A chromatographic model for water quality variations in the Aquia aquifer (Maryland, USA)

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Abstract

Flushing of marine sediments with fresh water will induce a chromatographic pattern of the cations which are displaced from the exchange complex. Upstream from the salt/fresh water boundary, a sequence of Na^+, K^+, Mg^{2+} and lastly Ca^{2+} dominated water is expected (Ca^{2+} is the displacing cation; HCO_3^- is the major anion). This sequence is present in the Aquia aquifer. Field data from this aquifer have been modeled with a 1D geochemical transport model to satisfactory agreement. The upper 30 miles of the aquifer must have been flushed about 8 times under the model conditions, which means that the now observed chromatographic pattern can have been established in 100 ka.

Introduction

Along flowlines in the Aquia aquifer, Chapelle and Knobel (1983) observed zonal bands with changes in the concentrations of the major cations that have been attributed to Ca^{2+} for Na^+ exchange and dissolution of Mg-calcites. The pattern is akin to a chromatographic sequence, where excess cations from the seawater exchange complex are flushed in order of increasing selectivity: first Na^+, then K^+, and lastly Mg^{2+}. The geochemical transport model PHREEQM (Appelo and Postma, 1993) was adapted to the hydraulic conditions in the Aquia, and run to see whether the sequence of water qualities could result from chromatographic transport.

Chromatographic modeling

PHREEQM is a 1D transport model that uses PHREEQE (Parkhurst *et al.*, 1980) to calculate the chemical reactions among water and sediment. It has been developed to model salt/fresh water displacements in Dutch aquifers, and includes cation exchange in the full dynamic sense. A form of the constant capacitance model was used for proton exchange. Exchange parameters are taken from literature.

The Aquia aquifer

The Aquia aquifer extends over 90 km from the outcrop near Washington D.C. to Chesapeake Bay in the East, where it is bounded by a facies change. The aquifer sediment has 10 to 35% glauconite and is sealed on top and bottom by clay layers. These properties make the Aquia probably the most ideal analogue of a laboratory chomatographic column that can be found on earth (fig. 1).

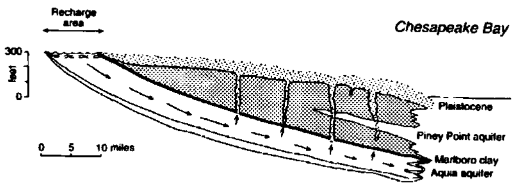

Figure 1. Schematic cross section of the Aquia aquifer (Maryland, USA).

Model results

Figure 2 illustrates that a chromatographic model fits the observed water quality. The model results are quite robust, and not much dependent on model parameters. The sequential appearance of K^+ and Mg^{2+} after Na^+ can be varied only by changing the K^+/Mg^{2+} selectivity. The apparent dip in alkalinity at the start of the $NaHCO_3$ water type is related to proton exchange at that front. Proton exchange makes CO_2 sources hypothesized by e.g. Foster (1950) and Chapelle and McMahon (1991) unnecessary; it explains the high $\delta^{13}C$ since all *TIC* originates from calcite.

The chromatographic pattern allows for a timespace estimate. The upstream 30 miles have been flushed 8 times in the model. Since an age of 12 ka has been found for water at 29 miles along the flowpath (Purdy *et al.*, 1992), about 100 ka have been necessary for the now observed water quality variations.

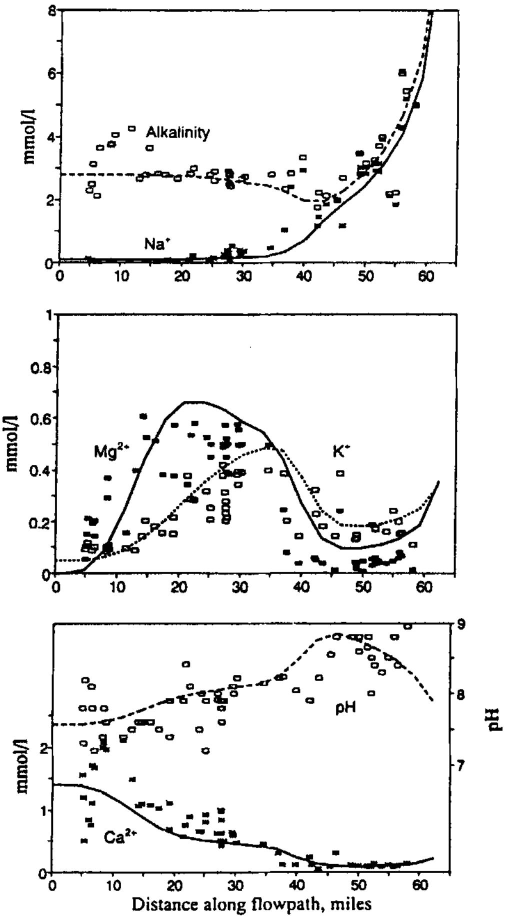

FIG. 2. Observed concentration changes along a flowline in the Aquia aquifer and PHREEQM model results.

References

Appelo, C.A.J. and Postma, D. (1993) *Geochemistry, groundwater and pollution.* Balkema, Rotterdam, 536 pp.

Chapelle, F.H. and Knobel, L.L. (1983) *Ground Water*, **21**, 343–52.

Chapelle, F.H. and McMahon, P.B. (1991) *J. Hydrol.*, **127**, 85–108.

Foster, M.D. (1950) *Geochim. Cosmochim. Acta*, **1**, 33–48.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. (1980) *US Geol Surv. Water Resour. Inv.*, **80-96**, 210 pp.

Purdy, C.B., Burr, G.S., Rubin, M., Helz, G.R. and Mignerey, A.C. (1992) *Radiocarbon*, **34**, 654–63.