The Geochemistry of a Seawater Intrusion Experiment in a Shallow Sandy Aquifer, Skansehage Denmark

M. S. Andersen, V. Nyvang, R. Jakobsen and D. Postma

Environment & Resources DTU, Technical University of Denmark, Denmark

ABSTRACT

A seawater intrusion experiment was carried out in a phreatic coastal aquifer characterized by a wide sea/fresh-water mixing zone near the coastline. The intrusion was accomplished by pumps installed in the aquifer. The mixing zone migrated to a position about 85 m landward. The distribution of dissolved ions during the intrusion experiment was dominated by landward migration of the existing mixing zone followed by the intrusion of surface seawater, but modified by geochemical processes associated with the intrusion. Ion exchange took place at the salinity front between the freshwater and the preexisting mixing zone releasing $\text{Ca}^{2+}$ from the exchanger. This $\text{Ca}^{2+}$, combined with the high bicarbonate concentration from the preexisting mixing zone, caused super-saturation and possibly precipitation of calcite at the salinity front. Behind the front, towards the sea, intruding sulfate is being reduced by organic matter. Acid production is associated with the sulfate reduction and causes a decrease in pH, resulting in subsaturation and possibly re-dissolution of calcite. The results show that the spatial separation of ion exchange- and redox-processes may trigger a sequence of calcite precipitation and dissolution in an aquifer affected by seawater intrusion. A PHREEQC 1D reactive transport model was constructed to quantify these processes.

INTRODUCTION

Many previous investigations on seawater intrusion have focused on monitoring the physical transport by a single non-reactive species like chloride. In the comparatively few studies dealing with the geochemical processes in relation to seawater intrusion, the data density is often sparse compared to the complexity of the problem. Furthermore, geochemical knowledge of the pre-intrusion situation is often
limited or non-existent. In this study, we document the physical and geochemical effects of seawater intrusion in a small scale field experiment with a high data density and good control on the initial conditions in the aquifer. The paper describes the geochemical processes taking place during the intrusion experiment. The geochemistry of the aquifer prior to the intrusion experiment was summarized in [Andersen et al., 2001].

The seawater intrusion experiment was carried out in a phreatic coastal aquifer. The aquifer is 9 m thick and consists 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. Seawater intrusion was accomplished through pumps installed 140 m from the coastline (Fig. 1), operated for about 10 months and abstracting a total of about 200,000 m³. The water composition was monitored in a 120 m long transect of about 100 piezometers (Fig. 1) placed parallel to the direction of the intrusion. Each piezometer is fitted with a 12 cm screen positioned from 1 to 9 m below the water table, marked as dots in Fig. 2,left. Water samples were taken from the piezometers for analysis of major ion chemistry.

RESULTS AND DISCUSSION

Chloride regarded as a non-reactive species describes the conservative advective transport in the experiment (Fig. 2). Fig. 2,left shows the natural sea-/freshwater interface prior to the intrusion. The interface consists of a 4-5 m thick mixing zone dipping gently landwards to intercept with the aquifer bottom about 40 m landward. The natural interface is maintained by out flowing freshwater in combination with a slow landward density driven advection of seawater along the bottom of the aquifer, and by occasional inundation of the field site caused by winter storms. Inundation causes seawater plumes to sink down through the aquifer. One such event was recorded 3 months prior to the intrusion experiment and in this case plumes of brackish water were recorded up to 80 m inland.

During the 10 months of intrusion the mixing zone became largely vertical and migrated to a position about 85 m from the coastline (the thick grey/red lines in Fig. 2 represents the 50 % seawater contour). Significant variation in the distribution of chloride is observed at the end of the intrusion experiment (Fig. 2,right). This is partly
due to small scale variation of the permeability in the aquifer. Some of the variation, notably the high Cl concentration seen between 100 to 120 m from the coast (Fig. 2, right), is caused by the earlier inundation and because the intrusion did not proceed exactly parallel to the transect. This causes an apparent early breakthrough of brackish water entering from the side into the transect. Leakage of freshwater up through the bottom of the aquifer at 40 to 50 m from the coast (Fig 2, right) is responsible for the lower Cl concentrations in the lower central part of the transect.

Chemical reactions prior to the intrusion experiment

Selected chemical parameters are shown in Fig. 3 prior to the intrusion experiment (left side), and at the end of the intrusion experiment (right side). The geochemical processes occurring in the pre-intrusion sea-/freshwater mixing zone are important for the geochemical effects caused by the intrusion experiment and will briefly be summarized (see also [Andersen et al., 2001]). The dominating geochemical process in the natural situation appears to be degradation of sedimentary organic matter. As a consequence the aquifer is anoxic with methanogenesis (1) occurring in the fresh parts of the aquifer and sulfate reduction (2) dominating in the saline part of the aquifer.

\[
2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (1)
\]

\[
\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- \quad (2)
\]

Reaction (2) leads to a general depletion of sulfate (Fig. 3a, left) compared to chloride (Fig. 2, left) and enrichment in dissolved sulfide (Fig. 3b, left). The degradation of organic matter also produces inorganic carbon causing the very high alkalinity in the saline part of the aquifer (Fig. 3c, left). The CO$_2$ production associated with the mineralization of organic matter appears to drive the dissolution of calcite.

\[
\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (3)
\]

The saturation index for calcite ($S_{\text{calcite}} = \log([\text{Ca}^{2+}][\text{CO}_3^{2-}]/K)$ is calculated in Fig. 3e, left showing general subsaturation for calcite. An exception is in the saline, lower and seaward part of the transect where saturation to slight supersaturation is observed. This is caused by the high alkalinity, the contribution of Ca$^{2+}$ from the seawater (Fig. 3d, left) and a possible release from the exchanger (see below).

In the natural interface the periodic inundations introduce Na$^+$ and Mg$^{2+}$ into the fresh part of the aquifer where Ca$^{2+}$ dominates the ion exchange complex. This leads to exchange reactions where Na$^+$ and Mg$^{2+}$ displace Ca$^{2+}$ from the ion exchange complex e.g.

\[
\text{Na}^+ + \frac{1}{2}\text{Ca} - \text{X}_2 \leftrightarrow \frac{1}{2}\text{Ca}^{2+} + \text{Na} - \text{X} \quad (4)
\]

where -X denotes the exchange sites. The released Ca$^{2+}$ is subsequently carried outward with the freshwater. Inundation therefore leaches Ca$^{2+}$ from the aquifer and leads to calcite depletion. For extended periods following inundation significant amounts of Na$^+$ and Mg$^{2+}$ remain adsorbed to the ion exchange complex in the fresh part of the aquifer. This was also the case prior to the intrusion experiment where Mg$^{2+}$ occupied a major part of the exchange complex in the central part of the transect.
Figure 3: Contoured vertical transects of selected chemical parameters prior to the intrusion experiment (left side) and at the end of the experiment (right side). a) sulfate (mM), b) sulfide (mM), c) alkalinity (meq/l), d) calcium (mM) and e) the calculated saturation index for calcite ($SI_{\text{calcite}} = \log([\text{Ca}^{2+}]\cdot[\text{CO}_3^{2-}]/K)$, where $K$ is the solubility constant). The thick grey/red line represents the 50% seawater contour. The black solid line at the bottom of the plots indicates the position of the aquifer bottom (dashed where uncertain).
Chemical reactions during the intrusion experiment

The distribution of sulfate at the end of the intrusion experiment (Fig. 3a,right) resembles that of chloride (Fig. 2,right). However, sulfate appears to be slightly retarded. This is mainly a remnant of sulfate depletion in the preexisting mixing zone and only to a lesser extent due to reduction of the sulfate introduced by the intrusion, because the reduction rate is small compared to the duration of the experiment. The high concentration of dissolved sulfide between 80 to 100 m from the coast (Fig. 3b,right) is accordingly a result of landward transport of the sulfide initially present at 0 to 20 m (Fig. 3b,left). An analogous development is seen for alkalinity (Fig. 3c). For both parameters the concentration remains high at the end of the experiment in the lower part of the transect near the coast (from 0 to 40 m), due to the low permeability in this zone.

At first inspection the distribution of Na\(^+\) and Mg\(^{2+}\) at the end of the intrusion (not shown) closely follow that of chloride. However, the distribution of Ca\(^{2+}\) (Fig. 3d,right) shows a distinct increase at the intrusion front (around 70-80 m) indicating that Ca\(^{2+}\) is expelled from the ion exchange complex by Na\(^+\) and Mg\(^{2+}\), according to reaction (4). Closer inspection of the Na\(^-\)distribution shows indeed depletion in the zone with high Ca\(^{2+}\) concentrations. For the Mg\(^{2+}\)-distribution the situation is more complex, with depletion at the lower part of the intrusion front and enrichment in the upper section. Apparently also Mg\(^{2+}\) is expelled from the exchanger by Na\(^+\). The Mg\(^{2+}\) on the exchange complex is probably a remnant of the inundation event.

Also the zone with saturation for calcite in the pre-existing mixing zone (Fig. 3e,left) moves landward with the intrusion (Fig. 3e,right). However, as a result of the additional release of Ca\(^{2+}\) due to ion exchange reactions, the size of the zone and the extent of supersaturation seem to increase as the intrusion advances and may possibly lead to a precipitation of calcite. The amount of calcite which can precipitate and possibly affect aquifer properties is, however, small.

Figure 4: Selected results of reactive transport modeling using PHREEQC. a) Observed and modeled calcium concentrations (mM) b) Observed and modeled calcite saturation index (SI).
In order to verify this set of processes a 1D-reactive transport model of the intrusion was constructed with PHREEQC [Parkhurst and Appelo, 1999]. The model includes ion exchange, organic matter degradation and redox-reactions using the initial distribution of species generalized to one dimension. The flow and transport parameters were obtained by fitting to the observed Cl distribution. Fig. 4 show the model results for Ca\(^{2+}\) and the SI for calcite compared with the field data. The reactive model for Ca\(^{2+}\) (Fig. 4a) shows a peak in the concentration at 80 m, resulting in a better fit to the field data than a simple conservative transport model can provide, (thin line in Fig. 4a), especially for the lower part of the aquifer. Ion exchange is apparently necessary to explain the Ca\(^{2+}\)-distribution. The observed SI (Fig. 4b) shows considerable scatter, but the model follows the trend in the field data with a zone of supersaturation (at 80-90 m from the coast) and a zone of subsaturation (at 10-70 m from the coast). In the model the subsaturation is caused by the acid produced by sulfate reduction. The implication is that calcite precipitating at the advancing intrusion front could subsequently re-dissolve.

CONCLUSION

The results show that the geochemical processes, such as degradation of organic matter in the natural sea-/freshwater mixing zone prior to an intrusion event have implications for the processes occurring during the intrusion. During the intrusion the spatial separation of ion exchange- and redox-processes may trigger a sequence of calcite precipitation and dissolution in an aquifer affected by seawater intrusion. These reactions could lead to changes in aquifer properties such as the permeability. However, quantitatively the effects on the mineral phase are small in this case because of the relatively short intrusion distance and because the affected part of the aquifer was partly affected by seawater due to the inundation prior to the experiment. In other settings with a larger intrusion distance these effects should be more pronounced.

References


Keywords: Geochemistry, seawater intrusion, calcite dissolution, redox-processes, ion exchange

Corresponding author: Martin Søgaard Andersen, Assistant Professor at Environment & Resources, Technical University of Denmark (DTU), Building 204, 2800 Kgs. Lyngby, Denmark. Email: msa@er.dtu.dk