

## Geochemical characteristics of salinization-zones in the Coastal Aquifer Test Field (CAT-Field) in North-Germany

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### ABSTRACT

The geochemical characteristics of a near shore inland aquifer system have been investigated in the Coastal Aquifer Test Field (CAT-Field) between Bremerhaven and Cuxhaven in the Northern Part of Germany which is described by Kessels et al. (this issue). Groundwater and sediment samples from the aquifer were taken at different locations on the flank of a glacial channel at depths between 5 and 100 m. Analyses of groundwater samples were carried out to determine possible zones of salinization, their origin, and associated geochemical processes in the transition-zone between salt and fresh water. Samples of aquifer material were used for a simulation of these processes in column experiments. Their results were modeled, using the computer program PHREEQC [Parkhurst and Appelo, 1999], and compared with the geochemical field data.

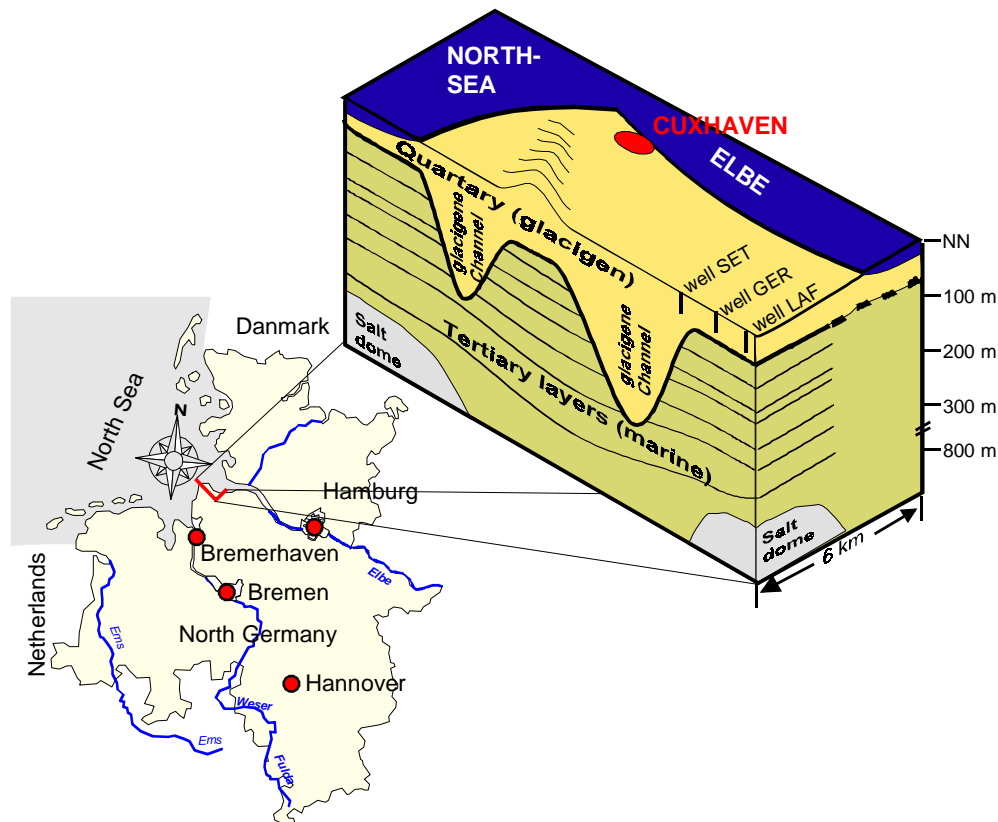
### INTRODUCTION

#### *Motivation*

In the subsoil of Northwest Germany a system of glaciogene channels can be found which were refilled at the end of the Elster ice age [Kuster, 1979]. In the CAT-Field one of these channels can also be found. Because of its partly coarse filling, the region seems to be suitable and may be interesting for a future groundwater exploration. The determination of possible influences of the exploration due to saltwater up-coming, a typical problem of coastal regions, is the aim of the project. Therefore different geophysical investigations were carried out [Fulda, Kessels et al., *subm.*; Kessels, Fulda et al., *subm.*; Siemon, Sengpiel et al., *subm.*; Willert, Behain et al., *subm.*] with the aim of a characterization followed by modelization [Gräsle, Willert et al., *subm.*] of the multilayered aquifersystem. Besides the necessarily intensily hydraulic investigations, this publication contents aspects of the geochemical interactions of the sediments with the underlying saltwater.

#### *Location and geological setting of the investigation area*

For the investigations an Coastal Aquifer Test Field (CAT-Field) was determined, which is located between Bremerhaven and Cuxhaven in the northwestern part of Germany.



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

At the surface, only quaternary glacigenic deposits can be found in this area, sometimes covered with some meters of Holocene marine mud near to the coast. Their grain size differs from clays (Lauenburger Clay) to medium sands. The base of these Pleistocene sediments lies in undisturbed areas at about 30 m below NN. In the western part of the investigation area the transition from tertiary to quaternary sediments is influenced by a glacigenic melt water channel, the “Bremerhavener Rinne”, which reaches down to more than 350 m below surface and is filled up with coarse glacigenic sands and gravels [Kuster, 1979].

If not eroded, the tertiary layers start with Pliocene limnic-terrestrial sediments which are underlain by marine deposits at about 60 m below surface in the investigation area [Besenecker, H. et al., 1981].

In the deeper subsoil salinarteconics from Halite, deposits of the Zechstein age, built up the salt dome Altenbruch. The salt dome rises up to 900 m below the surface [Besenecker, H. et al., 1981] and had also influenced the sedimentation process in the tertiary ages. The base of the tertiary layers lies at about 600-800 m in between the salt walls.

### *Geochemical introduction*

Corresponding to the geology, different sources of salinity have to be taken into consideration. Common for all sources is a saltwater with a high ion content (mainly built up by  $\text{Na}^+$  and  $\text{Cl}^-$ ) but also a freshwater with a low ion content (mainly built up by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ ). Between these two end-members a dispersion induced transition zone will build up depending on the source of the salt content and the groundwater flow [Reilly and Goodman, 1985].

A changing salt content will induce geochemical processes to obtain a new equilibrium as there are cation exchange, precipitation and dissolution of minerals

(Gypsum, Calcite, Dolomite), sorption and desorption and oxidation of organic matter. Therefore, water composition deviates from simple conservative mixing of the endmembers.

In the present case ion exchange seems to be the most important factor. Negative charged exchanger sites (e.g. clay-minerals) are balanced by adsorption of cations from groundwater. The adsorbed ions are in equilibrium with the ions in solution. A changing solution composition changes the occupation of the exchanger sites as described in the following literature [Appelo and Greinaert, 1991], [Appelo and Willemssen, 1987], [Appelo and Postma, 1996]. In general the coefficients for the exchange reaction follow the lyotropic series but it depends on the material and solution composition. Uncertainties about the exchanger composition results in two different model assumptions for heterovalent exchanges. Corresponding to the Gaines & Thomas convention [Gaines and Thomas, 1953] the activities of the adsorbed ions are assumed proportional to the number of exchanged cations and, according to the Gapon convention [Gapon, 1933] to the number of exchanger sites [Appelo and Postma, 1996].

Due to changes of the concentration or the ionic strength, changing ion activities may result in dissolution and precipitation processes. In our investigations calcite and dolomite might be concerned as major minerals. The decreasing  $\text{Ca}^{2+}$  concentrations with increasing seawater share may result in an undersaturation of calcite. At the same time, the  $\text{Mg}^{2+}$  concentrations increase what might lead to a precipitation of dolomite. If both processes occur at the same time, the net effect would be a dolomitisation as described by [Magaritz and Luzier, 1985]. Apart from these two minerals, others may be concerned as well (e.g. Gypsum precipitation has been described by [Gomis-Yagües and Boluda-Botella et al., 2000]) but should have a minor effect on solution composition.

Adsorption onto clay minerals may also modify the composition of the water. Only a few elements are sensitive to adsorption as Lithium, Potassium and Boron what should lead in low element/ $\text{Cl}^-$  ratio of these elements, compared to the seawater ratio [Jones, Vengosh et al., 1999]. Adsorption seems to have minor importance in our case and is therefore not further discussed here. The same is the case for the reduction of organic matter because of the low  $\text{C}_{\text{org}}$  content of the glaciogene sediments in the investigated area.

## **FIELD DATA**

### *Investigations*

In summer 2000 three multilevel wells have been installed in a distance to the coast of about 4 km. Geological drills went down to 90 m below surface and each well had five filter zones of 1 m length between 5 and 50 m below surface. Samples of the drilled aquifer material were taken every 5 m; additional samples in the filter regions were taken for column experiments.

Groundwater samples were taken at different times of the year and acidified for conservation. Sensitive parameters as pH, Eh,  $\text{O}_2$ -saturation and temperature were determined immediately by electrodes in a flow chamber, alkalinity by titration after filtration.. Analyses in the laboratory were performed of about 40 components. Cation concentrations were determined by inductively coupled plasma atom adsorption spectroscopy (ICP-AES), anion concentrations by ionchromatography.

**Table 1** Composition of the groundwater samples (major ions)

well	Depth M b.Surf.	Na+ mmol/l	K+ mmol/l	Mg2+ mmol/l	Ca2+ mmol/l	Sr2+ μmol/l	Li+ μmol/l	Mn2+ μmol/l	Fe2+ μmol/l	Cl- Mmol/l	SO42- μmol/l	HCO3- mmol/l
LAF 1	6,50	0,59	0,31	1,77	4,56	10,80	4,32	23,59	42,96	1,30	1365,94	9,53
LAF 2	13,50	4,86	0,42	0,82	0,52	2,10	1,66	2,46	0,49	4,38	15,13	3,55
LAF 3	23,50	3,99	0,10	0,35	1,37	3,29	2,31	6,50	5,14	4,31	0,59	3,19
LAF 4	33,50	6,93	0,13	0,47	1,66	5,50	3,60	3,47	1,18	8,38	4,09	2,92
LAF 5	43,50	29,20	0,59	2,80	5,07	29,20	10,66	13,74	4,03	40,74	1242,61	2,69
GER 1	10,00	3,30	0,07	0,28	1,44	3,17	2,59	13,47	9,76	4,00	3,59	3,00
GER 2	23,85	3,45	0,06	0,03	1,47	3,44	1,44	8,21		4,54	0,00	2,95
GER 3	31,50	6,51	0,11	0,44	1,62	6,23	3,60	5,05	3,50	7,96	5,10	2,94
GER 4	42,00	33,39	0,45	2,87	5,91	35,76	10,09	8,82		47,81	1884,58	2,69
GER 5	50,50	48,67	1,18	7,94	7,94	45,78	20,46	15,91	63,42	76,81	1972,24	3,17
SET 1	11,70	131,35	2,69	16,08	4,28	18,91	16,28	24,52	7,00	141,85		36,71
SET 2	21,80	6,52	0,15	0,46	1,63	3,20	2,16	11,24	11,08	7,00	0,00	3,68
SET 3	33,30	3,75	0,09	0,37	1,43	2,92	2,16	4,60	5,71	4,29	0,00	2,97
SET 4	37,10	4,22	0,09	0,40	1,55	3,57	2,59	4,02	3,05	5,15	0,00	3,06
SET 5	43,60	14,04	0,32	1,14	2,14	9,23	5,47	3,74	12,37	16,78	550,78	2,52

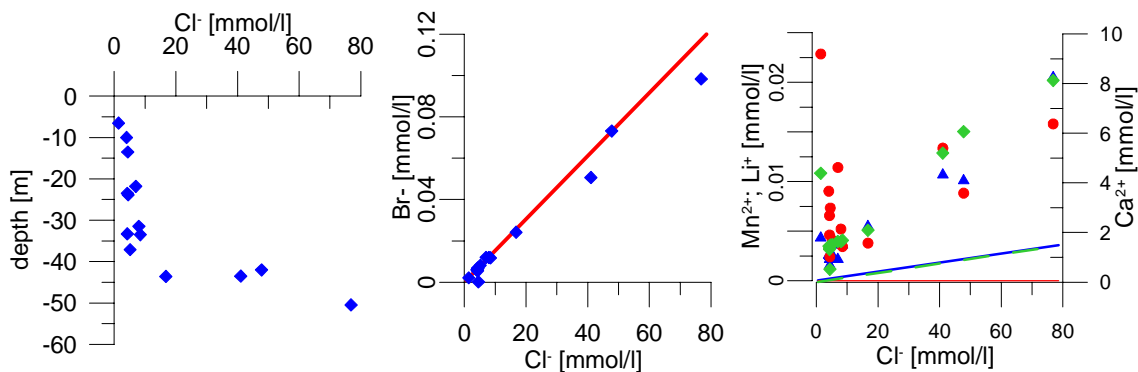
### Results and Discussion

The results of the chemical analyses of the groundwater samples are displayed in Table 1. The chloride concentrations show increasing values from 35 m below surface (Fig. 1) and determine the salinization zone. These results are supported by data from recent geophysical investigations [Siemon, Sengpiel et al., *subm.*; Willert, Behain et al., *subm.*] and older observations [Sindowski, 1969].

An important indicator for the source of the dissolved salt may be the contents of halogenides i.e. the  $\text{Br}^-/\text{Cl}^-$  ratio. At least, three different natural sources can be discussed. An obvious explanation for the chloride content in the groundwater might be the marine influence from the nearby North Sea or the underlying marine sediments. Other possible sources can be the dissolution of halite from the cited underlying salt dome or the weathering of minerals.

As discussed by [Stober and Bucher, 2000] the  $\text{Br}^-/\text{Cl}^-$  proportion should be higher than the seawater value if the salinity originates from the solution of halite and lower than the seawater value if mineral dissolution is the source.

The analyzed  $\text{Br}^-/\text{Cl}^-$  proportions of the deeper waters are in good accordance with the seawater values (Fig. 2). Therefore, a marine origin can be assumed for these waters. The origin of the marine salt content might be either a recent or an ancient seawater intrusion from the nearby coast, as demonstrated for the Wittmund area west of the river Weser by [Hahn, 1991], or a dispersion from underlying marine sediments with residual salt content as proposed by [Meinardi, 1991] for the Dutch brackish groundwaters.



**Fig. 2** left and middle: plot of  $\text{Cl}^-$  concentration v. depth and  $\text{Br}^-$  concentration (red line represents sea-water ratio); right: concentrations of  $\text{Ca}^{2+}$  (green rhombs);  $\text{Mn}^{2+}$  (red dots) and  $\text{Li}^+$  (blue triangles) vs.  $\text{Cl}^-$  concentration; lines represent seawater ratio.

An indication for the actual process might be the hydraulic data to proceed the flow directions of the groundwater. Piezometric data are rarely available at the moment but groundwater levels of the three examined wells lies mainly below sealevel, what might be an indicator for a seawater intrusion.

Another obvious evidence, which can be seen from the presented data in Fig.2 is an intense interaction of the sediments with the flushing water resulting in higher ion contents of Lithium, Calcium, Manganese and Iron (where the latter both are also controlled by redox reactions) with increasing depth and chloride content. The source of these enrichments seems to be different. Calcium originates probably predominant from exchange sites which will be occupied with increasing concentrations by sodium as described elsewhere (e.g. [Appelo and Postma, 1996; Jones, Vengosh et al., 1999]), but dolomitisation might be another possible source.

The source of Lithium, Manganese and Iron is more difficult to determinate. The higher concentrations in solution might be a product of mineral dissolution as discussed below. Especially the enrichments of Lithium are surprising. An expected adsorption resulted in an inverse effect.

## **EXPERIMENTAL AND NUMERICAL SIMULATIONS**

### *Method*

First laboratory experiments were carried out to simulate effects of an increasing salt content, i.e. a rising saltwater level in the ground. Therefore, a column experiment was carried out using natural aquifer material, sampled during the drilling campaign and stored meanwhile in close bottles at 3° C. The sediment samples originates from the filtered layer of the well GER 4 and were filled into two acryl columns (each of 50 cm length and 5 cm diameter) under wet conditions. The two columns were pursued parallel. During the condition phase the sediment was flushed with 0,6 ml/min (corresponding to a slope of 0,05) artificial groundwater (as analyzed at this location). The water was equilibrated to calcite by leading through two 200 cm<sup>3</sup> wash bottles filled with calcite. Electrical conductivity was measured continuously. Samples of input and effluent water were taken at different times and geochemical analyses of major components were carried out. After one week mineral equilibrium is presumed and reported by constant electric conductivity (EC) for over 100 hours. The geochemical analyses showed no significant differences between the input and the effluent water at the end of the condition phase. After the equilibrium phase the column was flushed with diluted (20 %), Calcite equilibrated seawater in the same manner (EC-measurements, sampling).

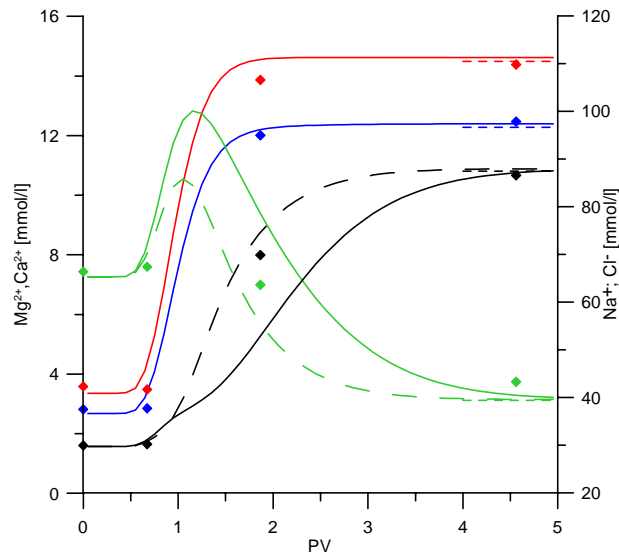
Using the computer program PHREEQC [Parkhurst and Appelo, 1999], the results of the column experiments were modeled. The transport through the column was simulated by separating the column into 50 cells each of 1 cm length. Input parameters for the transport module, which are displayed in Table 2, were determined by an EC-log fit. Only exchanger processes were considered so far and the initial composition of the exchange assemblage was defined implicitly by specifying that each exchanger is in equilibrium with the artificial groundwater used during the condition phase. The CEC (Cation Exchange Capacity) and exchange coefficients were gained by an CsCl-extraction of the original aquifer material. The results of the Gaines & Thomas convention [Gaines and Thomas, 1953] and of the Gapon convention [Gapon, 1933] were used in separated model runs and are also displayed in Table 2.

## Results and Discussion

The analyses of the effluent water showed the expected increase of the concentrations of Cl<sup>-</sup>, which is presumed to behave as an ideal tracer. An almost identical behavior shows the Na<sup>+</sup> concentration. Both of them match the modeled data of the transport/exchange simulation with the computer program PHREEQC [Parkhurst and Appelo, 1999] very well (Fig. 3). There can be found no significant differences between the two simulation runs (according to the Gapon and the Gaines & Thomas convention [Gapon, 1933]; [Gaines and Thomas, 1953]). An insignificant delayed concentration increase of Na<sup>+</sup> can be explained by a replacement of adsorbed cations which are released from the exchanger sites, for example Ca<sup>2+</sup>.

Even before Cl<sup>-</sup> reaches the level of the input water concentration, the Ca<sup>2+</sup> concentration of rises to a maximum value above the concentration of the local groundwater. After five pore volumes have been flushed the Ca<sup>2+</sup> concentration is still above the input value but stays more or less constant until the end of the experiment. The first Ca<sup>2+</sup> peak can surely be put down to an Ca<sup>2+</sup> release from the exchange sites of the sediment which is also observed and described in other experiments by [Gomis-Yagües, Boluda-Botella et al., 1997] and [Beekmann and Appelo, 1990] due to the higher Na<sup>+</sup> concentration. The simulation also reproduces this concentration peak. Our analytical data lies in between the results of the two simulation runs but tends toward the run relating to the Gapon [Gapon, 1933] convention. Surely, a closer sampling would give more detailed information about the preferable convention for our problem and will be done in the future. The later setoff might be an indicator for calcite dissolution or dolomitisation.

This assumption is supported by the simulation data. Speciations of the water analyses with PHREEQC [Parkhurst and Appelo, 1999] shows an increasing saturation index (SI) of Dolomite while the SI of Calcite decreases with higher salt content. The input water for the column experiment shows an SI of -0,4. Also Dolomite seems to be undersaturated, while the speciation of the groundwater samples show an increasing SI for Dolomite from -0,3 at well GER 3 (31,5 m b. Surf.) and 0 at GER 4 (42,0 m) to 0,3 at GER 5 (50,5 m).



**Fig.3** Simulated and experimental data of column transport of Cl<sup>-</sup> (red); Na<sup>+</sup> (blue); Mg<sup>2+</sup> (black) and Ca<sup>2+</sup> (green). Rhombs = exp. Data; solid line = simulation acc. to the Gaines and Thomas convention [Gaines and Thomas, 1953]; long dashed line = simulation acc. the Gapon convention [Gapon, 1933]; short dashed line = input water concentration

**Table 2** Experimentally determined column parameters and selectivity coefficients as used as input parameter for numerical simulation

		column A	column B	I	log K <sub>I/Na</sub>	log K <sub>I/Na</sub> <sup>G</sup>
<b>Kf</b>	m/s	9,50E-05	7,25E-05	Na <sup>+</sup>	0	
<b>Porosity</b>		0,36	0,29	K <sup>+</sup>	0,42	
<b>dispersivity</b>	M	0,017	0,013	Li <sup>+</sup>	1,62	
<b>length</b>	M	0,48		Ca <sup>2+</sup>	1,35	1,21
<b>diameter</b>	m <sup>2</sup>	1,96E-03		Mg <sup>2+</sup>	1,16	0,68
<b>slope</b>		0,05		Sr <sup>2+</sup>	1,29	-0,03
<b>CEC</b>	meq/ Kg	5,56		Mn <sup>2+</sup>	1,33	-0,24

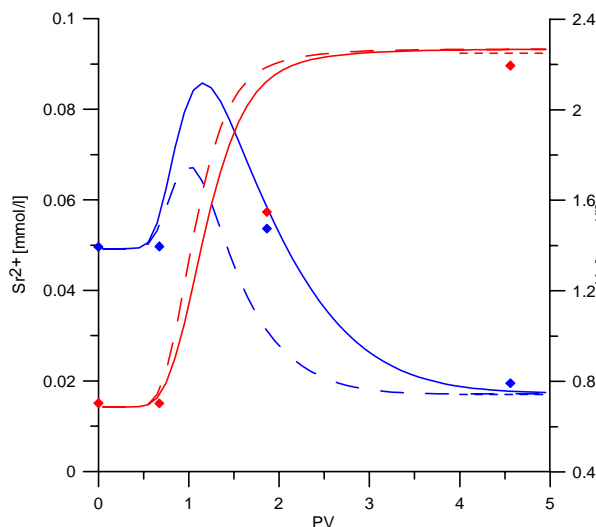
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The experimental data of the Magnesium shows increasing concentrations. Compared with the steep rising of the Sodium and Chloride concentration, the rising Magnesium

concentrations are delayed due to the replacement of Calcium on the exchanger sites. In fact, Magnesium has a bigger affinity to the exchanger sites than Sodium (cf. Table 2). This effect can be seen more clearly in the Magnesium concentration. Because of the bad resolution in the experimental data, an initial replacement of Magnesium due to high  $\text{Ca}^{2+}$  concentrations cannot be seen. But this is indicated in the model results according to the Gaines & Thomas convention [Gaines and Thomas, 1953]. In this simulation the selectivity coefficient for  $\text{Mg}^{2+}$  is higher, which is reflected in the curves. The experimental data tends toward the simulation data according to the Gapon convention [Gapon, 1933] as the Calcium data does. Also [Beekmann and Appelo, 1990] preferred the Gapon convention for multicomponent transport modeling. Besides, changing selectivity coefficients of  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$  during the breakthrough are discussed by [Beekmann and Appelo, 1990], which might be responsible for the differences between experimental and modeled data.

The concentration of  $\text{Sr}^{2+}$  shows the same behavior as  $\text{Ca}^{2+}$  does but with a less intense maximum. This also might be explained by exchange processes. If the two simulation runs are compared, the behavior of the exchange of  $\text{Sr}^{2+}$  on the exchanger sites seems to be better described by the Gaines & Thomas convention [Gaines and Thomas, 1953]. Even if there are only four samples, they have almost the concentration as predicted by the model run, using the Gaines & Thomas convention. In contrast to the  $\text{Ca}^{2+}$  concentration the concentration of  $\text{Sr}^{2+}$  reaches the input concentration and gives therefore no evidence for other mineral dissolution processes. This is according to the speciation results as  $\text{Sr}^{2+}$  is only present in solution.

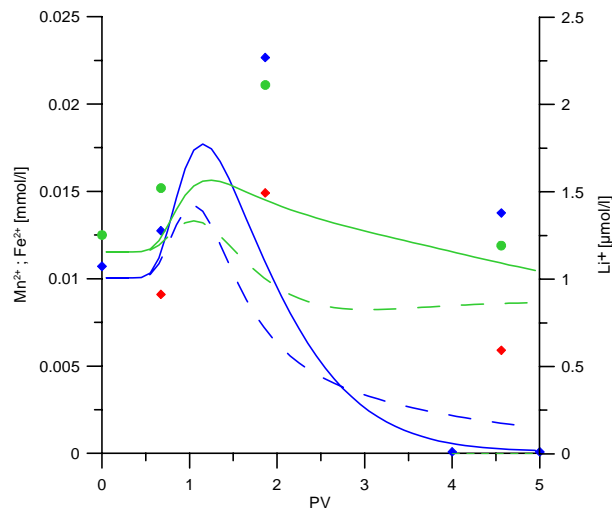
The analyzed concentrations of potassium shows increasing values with time as expected from simulations, but the simulation runs suggest a much faster concentration rise than measured. This is the matter for both model runs. A retardation of the potassium breakthrough was also noticed by [Beekmann and Appelo, 1990]. The lower concentrations as modeled might have be two reasons: First of all the selectivity coefficients depend on the concentration of the solution with a higher selectivity at lower concentrations of the solution [Stumm and Morgan, 1995]. The used solution for the column experiment was more concentrated than the groundwater where selectivity coefficients were determined for. Therefore, the preference of the alkaline earth metals could have been less during the experiment than simulated by the determined



**Fig. 4** Simulated and experimental data of column transport of  $\text{Sr}^{2+}$  (blue) and  $\text{K}^{+}$  (red) signature as before

coefficients. Secondly, a part of the potassium might be adsorbed nonreversible on the exchanger sites [Merkel and Sperling, 1996]. Also the  $\text{K}^{+}/\text{Cl}^{-}$  ratio of the deeper groundwaters lies below the seawater ratio, what might be another indication for the adsorption of potassium.

In addition  $\text{Mn}^{2+}$  shows a concentration peak at the start of the experiment. The input concentrations of these elements are to neglect in both runs (i.e. the condition phase and the flushing with salt water). Manganese is the only element whose concentration lies significantly above the input concentration after



**Fig. 5** Simulated and experimental data of column transport of  $\text{Li}^+$  (green);  $\text{Mn}^{2+}$  (blue) and  $\text{Fe}^{2+}$  (red, only experimental data): signature as before

of  $\text{MnCO}_3$  during the experiments, which might explain the excess ratio of  $\text{Mn}^{2+}$  in the output water. An increasing concentration of the solution might lead to enhanced dissolution due to a lower ion activity. This, coupled with the exchanger process, might explain the high concentration peak of  $\text{Mn}^{2+}$  at the beginning of the column experiment, which is much higher than the simulation implied. Also the relatively high concentrations, even after nine pore volumes flushed, indicate a slow process as mineral dissolution.

Iron shows the same concentration peak as Manganese. But no iron can be determined during the condition phase. The iron concentration drops down almost to its very small input concentration, but much slower than expected by a exchanger process. Unfortunately, the selectivity coefficient could not be determined, due to very small concentrations of iron in the extracted solution. Therefore, only the experimental data are presented in Fig. 5. As for manganese, the concentration peak seems to be too high to be explained only by exchanger processes; mineral dissolution might be another source which has to be considered.

Shortly after the beginning of flushing the column with diluted seawater, the concentration of Lithium shows also an concentration peak, even if the input concentration of  $\text{Li}^+$  has not changed during the experiment. This concentration peak seems to be too high for being induced by an exchange process. As for iron, the selectivity coefficient was hard to determine and the value given at Table 2 gives only an estimation (according to the theory, the coefficient for Lithium should be higher than for all other ions.) The simulated concentrations lie significantly below the experimental data, even if the Gaines & Thomas convention [Gaines and Thomas, 1953] results are in higher concentrations. A possible source of Lithium within the sediment might be the dissolution of Mica which is obviously present in the sediment. This might also be a source of iron up to an Fe/Li ratio of 5:1.

## CONCLUSIONS

In the water-containing layers of the CAT-Field, a zone of salinization could clearly be determined by an increasing  $\text{Cl}^-$  concentration from 35 m below surface onwards. The ratio of  $\text{Cl}^-/\text{Br}^-$  which correspond with the seawater ratio was used as indicator for the marine origin of the detected salt content. Further investigations have

the condition phase. A dissolution process must be assumed, as also indicated by the field data with a higher  $\text{Mn}^{2+}/\text{Cl}^-$  ratio than seawater. Another indication for mineral dissolution is given by water speciations with the PREEQC computer program [Parkhurst and Appelo, 1999]. While speciations of the sampled groundwater show a positive saturation index for Rhodochrosite ( $\text{MnCO}_3$ ) in the upper three filter zones of well GER, the lower two ones are in equilibrium ( $\text{SI} = 0$ ). Speciations of the input waters for the column experiments amount to a negative saturation index indicating a possible dissolution

to be done for a unambiguous determination of the source (i.e. marine intrusion or dispersion from tertiary marine layers). Oversized increasing ion contents of  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Li}^+$  indicate interactions of the aquifer material with the groundwater induced of increasing salt content.

A simple column experiment was carried out with the aim to get first indications of the geochemical processes at the fresh- saltwater interface. Analyses of the effluent water showed a significant increased concentration of the elements listed above. To separate well known exchanger processes from dissolution of minerals, a numerical model of the column transport with ion exchange using the PHREEQC [Parkhurst and Appelo, 1999] computer program was carried out. Input parameter for transport and exchanger composition were determined in separate experiments. The results showed a good accordance with experimental data, according the Gaines & Thomas convention [Gaines and Thomas, 1953] for the exchange of Strontium, Potassium and Sodium. The exchange of Magnesium and Calcium might be better represented by the data according to the Gapon [Gapon, 1933] convention. Higher output than modeled were found for  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Li}^+$ . These might originate from mineral dissolution of Calcite and Rhodochrosite which saturation indices change from saturated values to undersaturation with increasing salt content according to a water speciation with PHREEQC [Parkhurst and Appelo, 1999]. Increased  $\text{Li}^+$  concentration might originate from the weathering of Mica which can partly be found in high contents in the aquifer material. Potassium showed a retardation, which might be explained by changing selectivity coefficient or adsorption.

Further investigations will be done for an undoubted determination of the dissolution processes occurring during the salting of the coastal aquifer in the CAT-Field A higher resolution of the samples will facilitate a better determination of the exchanger processes.

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