

REACTIVE TRANSPORT MODELLING OF AMMONIUM: 1D CONCEPTUAL MODELLING AND COMPARISON OF REACTIVE TRANSPORT CODES

B. Haerens¹, A. Dassargues^{1,2} & D. N. Lerner³

¹Hydrogeology & Engineering Geology Group, Department of Geology-Geography, Katholieke Universiteit Leuven, Redingenstraat 16, B-3000 Leuven, Belgium.

²Laboratoires de Géologie de l'Ingénieur, d'Hydrogéologie et de Prospection Géophysique (L.G.I.H.), Université de Liège, Bât.B19, B-4000 Liège, Belgium.

³Groundwater Protection and Restoration Group (GPRG), Department of Civil and Structural Engineering, University of Sheffield, Sheffield S1 3JD, UK.

E-mail: bruno.haerens@geo.kuleuven.ac.be

Phone: +32-16-326449

Fax: +32-16-326401

Abstract Contamination of ammonium, as main inorganic contaminant, resulted from disposal of ammoniacal liquor at a former coal carbonisation plant at Mansfield, UK. Previous research for evaluating natural attenuation revealed strong retardation of ammonium in the aquifer due to ion exchange in the aquifer. In a first modelling approach a conceptual 1D-model example is considered where an ammonium contaminated aquifer is flushed by pristine background groundwater. Two multicomponent reactive transport models, PHT3D (Prommer et al., 2001) and PHREEQC-2 (Parkhurst and Appelo, 1999) were used for the model example and a comparison between the codes was made.

INTRODUCTION

Disposal of ammoniacal liquor coming from a former coal carbonisation plant at Mansfield, UK, gave rise to contamination of the groundwater by both organic and inorganic contaminants (Broholm et al., 1998; Jones et al., 1998). The ammoniacal liquor was dumped in small lagoons where it could infiltrate into the groundwater. High levels of dissolved ammonium (up to ~ 350mg/l NH₄-N) in the groundwater revealed ammonium as the main inorganic contaminant present in the aquifer. When entering the aquifer ammonium is retarded by ion exchange in the aquifer, where ammonium exchanges onto the aquifer sediment releasing the native cations of the sediment. After contamination has stopped leaking into the aquifer, the ammonium will be exchanged off the aquifer sediment by the flushing of the aquifer with pristine background groundwater under natural groundwater gradient conditions.

Because ammonium is competing for ion exchange with several other cations simultaneously, a multi-component reactive transport model is required that can handle ion exchange reactions among multiple cations. The modelling example, presented in this paper, serves as a first step for future 2D/3D simulations.

MULTICOMPONENT REACTIVE TRANSPORT MODEL

Recently (Prommer et al., 2001) developed a MODFLOW/MT3DMS-based reactive multicomponent transport model. The model couples via a sequential approach, the three-dimensional transport simulator MT3DMS (Zheng and Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999). The model uses total aqueous component concentration (Engesgaard and Kipp, 1992; Yeh and Tripathi, 1989) as primary dependent variable. The reactive transport equation is then given as (Prommer et al., 2001):

$$\text{for mobile components: } \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + r_{\text{reac}}$$

and for immobile components: $\frac{\partial C}{\partial t} = r_{\text{reac}}$

where v_i is the pore water velocity in direction x_i , D_{ij} is the hydrodynamic dispersion coefficient, r_{reac} is a source/sink rate due to the chemical reaction and C is the total aqueous component concentration, defined as: $C = c + \sum_{i=1, n_s} \gamma_i^s s_i$ where c is the molar concentration of

the (uncomplexed) aqueous component, n_s is the number of species in dissolved form that have complexed with the aqueous component, γ_i^s is the stoichiometric coefficient of the aqueous component in the i^{th} complexed species and s_i is the molar concentration of the i^{th} complexed species.

Since PHREEQC-2 can handle reactive transport calculations, yet only in 1D, as well, the code was used to compare results of the modelling example with the PHT3D code. Both codes use the same geochemical reaction module but a different scheme to couple the hydrodynamic transport and geochemical reactions (see figure 1).

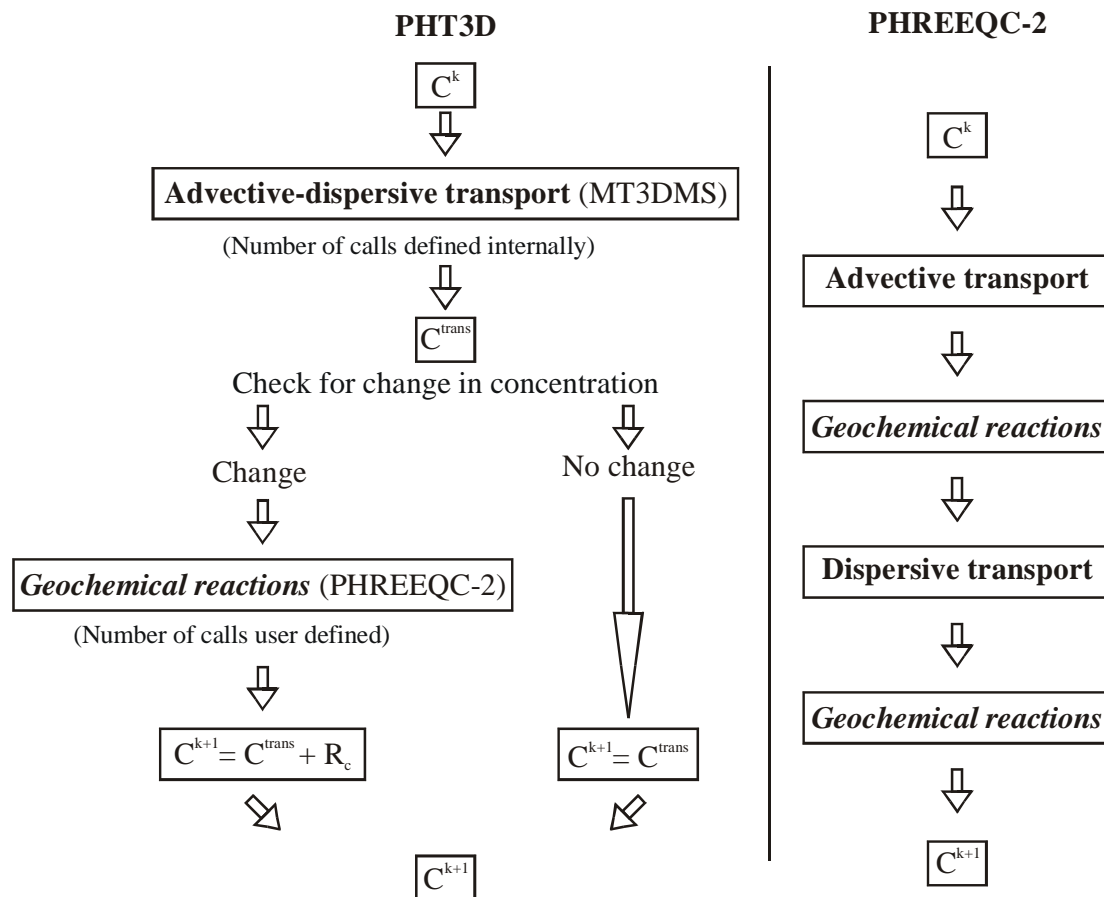


Figure 1: Coupling scheme between hydrodynamic transport and geochemical reactions. C^k and C^{k+1} are the total aqueous components concentrations at the old and new time levels, respectively, and R_c is the source/sink term linking the transport module with the reaction modules.

1D-MODEL EXAMPLE

The model example (figure 2) consists of a 1D flowtube that represents the ammonium contaminated aquifer with an injection well at the influent boundary to simulate the continuously flushing by pristine background groundwater after the contamination has stopped. The concentration at the end of the flowtube serves as observation point. Table 1 and 2 show the physical parameters and the hydrogeochemical initial and boundary conditions for the model example. For the reactive transport calculations the thermodynamic data from the PHREEQC-2 code are used (Parkhurst and Appelo, 1999).

Simulation results of the modelling example show that large numbers of pore volumes (i.e., a nondimensional time parameter where elapsed time is divided by the hydrodynamic residence time (Brusseau, 1994)) are needed to flush the ammonium (figure 3) off the aquifer sediment at the observation point at the end of the flowtube. When the exchange front has passed the entire flow tube the concentrations of the more selective cations in respect with ammonium (Ca and Mg) increase to reach the concentration levels of the background water. Figure 3 shows also the effect of flushing the aquifer on the pH. During the first twelve pore volumes ammonium is exchanged off from the aquifer sediments and the consequent release of ammonium into the groundwater causes a drop of pH due to the reaction: $NH_4^+ \rightleftharpoons NH_3 + H^+$. When the exchange front has passed the observation point after twelve pore volumes, the pH increases again and is in equilibrium with the incoming pristine background water.

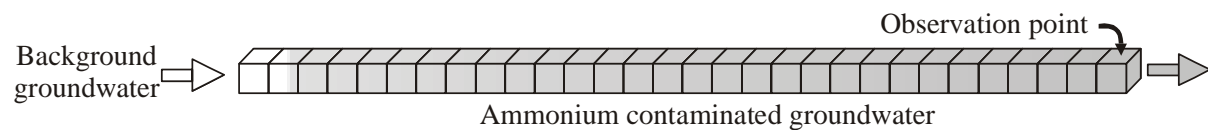


Figure 2: Conceptual 1D-model example

Table 1:

Physical parameters used for example problem. Data from (Jones, 2001).

| Parameter | Unit | |
|--|----------------------------------|---------|
| Length of flowtube | m | 30 |
| Spatial discretisation interval | m | 1 |
| Final solution time | days | 5000 |
| Longitudinal dispersivity | m | 0.5 |
| Hydraulic conductivity | m day ⁻¹ | 2.5 |
| Effective porosity | - | 0.2 |
| Prescribed flux influent boundary ^a | m ³ day ⁻¹ | 0.02375 |
| Prescribed head effluent boundary ^a | m | 1 |

^a Calculated based on the observed hydraulic gradient of 0.0095 and the hydraulic conductivity.

Table 2

Initial and boundary conditions: chemical concentrations (concentrations in moles per liter, unless otherwise specified) and hydrogeochemical parameters. Data from (Jones, 2001).

| Parameter | Contaminated groundwater (flowtube) | Background groundwater (influent boundary) |
|--------------------|-------------------------------------|--|
| CEC | 0.122 (eq/l) ^c | |
| pH | 7.9 | 8.3 |
| O ₂ | 2.5 x 10 ⁻⁴ | bdl |
| Na | 8.6 x 10 ⁻⁴ | 1.3 x 10 ⁻³ |
| K | 1.3 x 10 ⁻⁴ | 1.3 x 10 ⁻⁴ |
| NH ₄ -N | 6.9 x 10 ⁻³ | bdl |
| Mg | 1.4 x 10 ⁻³ | 5.0 x 10 ⁻⁵ |
| Ca | 1.8 x 10 ⁻³ | 1.5 x 10 ⁻⁴ |
| Cl ^a | 2.5 x 10 ⁻³ | 3.2 x 10 ⁻³ |
| SO ₄ | 1.6 x 10 ⁻³ | 9.9 x 10 ⁻⁴ |
| NO ₃ | ns | 8.9 x 10 ⁻⁴ |
| C(4) ^b | 2.8 x 10 ⁻³ | 2.9 x 10 ⁻³ |

^a Adjusted to achieve charge balance

^b Calculated based on alkalinity measures.

ns = not sampled

bdl = below detection limit

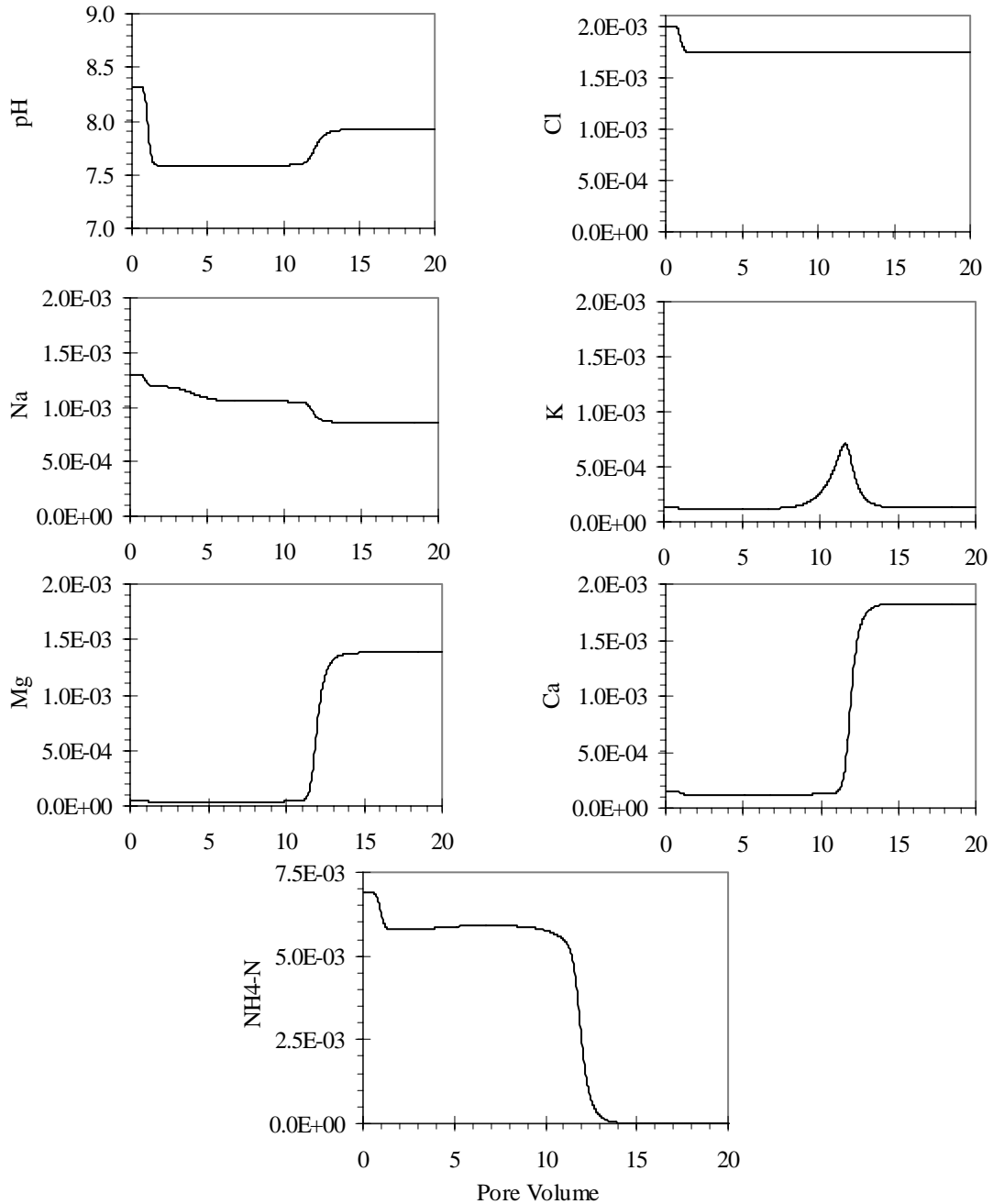


Figure 3: Total aqueous component concentration (moles per liter except for pH) versus pore volumes calculated at the observation point at the end of the flow tube.

COMPARISON OF SIMULATION RESULTS

Figure 4 shows the comparison of simulation results from the two codes. For transport of a non-reactive solute, as shown for Cl, both codes lead to the same results. For transport of a reactive solute, as shown for NH₄-N, there exists a discrepancy for a reaction time step, R_t , of 10 days in the PHT3D code. R_t defines the time step at which the code switches to the geochemical reaction calculation whereas the transport time step (advection-dispersion) is calculated internally by the MT3DMS code to meet the various stability criteria [Zheng, 1999 #251] (see also figure 1). A discrepancy arises when, as in the case with $R_t = 10$ days, several

transport time steps for advection-dispersion transport are performed before the program switches to the geochemical reaction calculation. This results in a loss in accuracy of the modeling of the exchange front in our example. This is confirmed by (Engesgaard and Traberg, 1996) who stated also that the accuracy of a sequential coupling approach is dependent on the time step. PHREEQC-2 simulation results don't show this behavior because only one single time step is used for the reactive transport calculation and the geochemical reactions are calculated after both the advective and dispersive steps (see figure 1).

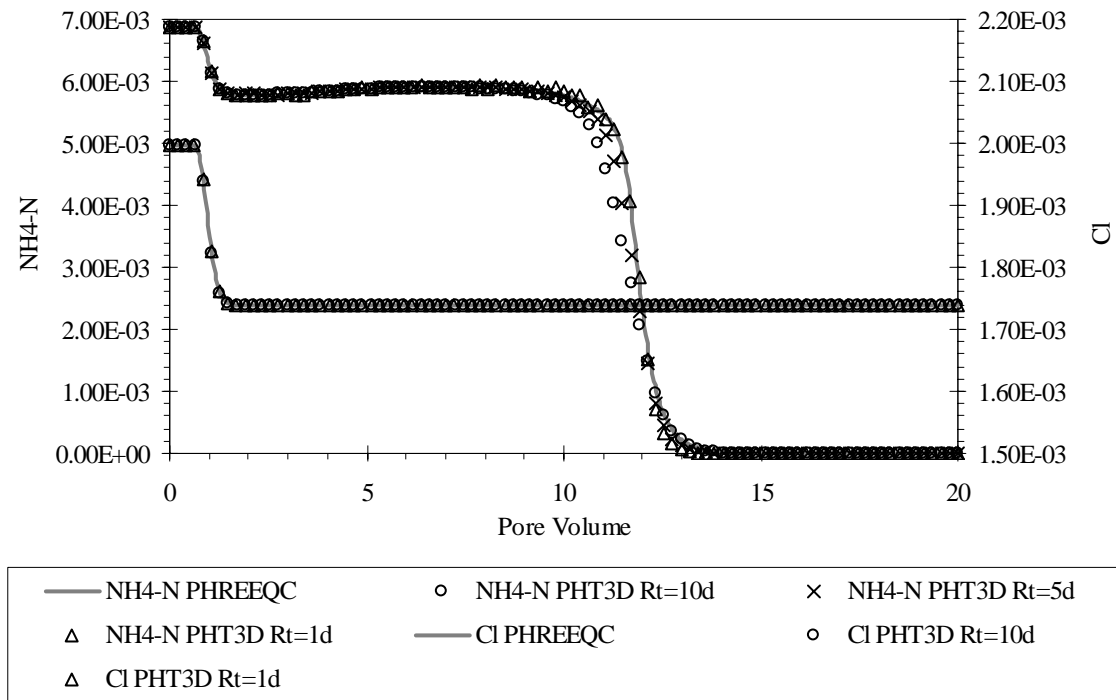


Figure 4: Comparison between the simulation results of PHT3D and PHREEQC-2 showing the effect of decreasing R_t upon the accuracy of the reactive transport modeling (concentrations are in moles per liter).

SUMMARY AND CONCLUSIONS

A 1D model example for multicomponent reactive transport of ammonium was set up for future 2D/3D simulations. The example showed strong retardation of ammonium due to ion exchange on the aquifer sediment and the consequent influence on pH. Furthermore simulation results obtained by two reactive transport codes were compared in order to assess their accuracy. It is shown that for the PHT3D code the reaction time step R_t should approach the time step calculated internally by the MT3DMS module for advective dispersive transport.

ACKNOWLEDGMENTS

We would like to acknowledge H. Prommer for providing and the help with the PHT3D code and the GPRG-group of the University of Sheffield for providing data from their research site.

REFERENCES

- Broholm, M.M., Jones, I., Torstensson, D. and Arvin, E., 1998. Groundwater contamination from a coal carbonization plant. In: D.N. Lerner and N.R.G. Walton (Editors), Contaminated land and groundwater: Future directions. Engineering Geology Special Publication. The Geological Society, London, pp. 159-165.
- Brusseau, M.L., 1994. Transport of reactive contaminants in heterogeneous porous media. *Reviews of Geophysics*, 32(3): 285-313.
- Engesgaard, P. and Kipp, K.L., 1992. A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite. *Water Resources Research*, 28(10): 2829-2843.
- Engesgaard, P. and Traberg, R., 1996. Contaminant transport at a waste residue deposit: 2. Geochemical transport modeling. *Water Resources Research*, 32(4): 939-951.
- Jones, I., 2001. Processes controlling the transport and attenuation of contamination from a coking plant in a sandstone aquifer. PhD Thesis, University of Bradford, Bradford, 247 pp.
- Jones, I., Davison, R.M. and Lerner, D.N., 1998. The importance of understanding groundwater flow history in assessing present-day groundwater contamination patterns: a case study. In: D.N. Lerner and N.R.G. Walton (Editors), Contaminated land and groundwater: future directions. Geological Society, London, pp. 137-148.
- Parkhurst, D.L. and Appelo, C.A.J., 1999. PHREEQC - User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigation Report 99-4259, USGS.
- Prommer, H., Barry, D.A., Chiang, W.-H. and Zheng, C., 2001. PHT3D - A MODFLOW/MT3DMS-based reactive multi-component transport model. In: Seo, E. Poeter and C. Zheng (Editors), MODFLOW 2001 and Other Modeling Odysseys, pp. 477-483.
- Yeh, G.T. and Tripathi, V.S., 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resource Research*, 25(1): 93-108.
- Zheng, C. and Wang, P.P., 1999. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems. Contract Report SERDP-99-1, U.S. Army Engineer Research and Development Center, Vicksburg, MS.