

# Aquifer recharge and exchangeable cations in a Tertiary clay layer (Bartonian clay, Flanders-Belgium)

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## Introduction

The survey area comprises the northern part of East- and West-Flanders in Belgium. The recharge of the Tertiary Ledo-Paniselian detrital aquifer is occurring by infiltration through the Bartonian clay in the highest regions in the south of the survey area. Both in the aquifer and in the overlying clay layer, marine conditions were prevailing until the last regression at the end of Tertiary times. The infiltration of fresh water has led to the gradual freshening of the aquifer. The present distribution of the groundwater types shows the increasing marine influence in the direction of groundwater flow to the north (Walraevens, 1990).

In the westerly recharge area around Ursel, the hydraulic head above and below the Bartonian clay is accurately known, by the presence of 56 piezometers. The local thickness of the Bartonian being known as well (on the average 10 to 20 m), the hydraulic conductivity of the clay layer could be deduced. In the modeling of groundwater flow, an excellent agreement between observed and calculated heads is obtained with a value of  $10^{-9}$  m/s (Walraevens, 1987). Laboratory measurements mostly lead to values that are at least an order of magnitude lower. The discrepancy has

been ascribed to the presence of preferential pathways in the clay, through which the flow is preferentially taking place.

## Exchangeable cations in the Bartonian clay and freshening of the sediment.

A cored boring at Ursel provided the opportunity for determining CEC and exchangeable cations, both of the clay and of the underlying aquifer. The determination of CEC and the extraction of the exchangeable cations were performed by means of  $\text{NH}_4^+$ -acetate at pH 7. As the salts soluble in water also dissolve in  $\text{NH}_4^+$ -acetate, they were determined separately, and the result was subtracted from the one in  $\text{NH}_4^+$ -acetate.

CEC for the Bartonian clay ranges around 27 meq/100 g and for the Ledo-Paniselian aquifer, CEC is 5.5 meq/100 g on the average. The exchangeable cations in the Bartonian clay were determined to be:  $\text{CaX}_2 = 12$  meq/100 g, ranging between 5–18 meq/100 g;  $\text{MgX}_2 = 13$  meq/100 g, ranging between 7–19 meq/100 g; and less than 3 and 0.2 meq/100 g for KX and NaX, respectively (Walraevens & Lebbe, 1989).

The Bartonian clay at Ursel shows a very clear depletion in adsorbed  $\text{Na}^+$ , and to a lesser extent

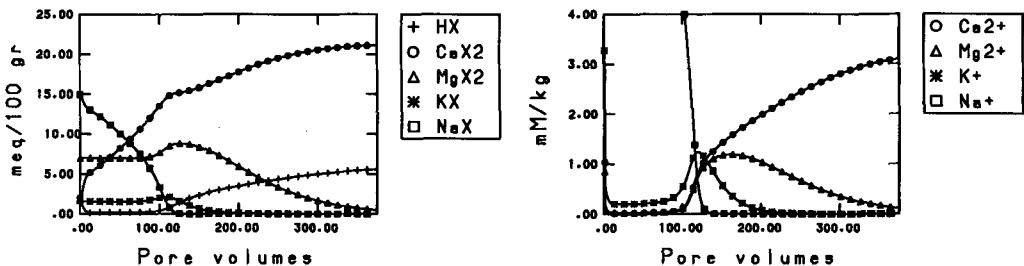


FIG. 1. Plot of the modeled amounts of exchangeable cations (in meq/100 g) and main cation contents (mM/kg) in the pore water of the Bartonian clay during the flushing (concentrations above 4 mM/kg in the first flushes are not shown).

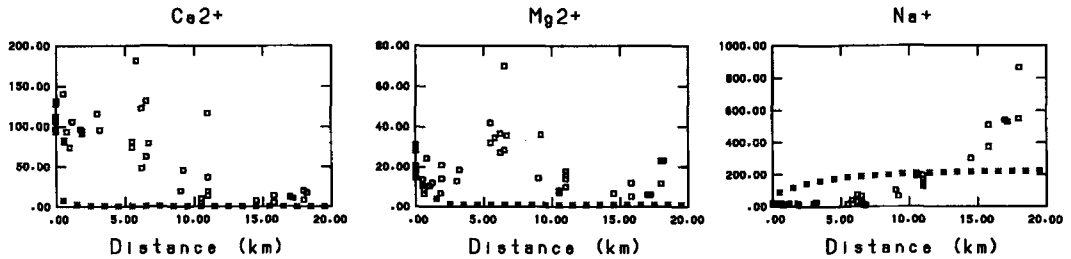


FIG. 2. Plot of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$  contents in the groundwater of Ledo-Paniselian aquifer along the flow path. Squares are field data and asterisk modeled data after the Bartonian clay has been flushed 150 times. Values in mg/l.

also in  $\text{K}^{+}$ , when compared to a boring out of the recharge area. Adsorbed  $\text{Ca}^{2+}$  is higher at Ursel. However, the analyzed samples of the Bartonian clay at Ursel do not at all show a depletion in adsorbed  $\text{Mg}^{2+}$ . This is a surprising result, as the Ledo-Paniselian aquifer in this recharge area is containing  $\text{CaHCO}_3$ -water, indicating that the flushing of the overlying clay layer has practically been accomplished.

A geochemical/mixing cell model (PHREEQM; Nienhuis *et al.*, 1993) has been used to simulate the freshening of the Bartonian and the subsequent recharge to the underlying aquifer. Details about the modeling can be found in another contribution (Cardenal & Walraevens, *this volume*). In short, the Bartonian, divided in 4 cells of 5 m each one, has been flushed with a 4mM  $\text{Ca}(\text{HCO}_3)_2$  solution, including cation exchange during transport, calcite equilibrium and gypsum dissolution. The initial pore water quality has been sea water equilibrated with calcite.

The computed data are shown in figure 1, which represents the main cation concentrations of the different solutions which are leaving the Bartonian and the distribution of the exchangeable cations in the clay during the flushing. After the clay has been flushed around 120–150 times, the distribution of the exchangeable cations is similar to that found in the boring at Ursel, although the amounts of  $\text{CaX}_2$  and  $\text{MgX}_2$  are slightly larger and lower, respectively, to the mean values found in the boring. At that stage the pore water solution which is leaving the Bartonian contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as main cations and no significant  $\text{Na}^{+}$  content. This water is very different from that found at present in the recharge area of the Ledo-Paniselian aquifer. When the different solutions leached out from the clay till this stage are used to flush the aquifer, it is not possible to model the observed distribution of the groundwater quality (Figure 2). The clay must be flushed near 400 times to obtain the present situation in the aquifer (Cardenal and Walraevens, *this volume*). This confirms the

existence of preferential paths in the Bartonian where the flow is faster. That means the flow line in the analyzed boring must be part of a slower pathway and the freshening here is still in process.

As shown in figure 2,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which are being leached from the clay (both around 1 mM/kg after the Bartonian has been flushed 150 times; figure 1), decrease drastically in the first 2 km of the aquifer. This implies that cation exchange is also important in the sandy aquifer although the CEC is 5 times lower than the CEC in the Bartonian, and that not only  $\text{Ca}^{2+}/\text{Na}^{+}$  but also  $\text{Mg}^{2+}/\text{Na}^{+}$  exchange occurs.

In figure 1 the amount of exchangeable  $\text{H}^{+}$  (HX) has been represented. Proton exchange has been included because the importance of this reaction has been recognized in column experiments (Appelo *et al.*, 1990) and in detrital aquifers in the Netherlands and the United States (C.A.J. Appelo, pers. comm.) to be responsible for calcite precipitation/dissolution processes and for alkalinity and pH distribution of the pore water. Research on this topic is continuing.

### Conclusions.

By means of a geochemical/transport model the freshening of marine sediments has been studied. This has confirmed the presence of preferential pathways, deduced by other techniques, in the clay layer through which a sandy aquifer is recharged. The modeling has also shown the importance of both cation exchanges:  $\text{Ca}^{2+}$  for  $\text{Na}^{+}$  and in less extent  $\text{Mg}^{2+}$  for  $\text{Na}^{+}$ .

### References:

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- Nienhuis, P., Appelo, C.A.J. and Willemsen, A. (1993) PHREEQM. Free University Amsterdam.