Reactive transport modeling of a groundwater contamination by ammoniacal liquor

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ABSTRACT

A reactive transport modeling study was carried out to assess the fate of a groundwater contamination by ammoniacal liquor from a former coking plant and the associated geochemical response. The simulations over a 45-year period provide a conclusive explanation and quantitative description of all measured data from observation wells down gradient of the contaminant source. It is shown that cation exchange exerts the main control on the fate of the ammonium plume as it strongly retards the migration of dissolved ammonium. The sorption of ammonium is accompanied by the elution of native cations, an effect that can be seen in some observation wells where ammonium is absent. While phenol has not been detected in the observation wells in recent years, the modeling results suggest that it has completely degraded in the aquifer, which is inferred from the agreement between the simulated and the observed geochemical fingerprint that the degradation of phenol imposes on groundwater composition.

INTRODUCTION

The general lack of knowledge about historical source terms, the high cost of field investigations, and the limited data density relative to the heterogeneity of the subsurface, make it difficult to determine reliably the risks from subsurface contaminants. For the current study, the MODFLOW/MT3DMS-based multicomponent reactive transport model PHT3D (Prommer et al., 2003) has been used as a tool for the interpretation of the geochemical fingerprint left behind by the contamination and also to unravel the history of the contamination. The analysis of the historical data provides important information on whether the contamination still provides a threat to potential receptors. In addition to the (primary) hydrochemical data (contaminant mixture, estimated source geometry and history) and physico-chemical processes (advective-dispersive transport, sorption and degradation), all secondary geochemical data from both, contaminated and uncontaminated portions of the aquifer, and the relevant processes to simulate these, were integrated into the modeling study as individual pieces of the puzzle.

SITE DESCRIPTION

The study area has been redeveloped into a light industrial estate, but was previously a typical coal mining area in the East Midlands, UK. Background information on the site was taken from Jones (2001), Davison (1998) and Davison et al. (2000). As part of the former mining activities, an on-site coal carbonization plant produced ammoniacal liquor as a by-product. This wastewater contaminated the underlying aquifer between 1956 and 1969 (approximately). The aquifer consists of sandstones from the Permo-Triassic Sherwood Sandstone Group overlaying impermeable Permian marls. Locally, the sandstone aquifer is approximately 80m thick and consists of loosely cemented medium to fine grained red/brown sandstones with some pebbles. The sandstones form one aquifer unit and generally act as an intergranular medium as a result of its relatively uncemented nature. There is no drift cover on top of the sandstones, which are therefore vulnerable to contamination.
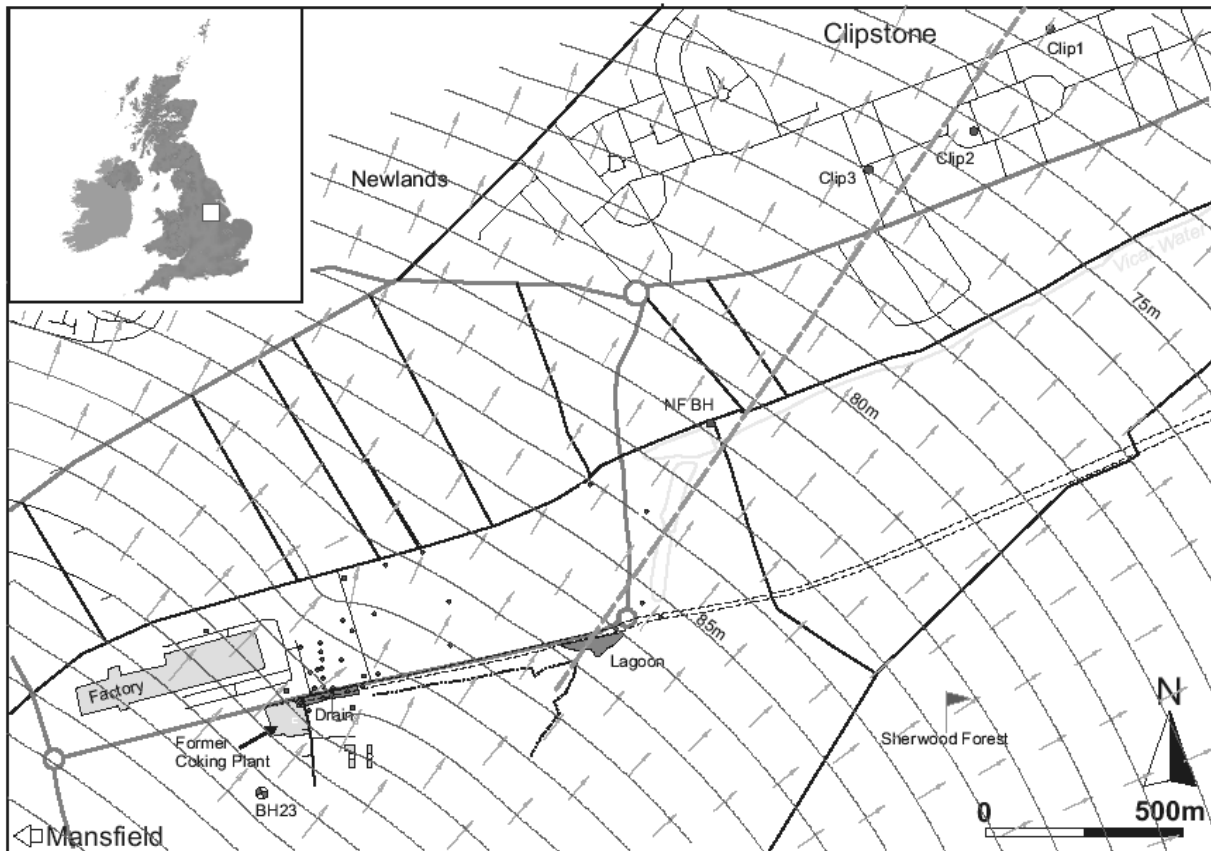
Figure 1. Site location map showing the 2D-cross-section and monitoring well locations used for transport modeling. Piezometric heads are taken from Davison's (1998) regional flow model.

PROBLEM DESCRIPTION AND CONCEPTUAL MODEL

The groundwater contamination was first discovered when a borehole was constructed to the NE of the coal carbonization plant in 1986 (NF BH in Figure 1). During the construction, high levels of phenol (77 mg/liter) and ammonium (276 mg/liter) were found in the groundwater. However, it was only after a newly built textile factory re-discovered high levels of ammonium in a new well that the remediation of the site was initiated. In 1994, the contaminated sandstone underneath the plant (top 7m of the vadoze zone) was excavated, backfilled and capped, and the groundwater was investigated to assess the size of the groundwater contamination. Geophysical surveys and detailed site investigations delineated two source input zones where the wastewater from the former coking plant had leaked into the aquifer. The worst groundwater contamination observed during these investigations was ammonium up to 465 mg/liter. Phenol, although present in the past, was not detected.

Using sandstone core material and groundwater from within the contaminant plume, Broholm and Arvin (2000) and Broholm et al. (2000) demonstrated in laboratory microcosm studies that phenol has the potential to degrade under the site-specific geochemical conditions. However, in the absence of field-based evidence for phenol degradation the risk for off-site migration was still present. Davison and Lerner (2001) installed three new monitoring wells in 2001 down gradient of the existing monitoring wells. Again, neither phenol nor ammonium were found in these monitoring wells, but the new data revealed a water composition that was clearly distinct from the background groundwater. It could be interpreted qualitatively as the geochemical fingerprint of phenol and ammonium attenuation. Due to their different physico-chemical properties, these two major constituents exhibit very different behaviors, (i) with respect to their own migration and (ii) with respect to the geochemical footprint of the attenuating processes.

During its migration in the subsurface, ammonium, which is the dominant cation within the contaminant liquid, exchanges with the cations that reside on the exchange sites of the sandstones under ambient conditions, mainly calcium and magnesium. Resulting from this exchange, the surface sites become successively filled with ammonium while the pristine cations are eluted from the exchange sites and their concentration in the groundwater increases. Consequently the ammonium plume travels at a significantly reduced velocity (compared to the water itself) while a plume with increased concentrations of calcium and magnesium travels in front of the ammonium plume. After active contamination has stopped, the process is reversed and cations in the uncontaminated (ammonium-free) groundwater displace the ammonium from the exchange sites into the groundwater.

Unlike ammonium transport, the migration of phenol is barely affected by partitioning effects between dissolved and sorbed phase. Thus, the conservative (non-reactive) transport of phenol does not trigger any significant hydrochemical changes. In contrast, if the transport of phenol is accompanied by the mineralization of phenol, considerable geochemical changes might occur. During the degradation process, microorganisms use dissolved electron acceptors (such as oxygen, nitrate, or sulfate) or the reductive dissolution of oxidized minerals (e.g., ferrihydrite, goethite, pyrolusite) to gain energy by converting phenol into harmless inorganic products (see, e.g., Spence et al., 2001). The changes that result from the oxidation of phenol include the decrease in electron acceptor concentrations, the production of reduced forms of the electron acceptors, and increasing alkalinity and pH changes. Ultimately those changes may trigger further, secondary geochemical changes such as the precipitation of sulfide or carbonate minerals. To quantify these effects, in particular when they occur simultaneously with advective-dispersive transport, a numerical modeling approach is required.

FLOW AND REACTIVE TRANSPORT MODELING

The MODFLOW/MT3DMS-based multicomponent reactive transport model PHT3D (Prommer et al, 2003) was applied to simulate the fate of both ammonium and phenol as well as the resulting geochemical changes. As a first step the transport of the conservative (i.e., non-reactive) groundwater constituents, chloride and bromide, was investigated.

Based on historical investigations, the total simulation time was divided into two stress periods for the transport simulation, a 13-year long period representing the time of active contamination and a second period (32-year) representing the time following active contamination. An overview of the simulation period is given in Figure 2.
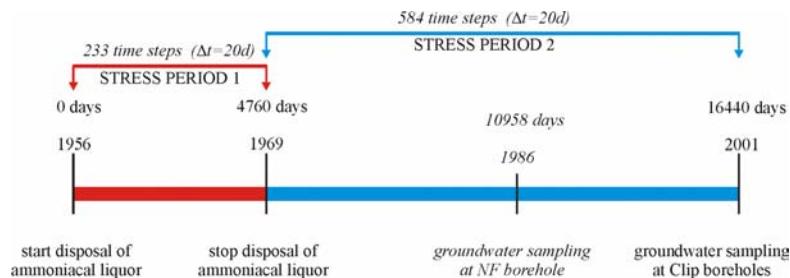

Figure 2. Schematic representation of the simulation time.

The model was discretised vertically to represent the layered structure that was identified earlier, e.g., by packer tests. The final values for the hydraulic conductivity attributed to the layers together with the source input concentrations for chloride and bromide were obtained through parameter estimation using PEST. Introduction of this layered heterogeneity improved the simulation of the non-reactive transport while the groundwater remained well calibrated.

To simulate the reactive transport of the ammoniacal liquor contamination, a site-specific reaction module was developed. The main reactive processes included for ammonium were (i) cation exchange with other cations, e.g., calcium and (ii) nitrification, i.e., the oxidation of ammonium to nitrate in the presence of molecular oxygen. Cation exchange reactions were included as equilibrium reactions, whereas

nitrification was included as a kinetically controlled reaction. The most important reactive processes involving phenol were its (bio)degradation and the corresponding electron acceptor reactions. The reactions were simulated by a partial equilibrium approach (see, e.g., Prommer et al, 2002). In addition to these reactive processes directly associated with the fate of ammonium and phenol other (secondary) geochemical reactions such as mineral precipitation/dissolution reactions were included as equilibrium reactions.
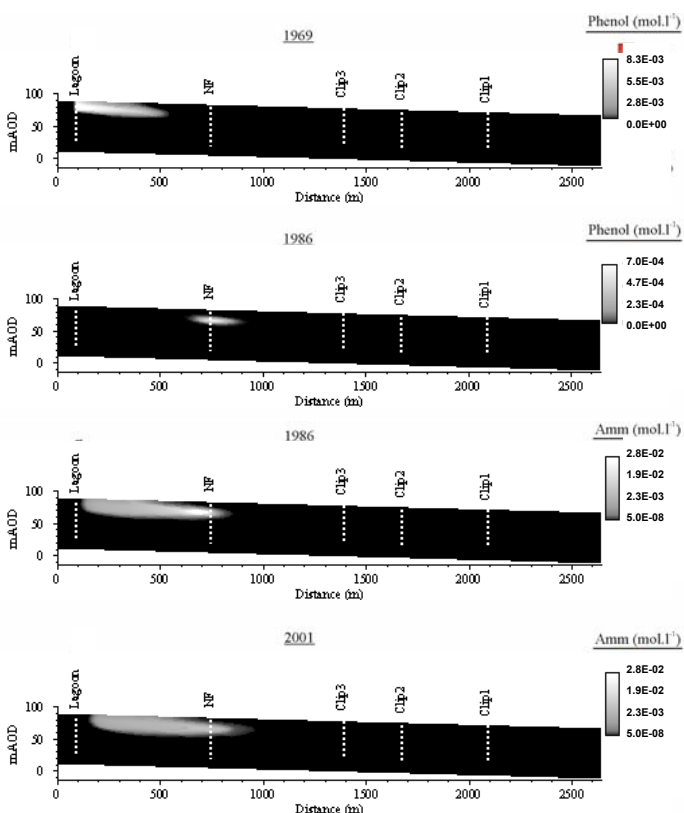

Figure 3. Simulation results for phenol and ammonium.

The reactive multicomponent transport simulations demonstrate that the dissolved fractions of phenol and ammonium have traveled at very different velocities during and after the active contamination as a result of the cation reactions, which lead to a chromatographic separation of the two plumes and their respective geochemical response. The simulation results can indeed explain the occurrence of phenol in the farm borehole in 1986 and its subsequent absence once site investigations had started in 1994 (see Figure 3). In a similar way, the persistent presence of ammonium in the groundwater nearby the source input locations as well as its observed presence and decrease in the farm borehole from 1986 towards 2001 and its measured concentration on the solid matrix, is well explained by the simulation results (see Figure 3).

Most importantly, the comparison between the simulated and observed geochemical response can now be used as additional evidence to support the hypothesis that phenol has mineralized and is unlikely to threaten potential downstream receptors. For example, the simulations show that the degradation of phenol and re-o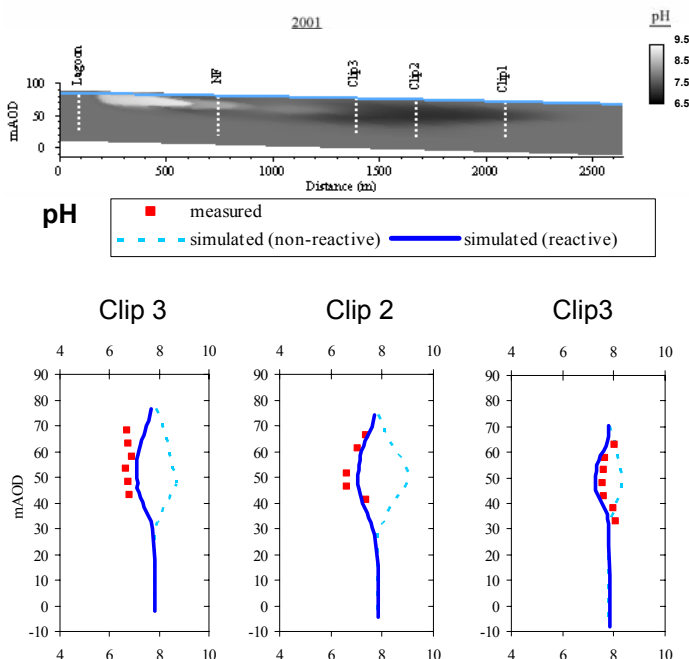xidation of its reduced reaction products by inflowing background groundwater is responsible for the observed depleted concentrations of dissolved oxygen and nitrate along the flow path of the contaminants. Furthermore, the simulated precipitation of siderite as a result of phenol degradation via iron reduction is consistent with the observed presence of siderite in the contaminated part of the aquifer while it also helps to explain the relatively low concentrations of iron in the groundwater. Due to the presence of sulfate in the contaminant source and at elevated concentrations in the aquifer, it is generally very difficult to assess its contribution to the degradation process of phenol. Based on the reactive transport simulations however, it can now be concluded that sulfate reduction provides an important contribution to the overall degradation of phenol and helps to explain the observed pH and alkalinity patterns in the aquifer.

The reactive transport simulations explain also how the elution of pristine cations as a result of the ion exchange process with ammonium produces the elevated concentrations of these cations at the downgradient Clip boreholes. Finally, the simulations show that the effect of these geochemical reactions on pH and alkalinity is partly buffered by precipitation and dissolution of carbonate minerals, and explain the decreased pH levels at the Clip boreholes as well as the observed increase in pH at the farm borehole from 1986 towards 2001.

Figure 4. Simulation results for pH and comparison of simulations results with observed values.

SUMMARY AND CONCLUSION

Simulations with the MODFLOW/ MT3DMS-based multicomponent reactive transport model PHT3D over a 45-year period provide a conclusive explanation and quantitative description of all measured data from observation wells downgradient of the contaminant source. It is shown that cation exchange exerts the main control for the fate of the ammonium plume as it strongly retards the migration of dissolved ammonium. The sorption of ammonium is accompanied by the elution of native cations, an effect that can be seen in some observation wells where ammonium is absent. While phenol has not been detected in the observation wells in recent years, the modeling results suggest that it has completely degraded in the aquifer, which is inferred from the agreement between the simulated and the observed geochemical fingerprint that the degradation of phenol imposes on groundwater composition.

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