

## GEOCHEMICAL PROCESSES IN THE SALT-FRESHWATER TRANSITION ZONE - PRELIMINARY RESULTS OF A 2D SAND TANK EXPERIMENT

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### INTRODUCTION

Most investigations concerning the subject of saltwater intrusion into aquifers look mainly on either the physical density flow system (Cooper 1964; Reilly and Goodman 1985) or the geochemical aspects (Beekmann and Appelo 1990; Appelo and Geirnaert 1991). The aim of this investigation is to combine both, geochemical processes and hydraulic aspects of seawater intrusion into a porous coastal aquifer system in Northwest Germany. Therefore a Coastal Aquifer Testfield (CAT-Field) was determined in the northeastern Part of the Elbe-Weser region. A two dimensional sand tank experiment is carried out to simulate the hydraulic and geochemical processes occurring in the salt-freshwater transition zone of the CAT-Field in a laboratory scale. The sand tank is filled with natural aquifer material, and after a condition phase with artificial groundwater, a density driven lateral saltwater intrusion against the hydraulic gradient is induced. Geochemical processes were recorded by intense sampling at 100 available monitoring points at different depths and intrusion lengths.

The ongoing laboratory experiment has two phases: The first phase is the intrusion of saltwater into the aquifer former conditioned with groundwater. The changing salt content during this phase will induce well known exchanger reactions (Appelo and Willemsen 1987; Appelo, Willemsen et al. 1990; Panteleit, Kessels et al. 2001). From previous investigations (Panteleit, Binot et al. 2001) we expect exchanger reactions to overlap and mask slower reactions as mineral dissolution and precipitation. Therefore the geochemistry of the porewater will be determined by the resulting salt concentration and the products of the exchanger processes during the first phase of the experiment.

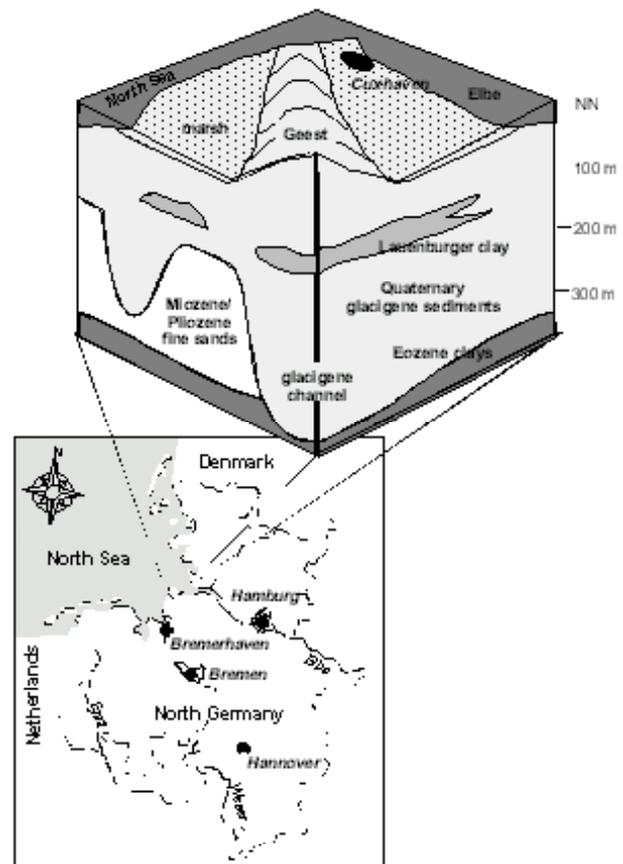
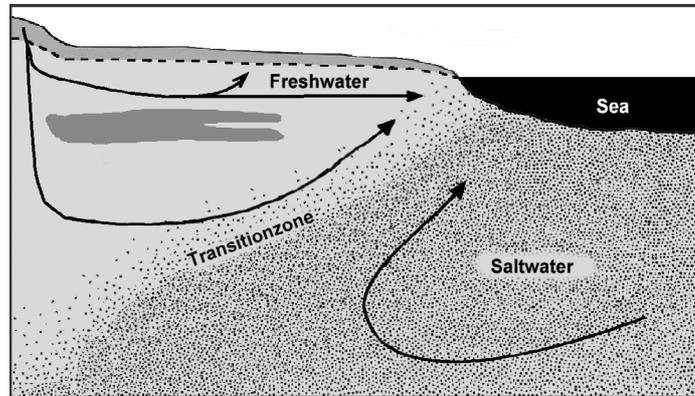


Figure 1 Sketch of the location and the geological setting of the CAT-Field.

In the second phase a steady state with a stable intrusion length is developed. Exchanger reactions will get less important as no further progress of salinization occurs. The former masked reactions are supposed to become more important concerning the composition of the pore water. These reactions will run off until a complete equilibrium between the porewater and the solid phase of the different areas of the transition zone between fresh- and saltwater is reached.



**Figure 2** Hydraulic flow pattern in the CAT-Field.  
(modified from (Cooper 1959))

For the determination of the micro flow pattern during the steady state additional tracer injections at the sampling points are planned after the end of geochemical sampling in the second phase.

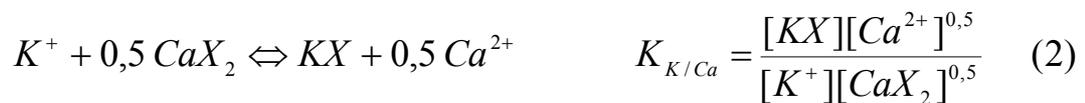
This presentation focuses on the first stage of the experiment, namely the exchanger reactions during saltwater intrusion. The geochemical results will be compared with results of former column experiments with the same aquifer material and results from a computer modelling with the computer program PHREEQC (Parkhurst and Appelo 1999).

The sand tank experiment simulates the natural processes during saltwater intrusion. These processes are affected by the natural hydrogeological setting of the waterconductive layers. Therefore it is described briefly in the following. The base of the aquifer system lies at about 200 m – 350 m b.s.l. and consists of Eocene clays. The waterconductive layers start with Miocene to upper Pliocene fine sands of a marine and a prodelta and deltaic-fluviatile regime. A speciality of the Pliocene sequence is a heavy mineral deposit in it's upper part (Besenecker, H. et al. 1981; Elsner and Simon 1994). Because of the partly coarse grained following quaternary glacial and periglacial sediments from the Elster and Saale glaciations the region seems to be suitable and may be interesting for future groundwater exploitation. Deeply incised glacial erosion channels cut down to the Eocene clays. They reach a depth of more than 350 m b.s.l., whereas the width is only 1 or 2 km. In most parts a thick (100m) clay layer (Lauenburger Clay) covers the channels and divides the aquifer in an upper and a deeper one. In places the Lauenburger Clay is thin or absent, also intercalations of more then 10 m of sands are common. The series is topped by Holocene sediments. These can be found in the flat topography marsh areas and start normally with a basal peat horizon, followed by fine brackish lagoon or tidal flat sediments.

Figure 2 shows the groundwater flow system in an orthogonal transect from the coast. Topographically seen the glaciogene sandwich deposits occur in slight ridges (the so called Geest). These are the important groundwater recharge areas in the CAT-Field even for the deeper groundwaters of the tertiary layers. From there the flow is directed toward the coastline in the east and the west. Due to the fine grained Holocene sediments and the extensive drainage for agricultural and land saving purposes, no recharge but upcoming groundwater in the marsh areas is documented by a negative water balance (Friedhoff 2001) and increasing hydraulic pressure heads with depth (Rifai, personal comm.). The upcoming groundwater is further focussed by a saltwater intrusion from the coastline, which is directed against the freshwater flow. This results in a groundwater flow pattern according to the typical Henry Problem (Henry 1959). The transition between salt- and freshwater does not occur in a sharp front. From dispersion and advection processes a transition zone with intermediate salt concentrations is build up (Panteleit, Binot et al. 2001). In the flat marsh topography exfiltration areas the transition zone shows a lower inclination than expected under static conditions (Hahn 1982; Fulda 2002) (Figure 2).

The saltwater intrusion represents a mixing of a high-salinity solution (seawater) with a dilute solution (fresh water) in a medium with many reactive solids. In a detrital sedimentary aquifer, cat ion exchange is one of the most important geochemical processes taking place during salinization. Sometimes it is difficult to distinguish between exchanger and dissolution or precipitation processes like the reaction of carbonate minerals, sulphate reduction, etc. (Sposito 1984). In any case these processes have a minor influence on the porewater chemistry during beginning of the saltwater intrusion, but are getting more important with increasing time and decreasing change of the salt concentration.

The solid surface charges of the aquifer material is balanced by adsorbed ions from the aqueous phase. The occupation of the exchanger sites may be changed facile by substitution of one ion by another. Characteristic cat ion-exchange reactions that take place when seawater intrudes are:

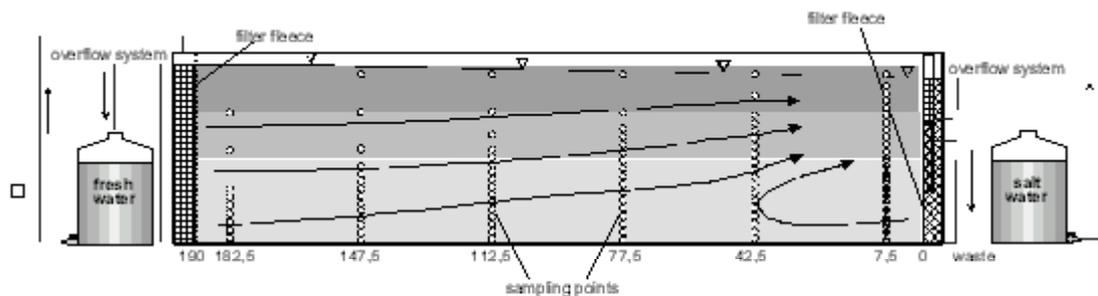


, where X indicates the exchanging solid surface. If the mass law is applied formally the affinity of the different ions can be expressed by the selectivity coefficient K. It must be pointed out that the selectivity coefficient represents not a constant value in a thermodynamically sense, but depends on the adsorbing material. As it can be seen from the equation the occupation of the exchanger sites of a certain material depends mainly on the composition of the porewater. This is the reason for the importance of the cat ion exchange process during the intrusion of higher saline waters.

## METHOD

### Hydraulic simulation

The flow pattern of the groundwater in the CAT-Field is simulated in a two dimensional sand tank experiment (Figure 3). The Perspex-lined box (200 x 50 x 5 cm) consists of a sediment filled flow chamber with a storage chamber on each side. The three parts are separated by a filter fleece to prevent the sediment from entering into the storage chambers but guarantees hydraulic contact. The flow chamber was filled with natural sediments from a research drilling project in the CAT-Field (November 2001). According to the natural setting of the aquifer system sediments from different depths of the quaternary deposits were built in. Because of the different sediment types hydraulic conductivity increases in three layers with depth. The flow chamber is covered with Plexiglas to minimize evaporation. Cat ion exchange capacity (CEC) and ion exchange coefficients of the sediment were determined by CsCl-extraction.



**Figure 3** Experimental set up of the sand tank experiment with (different colours represent different sediment types. Data of Figures 5&7 originate from the black marked sampling points on the lower right side of the basin)

The specific surface was determined via the BET-method (Brunauer, Emmett et al. 1938). Artificial calcite equilibrated groundwater as analysed from field samples at the drilling point was used as input water on the freshwater side. On the "seaside" artificial seawater was used. It was spiked with Uranine (Disodiumfluoresceine) to provide a quick observation of the saltwater intrusion. The water level in all chambers can be controlled separately by an overflow system. Two outflow chambers in the upper part of the saltwater storage chamber avoid the intrusion of mixed water and guarantees a constant salt concentration of the intrusion water. The intrusion length depends on the hydraulic gradient and can be controlled by varying the overflow height of the saltwater. During the experiment the level of the freshwater chamber was held constant, but the saltwater level was raised stepwise until a sufficient saltwater intrusion was reached. The freshwater flow follows the induced hydraulic gradient towards the "seaside" of the chamber, while the saltwater intrudes in the lower part of the chamber due to its higher density as described by Thorenz, Kosakowski et al. (in press).

### Numerical modelling

To give an idea of the resulting concentrations from exchanger reactions under idealised conditions a numerical modelling is done. That means no other reactions, a single exchanger site; horizontal flow only and a homogeneous material were presumed. For a first step the exchanger processes for the deeper part of the flow chamber were modelled with the PREEQC computer program (Parkhurst and Appelo 1999) as a horizontal one dimensional intrusion into an isolated soil layer. Sediment depending input parameters stem from the modelling of column experiments with material of same origin (Panteleit, Binot et al. 2001). The modelled intrusion length and slope is determined by the position of the corresponding sampling point.

### Geochemical sampling

For the determination of hydrochemical processes pore water samples have been taken. 100 sampling sites are arranged in six lines at different intrusion lengths with up to 25 sample points at different depths. The sampling points consist of soil moisture samplers, a porous polymer tube (diameter 2,5 mm) with a pore width of 1,1  $\mu\text{m}$  which penetrates the whole sediment thickness of 5 cm. Because of the relative high sampling surface of almost 8  $\text{cm}^2$  the irrigation of the hydraulic system and the risk of sealing of the sampling sites due to fine material is minimized. For the same reason samples were taken permanently with a peristaltic pump and a self constructed auto-sampler. At the beginning of the experiment samples were taken from 24 sites at the same time. After a transition zone has developed only 12 points, lying in the transition from fresh- to saltwater, were sampled. The position of the transition zone was controlled by the Uranine content in the samples. Samples were acidified immediately after sampling and later analysed by inductive coupled plasma atom emission spectroscopy (ICP-AES) for major cat ions (Na, Ca, K, Mg) and for further investigations as well for Li, Sr, Ba, Mn, Fe. Anion analysis for sulphate and borate was done also by ICP-AES. The determination of the Chloride concentrations lead to some problems due to interactions of the analysis system with the UV active tracer Uranine in the samples. Therefore the Chloride concentration is unknown so far, but will be determined in the future. Alkalinity was determined periodically from extra samples immediately after sampling by titration as described by (Grasshoff, Ehrhardt et al. 1983).

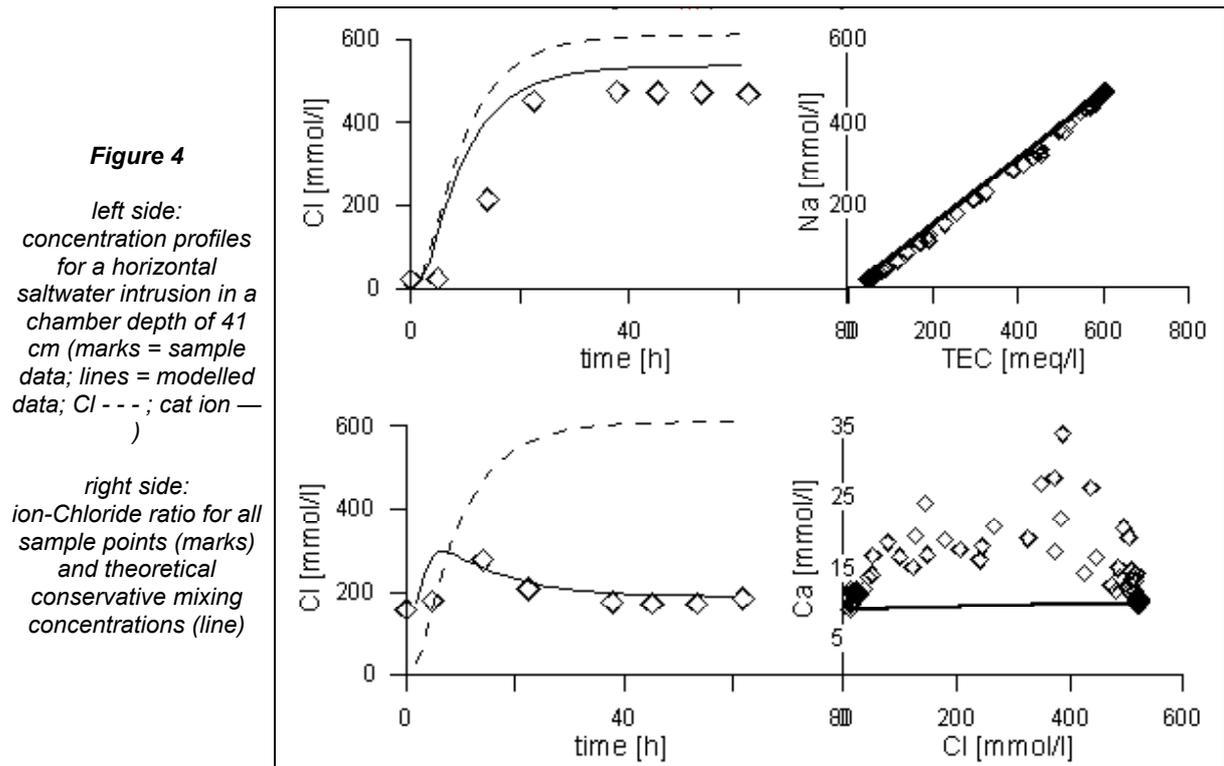
## DISCUSSION AND RESULTS

From the experimental salinization of sediment columns (Appelo and Willemssen 1987; Beekmann and Appelo 1990) it is known that exchanger processes determine the composition of the porewater. In a first step this assumption will be proved for the present chamber experiment. Due to the analytical problems of Chloride mentioned above the intrusion of saltwater into the flow chamber is documented in this first step by the Sodium concentration. Of cause Sodium is also expected to be involved into the exchanger reactions. The error of the amount of Sodium attached on the exchanger sites might be neglected due to the high Sodium concentration compared to the CEC. This approximation is supported by the results and modelling of column experiments with diluted (20%) seawater (Panteleit, Kessels et al. 2001).

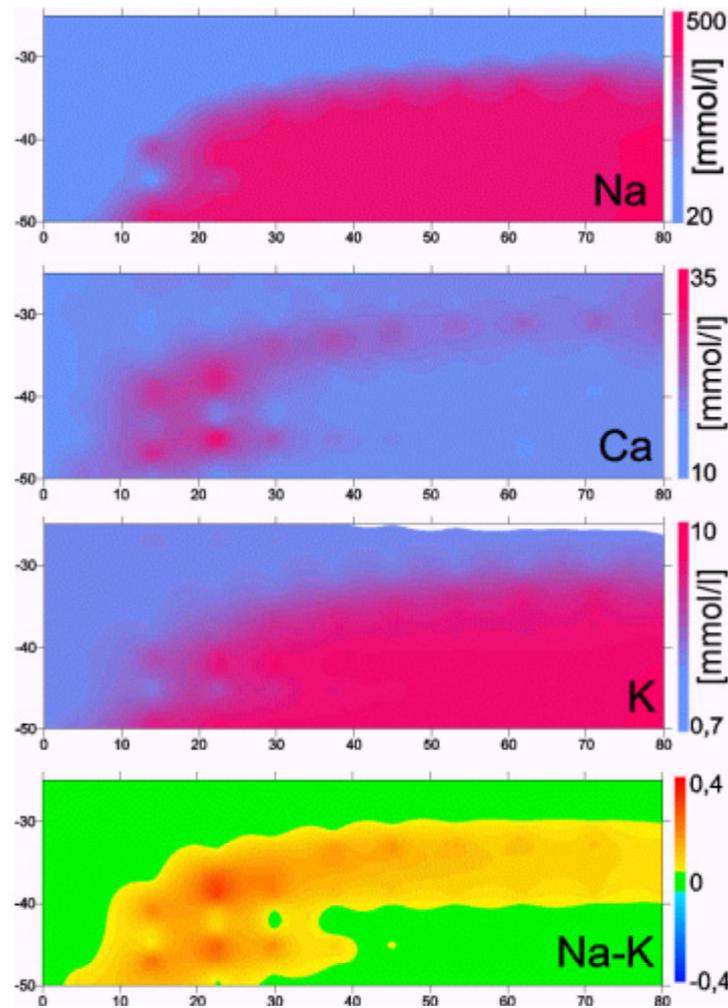
Furthermore the modelled data shows no significant differences between the run of the Chloride and Sodium concentration curves (Figure 4 upper part, left side). On the right side of Figure 4 the total cat ion equivalent concentration (TCE) is plotted against the Sodium concentration. The TCE of the samples correspond well with the theoretical TCE of a conservative mixing of fresh- and seawater. A slightly negative curvature might be caused by the mentioned Sodium depletion due to exchanger processes, but

in general it shows curve linearity with a regression coefficient of 0,9993. As expected the geochemical process of ion exchange seems to dominate during the saltwater intrusion. They result only in a qualitative change of the TEC, while precipitation or dissolution processes would cause a quantitative change of it. For the following discussion of the exchange of major cat ions a theoretical Chloride concentration, calculated by the charge difference between the analysed TEC and the anions (sulphate and alkalinity) is used.

In Figure 5 the concentration of Sodium at the lower part of the chamber (first sample line, see Figure 3) is displayed versus experimental time. The saltwater intrudes from the right side and is indicated by high sodium concentrations in red colours. In general the level of the saltwater rises with time up to a certain level of equilibrium. Only in the region of about 45 cm depth it is delayed due to a higher content of fine material and the coinciding lower permeability.



The exchanger reactions occurring during the intrusion of the saltwater can be seen best in the concentration behaviour of Calcium (Figure 5). If the distribution is compared with the Sodium figure it becomes obvious that the Calcium concentration rises during the transition from fresh to saltwater before it drops down again to the saltwater concentrations. Calcium is the dominating cat ion (42,6 meq%) in the freshwater. The selectivity coefficients from literature and the CsCl-extraction (Table 1) reflect a high affinity for the exchanger sites. For these reasons the negative surface charges of the sediment are predominantly equilibrated with the Calcium ions. With rising salt content the Calcium ratio in the porewater decreases down to 3,3 meq%. As the occupation of the exchanger sites is always in balance with the porewater composition, Calcium is released from the exchanger sites during salinization, even if it has a greater affinity than the adsorbed ions (K, Na, Mg). This leads to a maximum in the calcium concentration as it can be seen in Figure 5. A peak of the Calcium concentration was measured at 45 cm depth. As mentioned above a higher content of fine materials respectively clay is present in this region. The exchanger sites are situated on the surface of the material, thus a higher specific surface of the finer material leads to a higher CEC. This results in an enhanced Calcium release from the exchanger sites in this region.



**Figure 5** Concentration distribution of different ions versus depth and time for the sampled points (see Figure 3); lower graphic: difference between the normative concentrations of Sodium and Potassium.

The general trend of the concentration profile can also be seen in the results of the numerical modelling (Figure 4 lower part left side). The data for the corresponding sampling point is also displayed and agree well with the modelled data.

On the right side of Figure 4 the Ca/Cl ratio from all sampling points is displayed together with the theoretical conservative mixing concentration. Calcium rates up to almost four times above the theoretical conservative mixing concentration during the transition from fresh- to saltwater. This is an obvious result of the Calcium release from the exchanger sites. The analysed concentrations above the modelled data originate again from the sample points at a chamber depth of around 45 cm. Here the Calcium release is locally higher than predicted by the model due to the higher CEC, while for the modelling an intermediate CEC was used as input parameter.

The influence of the exchanger reactions on the concentration of Potassium is less obvious. At first glance it shows a direct rising up to the higher saltwater concentration as it can be seen in Figure 5.

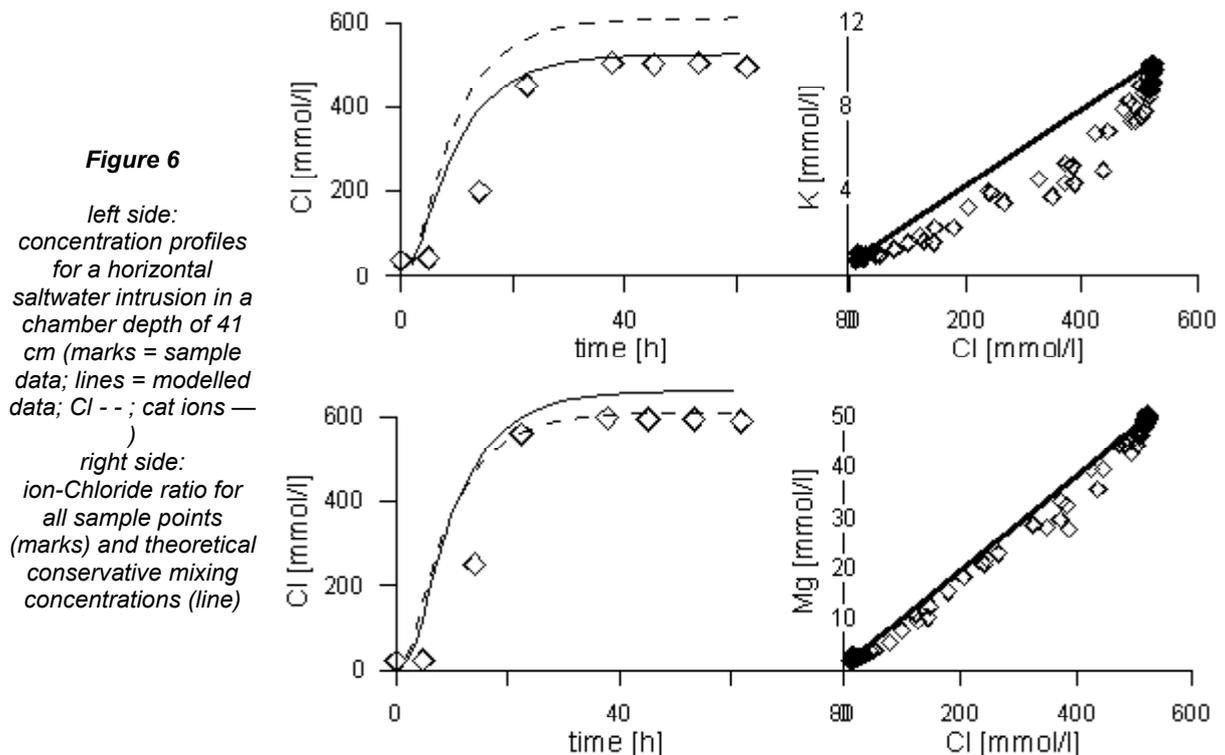
**Table 1** Selectivity coefficients for the exchange of adsorbed Calcium by different ions. Results from CsCl extraction and a compilation in (Appelo and Postma 1996).

Ion	$K_{I/Ca}$ from extraction	$K_{I/Ca}$ median from literature
$Na^+$	0,06	0,40
$K^+$	0,16	0,50
$Mg^{2+}$	0,73	0,64
$Ca^{2+}$	1	1

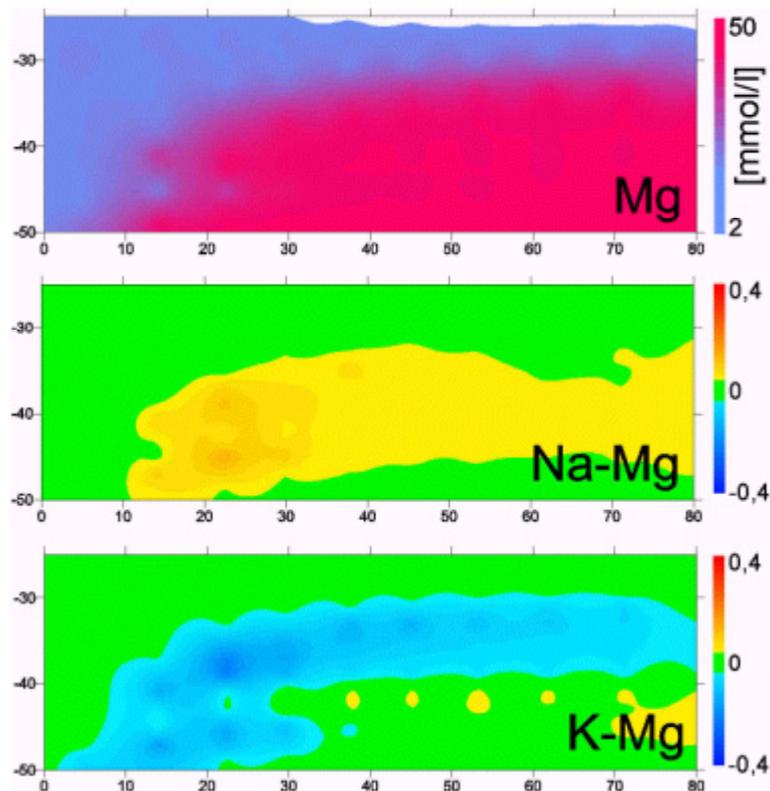
There are no obvious differences between the behaviour of Sodium and that of Potassium. Also the modelled concentrations (Figure 6, left) show an immediate rising, just like the concentration of the Chloride ion, which should behave as an ideal tracer. The Potassium-Chloride rate shows (Figure 6, right) a depletion of Potassium at medium salt concentrations compared to the conservative mixing concentrations. This might result from an adsorption onto the exchanger sites released from Calcium. Sodium should show this behaviour as well, but the stronger negative variation to the conservative mixing ratio compared to Sodium (Figure 3) expresses a higher affinity to the exchanger sites of Potassium compared to that of Sodium.

This can also be seen by a comparison of the two dimensional data of Sodium and Potassium (Figure 5) in detail. Therefore the maximum concentrations of the ions were set to one, while the minimum concentrations were set to zero. Make use of the difference between these normative concentrations, a retardation of the rising Potassium concentration compared to that of Sodium becomes obvious (Figure 5 bottom). The positive values (yellow colours) indicate the retardation of Potassium compared to Sodium during the transition from fresh- to saltwater. The green areas represent a Potassium Sodium ratio according the conservative mixing after respectively before the influence of exchanger processes.

The higher affinity of Potassium results from a smaller hydration shell of water molecules that stick to the ion and is also expressed in exchange coefficients from literature (Appelo and Postma 1996) as well as from the performed CsCl-extraction (Table 1). Here Potassium shows a 2.6 times higher affinity than Sodium does.



The fourth parameter, which might be affected by exchanger processes, is Magnesium, which shows also an almost conservative concentration rise (Figure 6&7). But again the ratio versus Chloride (Figure 6, right side) indicates a slight depletion compared with the conservative mixing concentrations. To visualise this in the 2D diagram, again the difference between the concentrations of Sodium and Magnesium is used (Figure 7, middle). Coinciding with literature data and the CsCl-extraction (Table 1) Magnesium is restrained compared to Sodium. Comparing Magnesium and Potassium concentrations in the same way we can see that the Magnesium concentration raises quicker than the Potassium concentration does (Figure 7, bottom).



**Figure 7** Concentration distribution over time and depth for Magnesium; Differences of normative concentrations between Na-Mg and K-Mg

This observation also agrees with the data compiled by (Appelo and Postma 1996). (Hahn 1972) describes even a release of Magnesium during salinization with a competing simultaneous depletion due to the formation of clay minerals. In contrast to these data the results of the CsCl-extraction would suggest a stronger retention of Magnesium only by the exchanger reactions. But already concentrations of Potassium from former column experiments showed an enhanced sorption than predicted by the PHREEQC modelling (Panteleit, Binot et al. 2001). A retardation of the Potassium breakthrough curve was also noticed by (Beekmann and Appelo 1990). A possible mechanism for this might be also the formation of clay minerals with the incorporation of Potassium. Alternatively a multi site exchanger can be considered which has not been registered by the CsCl-extraction.

## SUMMARY / OUTLOOK

Results from the first phase of the 2D simulation of a saltwater intrusion into an aquifer system have confirmed the presumption of dominating exchanger processes by a linear rising of the total cat ion equivalent concentration. The concentration of Calcium shows a maximum resulting from the release of Calcium ions from the exchanger sites with decreasing share of Calcium in the porewater. This is equalized by the depletion of cat ions with are enriched in seawater (Na, K, Mg) due to the adsorption on the exchanger sites. The intensity of the depletion of the different ions corresponds in general to the measured selectivity coefficients used as input parameters for a one-dimensional numeric modelling. Discrepancies resulted from inhomogeneities in the flow chamber filling. The formation of clay minerals seems to have an impact on the concentration profiles of Magnesium and Potassium due to enhanced adsorption. This will be investigated in the second phase of the experiment with a stabile intrusion zone, where exchanger processes are less important and the porewater chemistry is controlled by the formation and dissolution of minerals. The influence of the two dimensional flow regime on porewater chemistry will be taken into consideration of the numerical model using the computer program Processing SCHEMAT (Kühn and Chiang 2000).

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