On the use of reactive multicomponent transport modelling for assessing water quality changes during managed aquifer recharge

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Abstract

Managed aquifer recharge is an increasingly used technique to supplement water supplies. Following recharge the water quality of the injectant is typically altered by a multitude of geochemical processes during subsurface passage and storage. Relevant geochemical processes that affect the major ion chemistry include microbially mediated redox reactions, mineral dissolution/precipitation, sorption and ion-exchange. Reactive multi-component transport modelling provides an ideal platform for the simultaneous quantification of these processes and to develop an understanding of how they interact. The present paper demonstrates this for the analysis of a comprehensive data set that was collected during the deep-well injection of aerobic surface water into an anoxic, pyritic aquifer in the Netherlands.

INTRODUCTION

Managed aquifer recharge is increasingly used to enhance the sustainable development of water supplies. Common recharge techniques include aquifer storage and recovery (ASR), infiltration ponds, river bank filtration and deep-well injection. Following recharge the water quality of the injectant is typically altered by a multitude of geochemical processes during subsurface passage and storage. Relevant geochemical processes that affect the major ion chemistry include microbially mediated redox reactions, mineral dissolution/precipitation, sorption and ion-exchange. The hydrochemical conditions and changes that occur under these circumstances, in particular the temporal and spatial changes of pH and redox conditions, are in many cases the controlling factor for the fate of micropollutants such as herbicides and pharmaceuticals. Similarly, changes in mineralogical composition such as dissolution and precipitation of iron- or aluminiumoxides may affect the mobility of trace metals as well as the attachment and subsequent decay of pathogenic viruses (Schijven et al., 2000, Zhuang et al., 2003). Laboratory and field-scale experimental studies are aimed at investigating such processes under controlled conditions and to eventually develop a better qualitative and quantitative understanding of their complex interactions, both site-specific and at a fundamental level. However, a comprehensive and integrated in-depth analysis of the recorded experimental data is often omited, despite the sometimes significant cost for the experimental work and despite the potential long-term benefits for designing and operating efficient, sustainable and safe recharging schemes. The present paper gives a summary on how reactive multicomponent transport modelling was used at a recharge site as a technique for a more rigorous analysis and the quantification of physical and biogeochemical processes that can explain the observed data. A full description of the modelling study can be found in Prommer and Stuyfzand (2005). A second modelling example is presented in the companion paper by Greskowiak et al. (2005).

DEEP-WELL INJECTION EXPERIMENT

The technical feasibility for deep well recharge of canal water was investigated by two Dutch water supply companies (Brabant Water and WML) in order to halt and reverse water table drawdown and to minimise the potential negative impact on wetlands within the capture zone of water supply wells. A pilot plant was built near Someren in Southern Netherlands and a trial injection of initially 720 m^3 day^{-1} (between day 0 and 726) and later of 960 m^3 day^{-1} (between day 727 and day 854) was carried out. It was accompanied by a detailed site character-isation and a comprehensive water quality monitoring program. Pre-treated surface water from a canal was injected by one well at ~300 m depth (273 m−312 m below the land surface) and withdrawn by an extraction well located 98 m away from the injection well. The target aquifer is anoxic (pyritiferous), very low in calcite (probably absent) and has a near-neutral pH. Its geochemical reactivity is largely defined by locally varying concentrations of pyrite and sediment-bound organic matter (BOM). Both, the hydrochemical composition and the temperature of the injection water changed significantly during the course of the trial period. Most notably the temperature varied seasonally between a minimum of 2 °C and a maximum of 23 °C The field observations show that oxygen depleted rapidly in the vicinity of the injection well while nitrate was removed at a slower rate. However, no elevated nitrate concentrations were found in the extraction well. More details can be found in Stuyfzand (1999).

FLOW, CHLORIDE AND HEAT TRANSPORT SIMULATIONS

The deep well injection and extraction scheme created a three-dimensional flow field that strongly determined the hydraulic gradients and mass transport in the vicinity of the wells. The symmetrical flow-field that resulted from the injection was approximated by a half-model of 263 m length (in flow direction) and 124 m width, i.e., perpendicular to the main flow direction. In vertical direction the model was discretized into 12 layers of different conductivities between −273 m and −340 m depth, as proposed in the conceptual model by Stuyfzand (1999). Initially nonreactive transport of chloride was simulated and the results compared with the measured con-centrations. A good agreement between simulated and observed data was achieved after small adjustments of the initially attributed hydraulic conductivities were made. This step was followed by a fine-calibration that used the simulation of heat transport and its comparison with measured temperature data as an additional constraint for the flow and nonreactive transport model. Heat transport was modelled in a simplified manner by defining the water temperature as a retarded, mobile species.

REACTIVE MULTICOMPONENT TRANSPORT

Based on the field observations a reaction network was defined and a corresponding reaction module was formlated for the multicomponent transport model PHT3D (Prommer et al., 2003), a model that couples the transport simula-tor MT3DMS (Zheng and Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999). The reaction network included complexation reactions of all major ions, dissolution/mass transfer of sediment bound organic matter to dissolved organic carbon (DOC), kinetically controlled DOC mineralisation, ion-exchange reactions and the kinetically controlled, temperature-dependant oxidation of pyrite by oxygen and/or nitrate. The duration of the pilot test was subdivided into 39 stress-periods of variable length and the measured injection water compositions were used to define the source concentrations at the injection well. The ambient water composition was assumed to be homogeneous, however, pyrite and BOM contents as well as the cation exchange capacity varied with depth, according to the zonation proposed by Stuyfzand (1999). The model calibration was used to determine both the magnitude and the relative importance of pyrite oxidation in comparison with the organic carbon mineralisation. Matching simulated and measured sulfate concentrations served as the major con-straint for the estimation of the parameters that determined the magnitude of the pyrite oxidation rates, while

matching simulated and observed oxygen and nitrate concentrations served as the main constraint for the combined effect of pyrite oxidation and DOC degradation.

MODELLING RESULTS

The calibrated model reflects in great detail the spatial and temporal changes of the major ion and redox chemistry that occurred in response to the injection of the aerobic surface water. For example, the model is capable of accurately reproducing the extent and the seasonal variability of the oxygen and nitrate plumes that are created during injection. Fig. 1 illustrates the extent of those plumes 730 days after the start of the experiment. The snapshot shown corresponds to a period where low temperatures of the injected water leads to comparatively large oxygen and nitrate plumes. The degree of variability is indicated in Fig. 2, which shows the breakthrough curves of
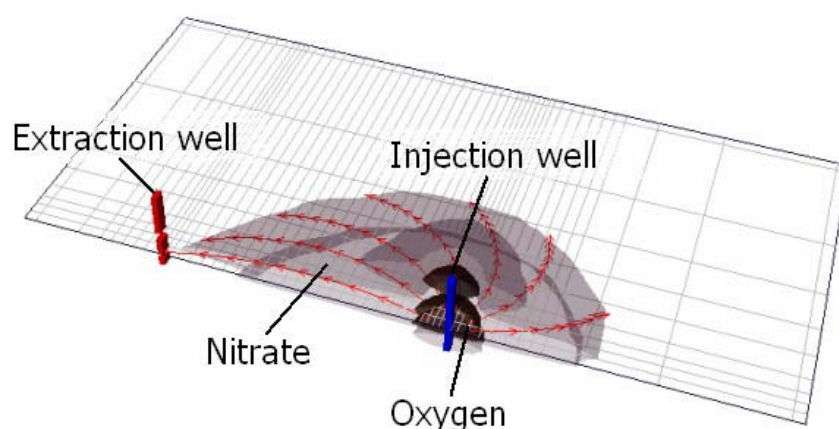

Figure 1. Illustration of the modelled redox-zonation - Iso-concentration surfaces
of oxygen and nitrate at 730 days after the start of the deep well injection experiment.
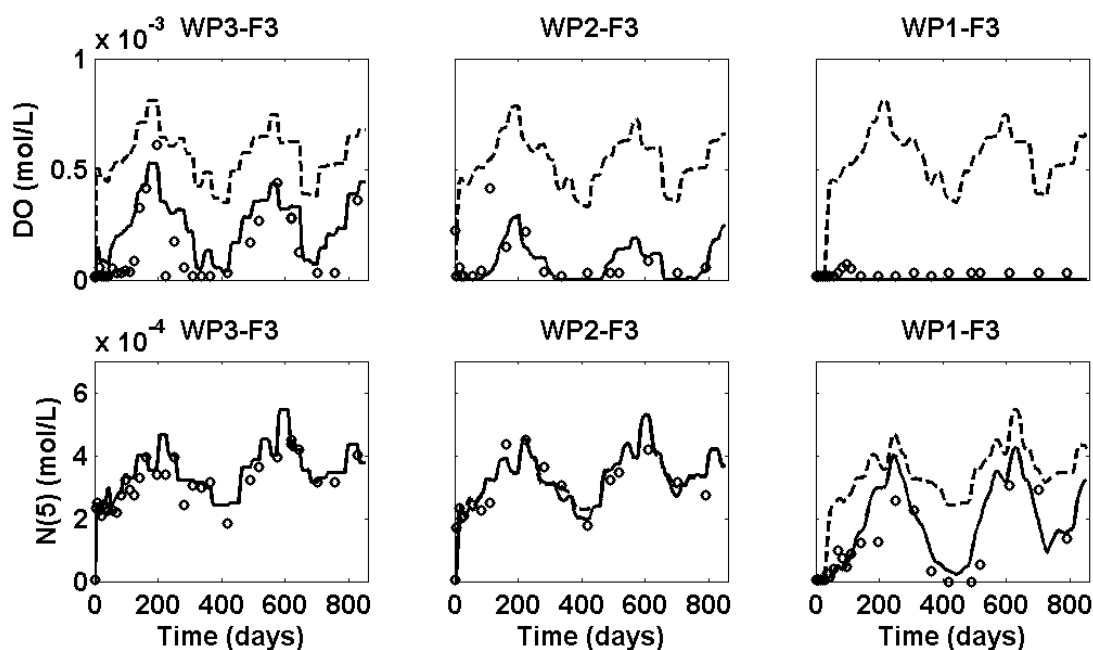*Also shown are pathlines between injection and extraction well.*

Figure 2. Measured (circles) and simulated (solid lines) breakthrough curves of oxygen and nitrate
at three different distances from the injection well (WP3 = 8 m, WP.2 = 12 m, WP.1 = 38 m).
Dashed lines show the simulated breakthrough curves for advective dispersive only (no reactions).

oxygen and nitrate at three different distances from the injection wells, at 8 m, 12 m and 38 m, respectively. The plots show how, influenced by a seasonal variability, initially oxygen and with increasing distance also nitrate concentrations are decreasing. The results of model runs where only advective dispersive transport was considered, that is, all reactions were switched off, are plotted in comparison. The results illustrate that nitrate is transported conservatively as long as oxygen is present.

The model calibration identified pyrite oxidation as the dominant process with respect to oxygen and nitrate removal, consuming 6.34 of the 9.11×10^6 mol electron equivalents (Eeq) injected into the aquifer. This is indicated in Fig. 3, where the simulated rates of the spatially integrated oxygen and nitrate consumption are plotted in comparison with the removal rates of pyrite and BOM. Through a more detailed modelling analysis (Prommer and Stuyfzand, 2005) it was shown that pyrite oxidation rates exhibit a strong temperature dependency, which can explain a large fraction of the observed seasonal variability of the breakthrough curves at the monitoring wells. For that study the temperature-dependency was approximated from the rates of measured oxygen consumption in the proximity of the injection well and incorporated into the appropriate rate expressions through an Arrhenius-type term in the equations for pyrite oxidation and BOM mineralisation.
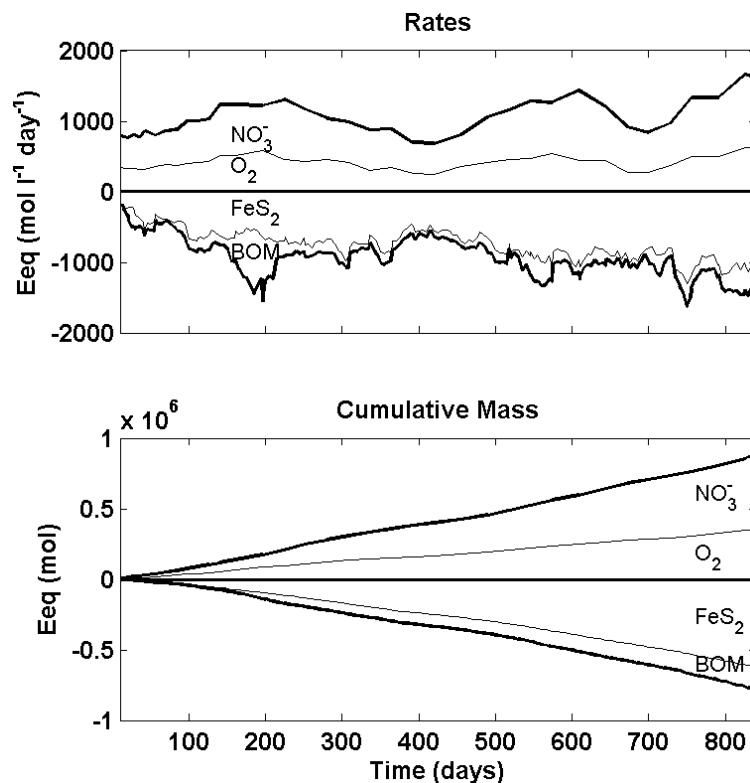

Figure 3. Modelled rates and cumulative mass of electron equivalents (Eeq)
added to the aquifer via deepwell injection (as O2 and NO3-) in comparison with the modelled,
spatially integrated consumption of pyrite and BOM, respectively.

In contrast to the observed variability of concentrations at the monitoring wells the extraction water quality showed only a minor impact of seasonality and of temperature variations. This can be seen in Fig. 4, where the results of the reactive transport simulations are plotted in comparison with measured concentrations for some of the key species and water quality parameters. The extraction well collects water with a wide range of differing travel times, which explains why the locally observed variability observed in the monitoring wells are dissipated in the extraction water. Through the comparison of the modelling results for reactive transport with those of conservative (i.e., advection-dispersion only) transport simulations, the impact of physical and chemical processes on the extraction water

quality can be distinguished. For example, it can be seen that 30–40% of the increase in sulfate concentrations can be attributed to pyrite oxidation, whereas the remainder is determined from the dynamically changing mixing ratio between ambient water and the more sulfate-rich injectant. Similarly it can be seen that the dissolved inorganic carbon concentrations in the extraction water remain essentially unaffected by reactive processes.
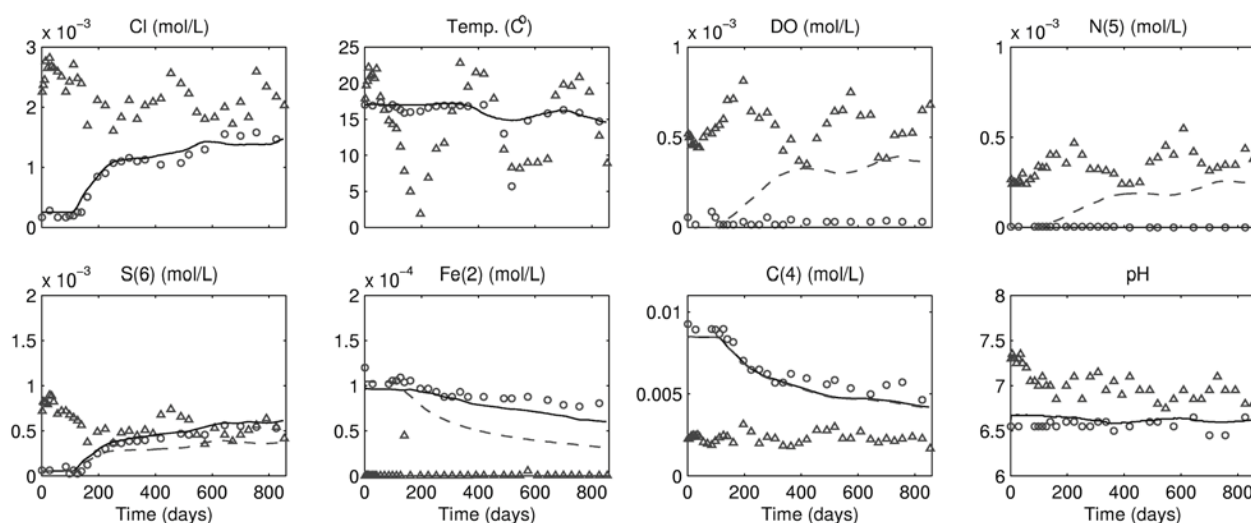

Figure 4. Selected simulated (solid lines) and measured (circles) aqueous component concentrations at the extraction well PP.1 in comparison with measured concentrations at the injection well IP.2 (triangles). The dashed lines indicate the simulated extraction well concentrations for purely advective-dispersive transport (no reaction).

CONCLUSIONS

Reactive multicomponent transport modelling combines the more widely established modelling techniques of groundwater flow modelling and that of batch-type geochemical modelling. It was shown here to be an adequate tool for the in-depth analysis of the comprehensive data set collected during the deep-well injection experiment. The model was for the particular case here, like for the case described in the companion paper by Greskowiak et al. (2005), used in a mode that included the development and testing of hypotheses how physical, chemical and biological processes interact. In the deep-well injection case the resulting major outcome was the model-based identification and quantification of the impact that the variable temperature of the injection water had on reaction rates. This allowed to accurately describe the spatial-temporal evolution of the major ion chemistry, pH and redox changes that had developed during the trial injection. The capacity to reliably quantify those hydrochemical parameters for artificially recharged aquifers provides the key for the assessment of the fate of potential micropollutants and, for example, to pursue a process-based description of the mobility of pathogenic viruses. The mobility of the latter, which might be controlled by the electrostatic repulsion between viruses and grains, is strongly affected by hydrochemical parameters such as pH, ionic strength and the concentration of divalent cations. Those parameters are of course all intrinsically determined by reactive multicomponent transport models, making it an ideal platform for more detailed studies of those issues.

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