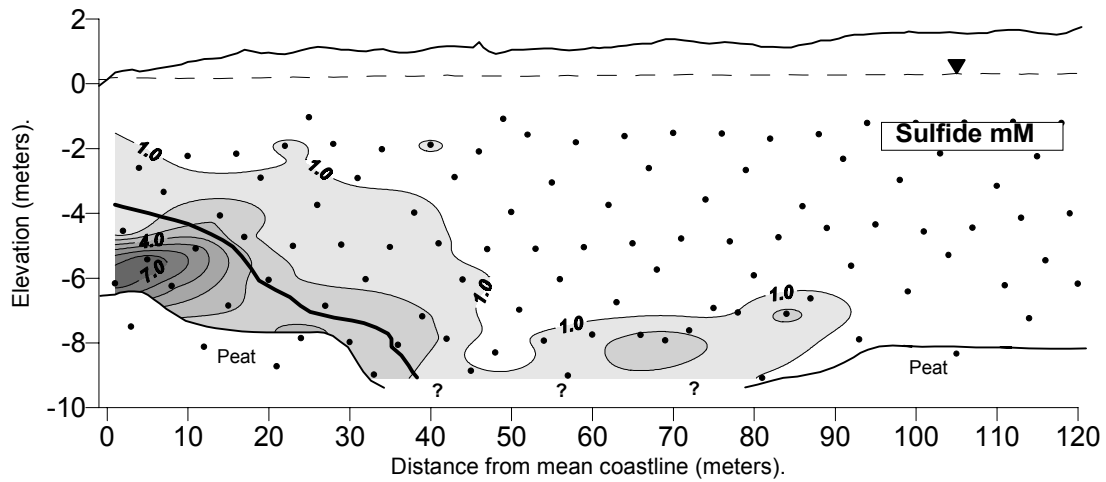


Figure 2: Sulfide concentrations (mM) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater from Cl⁻). Vertical exaggeration is 4.

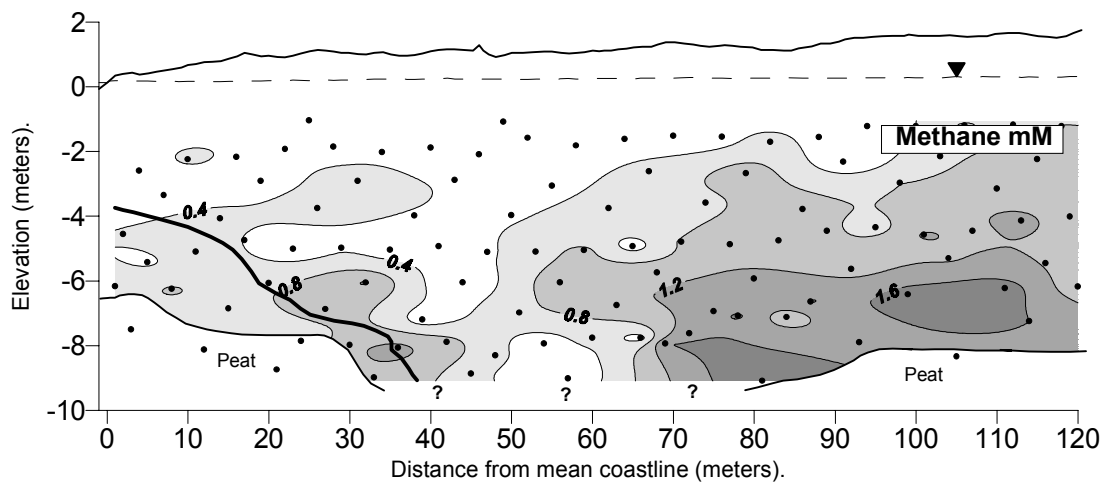


Figure 3: Methane concentrations (mM) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater from Cl⁻). Vertical exaggeration is 4.

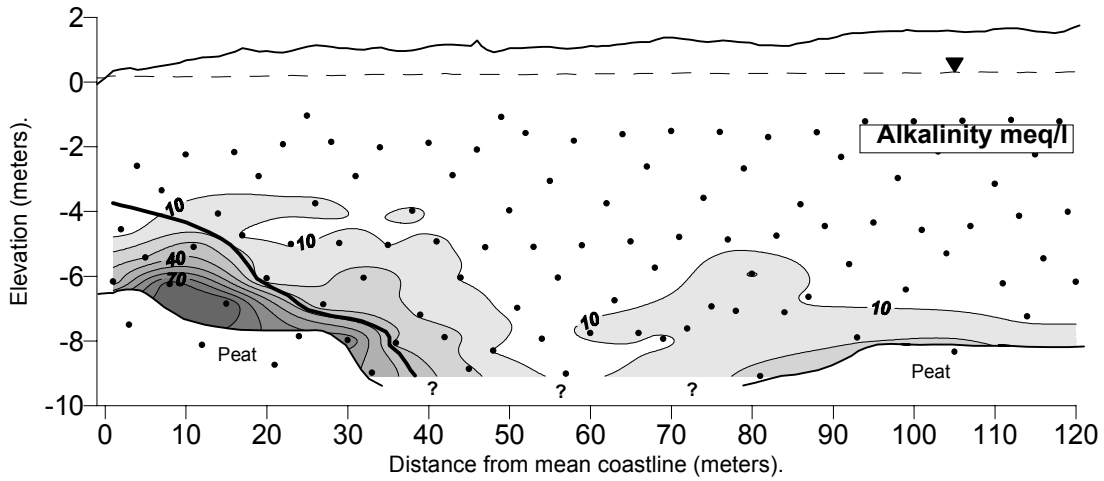


Figure 4: Alkalinity concentrations (meq/l) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater from Cl⁻). Vertical exaggeration is 4.

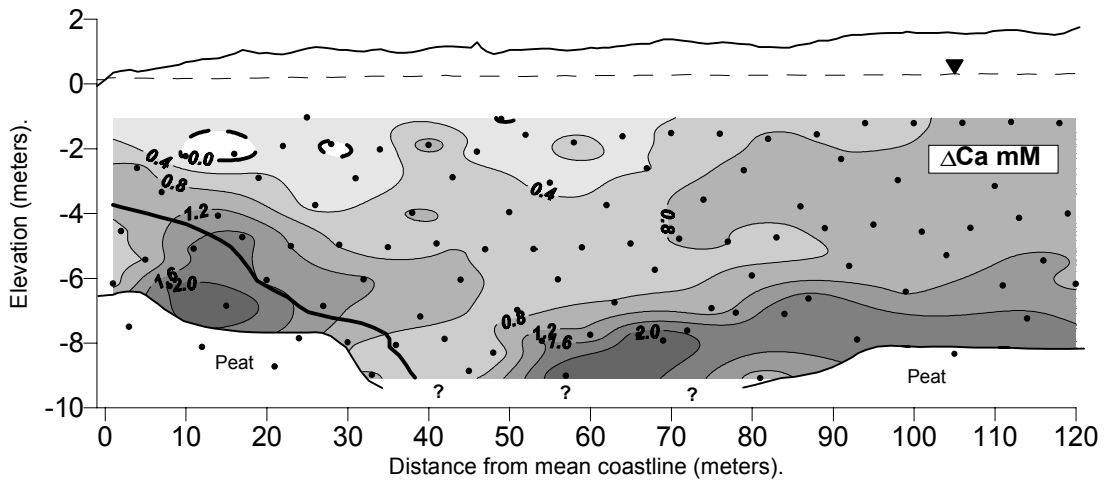


Figure 5: ΔCa (mM) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater from Cl⁻). Dashed line: $\Delta Ca = 0$. Vertical exaggeration is 4.

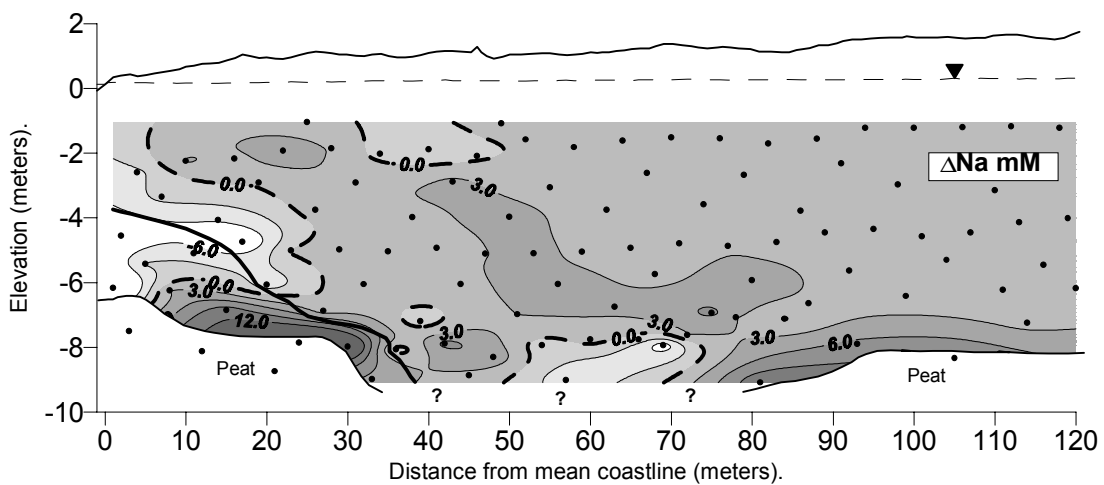
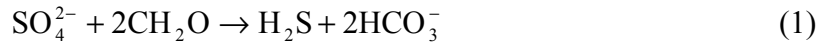


Figure 6: ΔNa (mM) in vertical transect perpendicular to the coastline (thick line represents 50 % seawater from Cl⁻). Dashed line: $\Delta Na = 0$. Vertical exaggeration is 4.

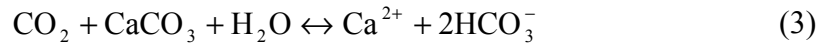
in dissolved sulfide (Fig. 2), indicating that sulfate reduction (1) is the dominant redox-process in this part of the aquifer. Further inland high methane concentrations (Fig. 3) are found showing methanogenesis (2) to take over as the dominant redox-process in the freshwater zone, but also in the saline parts where sulfate is depleted.



A high concentration of inorganic carbon is present in the most saline part of the aquifer as represented by the alkalinity in figure 4. This suggests a relation to mineralization of organic matter. Alkalinity is produced directly by sulfate reduction (1) but the concentration of alkalinity is too high to be explained by sulfate reduction alone.

Calcite dissolution

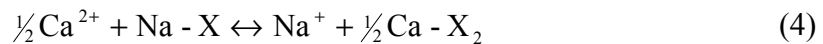
An additional source of alkalinity could be the dissolution of calcite (3). Compared to conservative mixing, the groundwater has become enriched with calcium, as seen in fig. 5 showing ΔCa , which also supports the dissolution of calcite.



CO_2 from methane production (2) could be the driving force for the calcite dissolution. But also simple mixing of fresh- and seawater, both in equilibrium with calcite, can lead to subsaturation for calcite in the mixed water creating a potential for additional calcite dissolution.

Ion exchange

The dissolution of calcite causes an increase in the Ca^{2+} concentrations, which will disturb the equilibrium between solution and cation exchanger. In the saline part of the aquifer, sodium, magnesium and potassium dominate the cation exchange complex. An increase in the Ca^{2+} concentration will lead to exchange with mainly Na^+ and can be written as:



X indicates the sediment exchanger. In figure 6 ΔNa shows a large enrichment of sodium in the more saline portion of the aquifer supporting reaction (4). A similar pattern is found for magnesium and potassium.

The processes described above can be summarized in the following conceptual model for the evolution of the saline groundwater in the mixing zone: First sulfate reduction causes an increase in HCO_3^- . Once sulfate is depleted CO_2 production by methanogenesis takes over and induces CaCO_3 dissolution releasing calcium and bicarbonate. Through ion exchange the calcium is exchanged for sodium and additional calcite can be dissolved. The result is anoxic groundwater enriched in bicarbonate and sodium.

Keywords: Geochemistry, sea-/freshwater interface, redox-processes, calcite dissolution, ion exchange

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