432

Multicomponent reactive transport modelling of ammonium contamination at a former coal carbonisation plant

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ABSTRACT

Ammonium is observed as the main inorganic contamination in groundwater at a former coal carbonisation plant in Mansfield UK. Natural attenuation of ammonium occurs primarily due to retardation by cation exchange with the native cations present in the aquifer and to a lesser degree due to re-oxidation by recharge and flushing with oxygenated water. In order to simultaneously account for ion exchange of multiple, competing cations and aqueous complexation reactions, a multicomponent reactive transport model was selected to simulate the fate, i.e., transport and reactions, of ammonium. This paper gives an overview of the employed multicomponent reactive transport model, PHT3D (Prommer, 2002; Prommer et al., 2001) and shows an application to the field site.

KEYWORDS

Ammonium, cation exchange, reactive transport modelling, natural attenuation

Introduction

Disposal of ammoniacal liquor in small lagoons at a former coal carbonisation plant resulted in contamination of the underlying Permo-Triassic sandstone aquifer with both organic and inorganic contaminants (Broholm et al., 1998; Jones et al., 1998). High levels of dissolved ammonium (up to ~350mg/l NH4/N) revealed ammonium as the main inorganic contaminant in the aquifer. Cation exchange sites of the pristine aquifer material are in equilibrium with the hydrochemistry of the pristine groundwater and are mainly occupied by calcium and magnesium (Jones, 2001). Since high levels of ammonium are leached into the groundwater, ammonium exchanged with the native cations on the exchange sites, resulting in attenuation of ammonium and in a calcium and magnesium peak (and to a lesser degree a peak of the other native cations) migrating with the groundwater flow velocity. Based on historical data from the former plant and field measurements, Jones (2001) concluded the contaminant input lasted for approximately 18 years, from 1956 till 1974. Once contaminant input had

stopped after 18 years, the reverse cation exchange occurred, i.e., the ammonium on the exchange sites were replaced by the cations of the flushing background water, thereby creating a retarded ammonium plume.

Multicomponent reactive transport models

When dealing with reactive solutes in groundwater several approaches exists to handle the geochemical reactions: a pure kinetic, an equilibrium (i.e., local equilibrium approach or LEA) or a mixed kinetic-equilibrium approach. The choice between these approaches depends upon the problem that is concerned. Cation exchange reactions are generally known to be relatively fast, i.e., have reaction half times of seconds to hours (Langmuir, 1997). For these reaction half times, the observed groundwater flow velocities of 0.25m/d and a grid spacing of 10m, the resulting range of Damkohler numbers, D_a, is $3.456e^6$ to 960. The Damkohler number is a dimensionless parameter representing the ratio of a reaction rate to an average transit time with (Boucher & Alves, 1959):

$$D_a = \frac{r \cdot L}{v_e}$$

where, r is the reaction rate (s^{-1}), L is a reference length (m) and v_e is the pore water velocity ($m.s^{-1}$). Comparing this range with the limiting D_a of 100 necessary for the LEA to be applicable (Jennings & Kirkner, 1984), indicates that the LEA approach can be expected to be a good approximation for modelling cation exchange reactions.

Both, single-species transport and batch-type geochemical modelling are established techniques for practical hydrogeological and hydrogeochemical investigations. In addition, more recently an increasing number of models that combine those techniques have appeared in the literature (Chilakapati et al., 2000; Gao et al., 2001; Gwo et al., 2001; MacQuarrie & Sudicky, 2001; Prommer et al., 2001; Saaltink et al., 2001; van der Lee & De Windt, 2001; Zhu et al., 2001). One of these models is PHT3D (Prommer, 2002; Prommer et al., 2001) that couples via a sequential approach, the three-dimensional transport simulator MT3DMS (Zheng & Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst & Appelo, 1999). The

PHREEQC-2 model is capable of solving complex sets of equilibrium and/or kinetic geochemical reactions. This and other geochemical models are using the concept of components in a standard way. Components are defined as a set of chemical entities that permits a complete description of the stoichiometry of the geochemical system (Bethke, 1996; Morel, 1983; Westall et al., 1976). Applying this concept, the set of non-linear equations governing the geochemical equilibrium reactions includes a mass action law for each species and a mass- or mole-balance for each component. For the cation exchange reaction, this leads to the following mass action equation:

$$mA^{n+} + nB\text{-}X_m \leftrightarrow nB^{m+} + mA\text{-}X_n$$
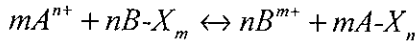
and a mass-balance following the Gaines & Thomas (1953) approach:

$$K = \frac{a_B^m N_{A\text{-}X_n}^n}{a_A^m N_{B\text{-}X_m}^n}$$

where K is the selectivity coefficient for the cation exchange reaction, a denotes activity, and N equivalent fraction given by:

$$N_{A\text{-}X_n} = \frac{meq\ of\ A^{n+}\ per\ 100g\ of\ sediment}{CEC\ (meq\ per\ 100g\ sediment)}$$

Analogously mass action and mass balance equations can be defined for other geochemical reactions such as aqueous complexation and precipitation/dissolution.

The model used in this research, couples an existing, well tested geochemical model with an existing, also well tested and widely applied transport model through a sequential operator-split approach. Thereby the total aqueous component concentrations serve as the primary dependent variable (Engesgaard & Kipp, 1992; Yeh & Tripathi, 1989). This gives the following governing equation for mobile aqueous components (Prommer et al., 2001):

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

and for immobile components:

$$\frac{\partial C}{\partial t} = r_{reac}$$

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 reactions 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 ith complexed species and s_i is the molar concentration of the ith complexed species.

Field site: hydrogeology and cation exchange pattern

The aquifer geology consists of 80m Permo-Triassic Sherwood sandstone overlying relative impermeable Permian Marls and Lower Magnesian Limestones. The sandstone aquifer is composed of two principal sedimentary facies. The Pebble Beds form the upper 30 to 40m of the sandstone aquifer, with the Mottled sandstones making up the lower 40 meters of aquifer. The Pebble Beds, more coarse grained than the Mottled Sandstones, have consequently a higher conductivity and porosity than the Mottled Sandstones as was shown by hydraulic packer tests (Jones, 2001).
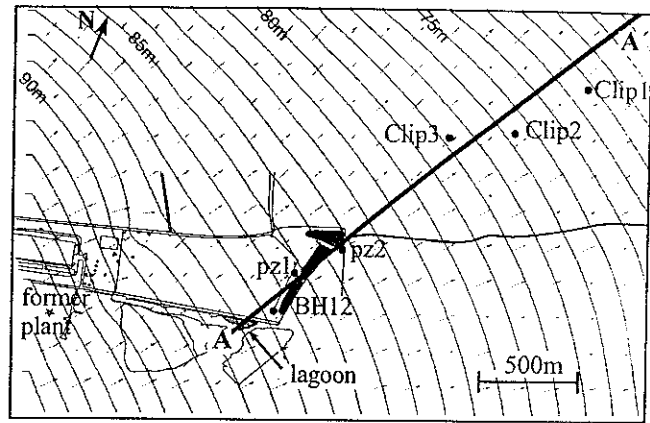

Fig. 1. Location and piezometric map of the field site with groundwater velocity directions.

The research of the present study focuses on the contamination resulting from the disposal of ammoniacal liquor at the lagoon plume (see figure 1). This contaminant plume was selected because of the relative steady-state conditions of the groundwater flow as was shown by a regional modelling exercise for the site (Davison, 1998) (see also Fig. 1). Recent groundwater analyses (Davison & Lerner, 2001) downgradient of the lagoon plume (observation points Clip 1, 2, 3 in figure 1) showed enhanced concentrations in the major cations with respect to background groundwater geochemistry, suggesting the existence and location of a cation exchange front. This observed pattern is studied in more detail in the present modelling work.

Modelling the cation exchange reactions at the field site

Since concentration gradients in horizontal transversal direction are negligible and primarily occur in the vertical direction, a 2D-cross section (A-A' in figure 1) along the groundwater flow direction starting upgradient of the lagoon

plume was chosen for the modelling. The selection of appropriate boundary conditions was based on the results of
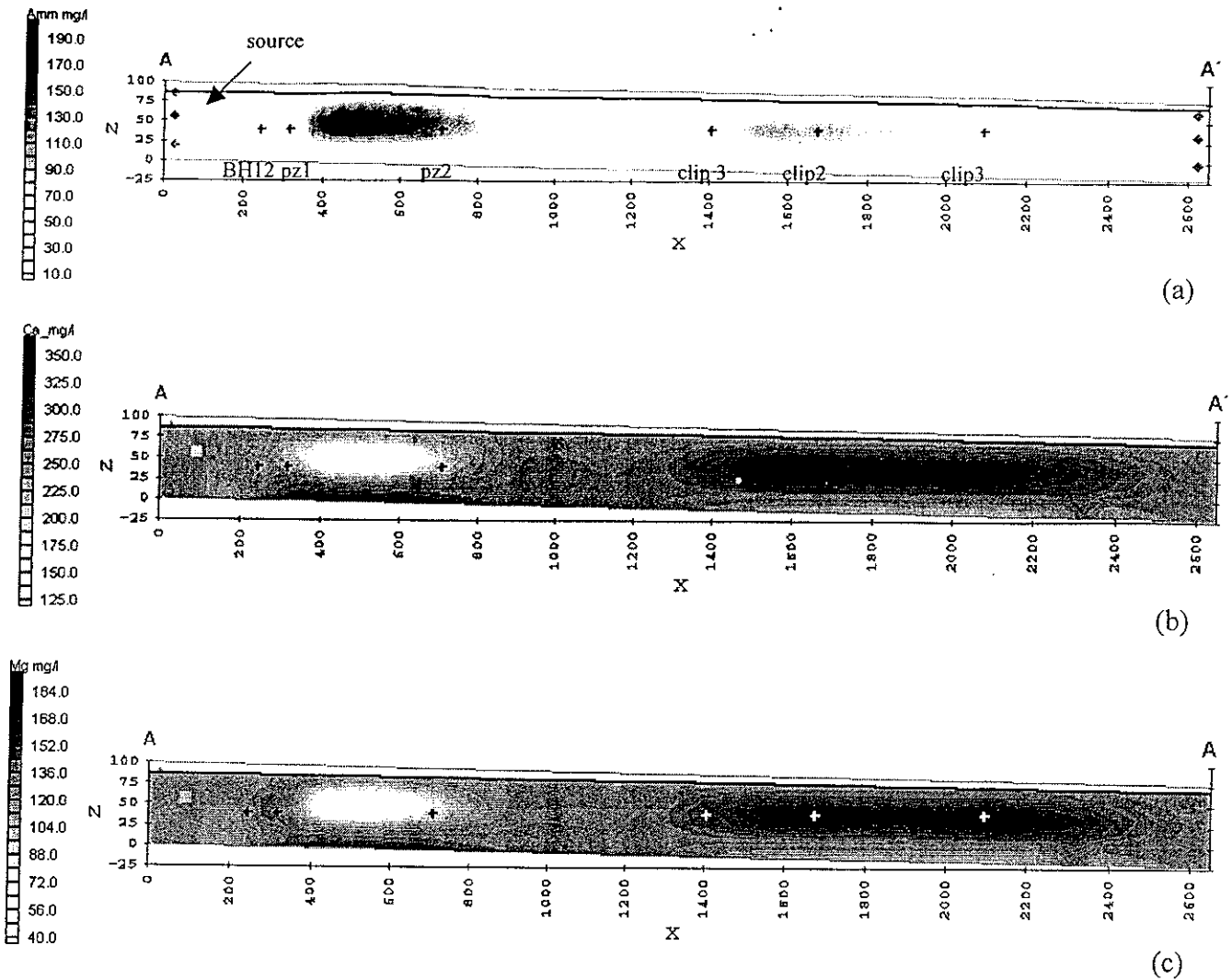

Fig. 2. Simulation results (mg/l) of respectively NH4-N (a), Ca (b) and Mg (c).

the regional flow model. The hydrogeological parameters were taken from this regional model and/or the site investigations performed at the site (Jones, 2001). In a first approach the source term is simplified by assuming a constant and continuous source term over the 18 years period of contamination with concentrations based on previous 1D modelling (Jones, 2001). After this contamination period the source term is set to zero for the following 27 years, i.e. till the recent sampling campaign (Davison & Lerner, 2001), to simulate aquifer flushing by background groundwater

Results of this modelling show the appearance of elevated concentrations of calcium and magnesium resulting from the cation exchange with ammonium near the three Clip boreholes (see Fig. 2), which is confirmed by the groundwater analyses. The (strongly) retarded ammonium plume emanating from the flushing of the contaminated aquifer show elevated concentrations of ammonium that is exchanged mainly by calcium and magnesium. Both these cations show in return a decrease in concentration where the ammonium is flushed off the aquifer sediments.

Conclusions and further work

This paper reports a groundwater contamination involving multiple solutes, i.e., cations, that interact with sediments through ion-exchange reactions and which control the distribution of the ammonium contamination. A preliminary modelling study was carried out for a 2D cross sectional model along a flow line. The modelling results confirm observed distribution of the major cations at the field site. For example, ammonium is retarded, which results in elevated concentrations of calcium and magnesium at the Clip boreholes downgradient of the lagoon plume. The agreement between observed and simulated patterns is encouraging and it is concluded that the present reactive transport modelling of ammonium sufficiently represents the ion exchange process affecting the ammonium transport at the site. Further work will be continued to include the re-oxidation of ammonium and precipitation/ dissolution of minerals in the reactive transport modelling, in order to investigate the influence of these processes on the transport of ammonium.

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