

# Chromatographic pattern in a freshening aquifer (Tertiary Ledo-Paniselian aquifer, Flanders-Belgium)

J. Cardenal

*Instituto del Agua-University of Granada. 18071-Granada  
(Spain).*

K. Walraevens

*National Fund for Scientific Research-University of Ghent. 9000-  
Ghent, Belgium.*

## Introduction.

The freshening of a detrital aquifer, by fresh water intrusion in sediments deposited in a marine environment, has been studied. The survey area comprises the northern part of East- and West-Flanders in Belgium. The Ledo-Paniselian aquifer (LPa), with around 60 m of thickness, is semi-confined by a clayey formation, the Bartonian clay, which has a variable thickness of 20–60 m. The LPa is being recharged by infiltration through the Bartonian. This infiltration occurs mainly in the highest regions in the southern parts of the survey area (Walraevens & Cardenal, this volume). The marine conditions (represented by marine-cations,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , adsorbed in the clay) prevailing in the sediments before the last regression in Tertiary times, are being gradually expelled by infiltrating fresh water. Cation exchange plays an important role, mainly in the Bartonian clay, so  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  from the clay surfaces are being exchanged against  $\text{Ca}^{2+}$  from the fresh water. This implies that the LPa shows bands with different watertypes (Walraevens, 1990). In the recharge area, the groundwater is fresh, hard and  $\text{CaHCO}_3$ -type, which represents the end member of a freshening pattern. Downward the flow (to the NNE) the  $\text{MgHCO}_3$ -type, also fresh and hard, appears. The  $\text{NaHCO}_3$ -type is found in the northern part of the survey area. This last watertype is fresh or fresh-brackish and the hardness has clearly been lowered as a result of the cation exchange. Moreover, a net increase in  $\text{K}^+$  and  $\text{NH}_4^+$  (this last ion is also affected by cation exchange) concentrations in groundwater has been found just between the  $\text{MgHCO}_3$  and  $\text{NaHCO}_3$  types. This agrees with the expected chromatographic pattern in the freshening of an aquifer (Appelo, 1992) or a column experiment (Appelo *et al.*, 1990).

## Discussion.

The observed chromatographic pattern in the aquifer has been modeled by means of a geochemical/mixing cell model (PHREEQM; Nienhuis *et al.*, 1993) in order to show that the variation of watertypes in the LPa mainly responds to cation exchange processes in the overlying Bartonian clay and to a smaller extent in the LPa. The modeling has consisted in two parts.

First, the freshening of the Bartonian has been modelled. The Bartonian clay was considered as a column of 20 m, divided in 4 cells. The initial pore water quality was sea water equilibrated with calcite and the exchange complex in the clay (around 27 meq/100 gr). For the recharge water, pure water equilibrated with calcite and a  $P_{\text{CO}_2}$  of  $10^{-2.5}$  atm, which at 11°C means a 4mM  $\text{Ca}(\text{HCO}_3)_2$  water, was used. Another condition imposed during the freshening of the clay is related with the gypsum content observed in borings in the Bartonian. The gypsum results from the oxidation of the pyrite contained in the clay.  $\text{SO}_4^{2-}$  concentrations around 100–200 mg/l are usually found in the southern part of the survey area, so a limited source of gypsum dissolution has been maintained during simulation (0.5 mM per cell). After the column was flushed around 400 times, the water quality at the end of the column, that is the bottom of the Bartonian, was similar to that found in the recharge area of the LPa (fresh and  $\text{CaHCO}_3$ -type) and so, the simulation was stopped.

Next to the model of the Bartonian, the sequential watertypes obtained (first  $\text{NaHCO}_3$ -type, then  $\text{NaHCO}_3$  with high  $\text{K}^+$  and  $\text{Mg}^{2+}$  contents and, finally,  $\text{CaMgHCO}_3$  and  $\text{CaHCO}_3$ -types; figure 1 in Walraevens & Cardenal, this volume) have been flushed through a column of the LPa, simulating the subhorizontal flow in this aquifer. A column of 20 km, divided in 20 cells,

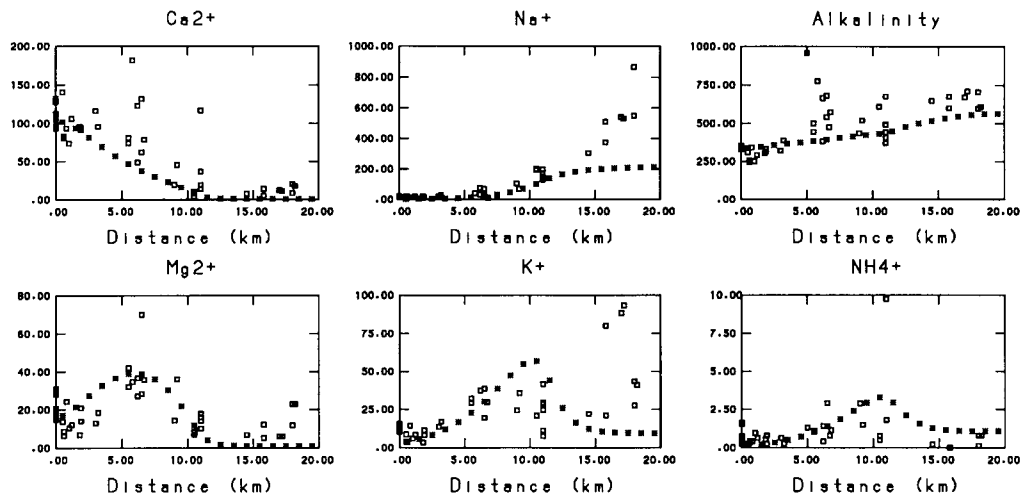


FIG. 1. Plot of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ , Alkalinity,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  and  $\text{NH}_4^{+}$  contents in the groundwater of Ledo-Paniselian aquifer along the flowpath. Squares are field data and asterisk modeled data. Values in mg/l.

was chosen. The initial watertype in the aquifer was also sea water equilibrated with calcite and the exchange complex in the LPa (5.5 meq/100 gr). With the former changing water qualities, it has been necessary to flush the aquifer 14 times to obtain the peaks of the main cations at the right positions, which were marked by the field data (Figure 1).

Other effects are related with the dissolution of the calcite contained in the sediment, which controls the alkalinity distribution. In order to maintain equilibrium with calcite, following the depletion of  $\text{Ca}^{2+}$  fixed by the clay, more of this mineral must be dissolved. In fact, Walraevens (1990) shows the relation between  $\text{HCO}_3^-$  contents and the extent of the cation exchange. But the alkalinity values modelled in this way (with calcite equilibrium) are clearly lower, between 200 and 400 mg/l, than those found in the field. It is possible to explain this disagreement between the observed data and the modelled ones by the reducing conditions existing in the LPa, which cause an important sulfate reduction (from more than 100 mg/l in the recharge area to less than 10 mg/l a few km downward the flow; Walraevens, 1990).

The  $\text{NH}_4^+$  content also rises between 6–12 km, which is attributed by Walraevens (1990) to cation exchange. Taking in mind the  $\text{NH}_4^+$  content in sea water is very low (<0.05 mg/l), it is necessary to think of an additional source of this cation, like diagenetic processes in pore water of seafloor sediments controlled by reactions with organic matter and subsequent adsorption of  $\text{NH}_4^+$  by the

clays, as it has been described by Murray *et al.*, (1978). Choosing an initial  $\text{NH}_4^+$  content in the sediment pore water of 2mM, it is possible to explain concentrations over 2 mg/l (exchanged for the  $\text{Ca}^{2+}$  from the infiltrating water) found in some parts of the aquifer.

With respect to the last 8 km of the aquifer, the model can not fit the field data at the end of the column. Two aspects that the modelling technique employed can not solve must be mentioned here. First the model considers a constant flow velocity through the whole column, which is not correct for the northern part of the aquifer, where the flow is limited and the water is leaving the LPa by an upward flow through the Bartonian (Walraevens, 1990). And second a mix with fossil sea water occurs in this part of the aquifer, so all cations, especially  $\text{Na}^+$ , increase in the northern part.

### Conclusions.

The modelling technique employed confirms the large extent of the cation exchange in the control of the water quality in the LPa and the importance not only of the  $\text{Ca}^{2+}/\text{Na}^{+}$  exchange, but also of  $\text{Ca}^{2+}/\text{K}^{+}$ ,  $\text{Ca}^{2+}/\text{Mg}^{2+}$  and even  $\text{Ca}^{2+}/\text{NH}_4^+$  exchanges.

### References

- Appelo, C.A.J. (1992). *Proc. 12th SWIM*, Barcelona. 193–206.
- Appelo, C.A.J., Willemsen, A., Beekman, H.E. and Griffioen, J. (1990). *J. Hydrol.*, **120**, 225–50.