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A post audit and inverse modeling in reactive transport: 50 years of artificial recharge in the Amsterdam Water Supply Dunes

R.H. Karlsen [a,*], F.J.C. Smits [b,c], P.J. Stuyfzand [a,d], T.N. Olsthoorn [b,c], B.M. van Breukelen [a]

[a] Department of Earth Sciences, Faculty of Earth and Life Sciences, VU University Amsterdam, De Boelelaan 1085, NL-1081 HV Amsterdam, The Netherlands
[b] Hydrology Department, Amsterdam Water Supply, Waternet, Vogelenzangseweg 21, 2114 BA Vogelenzang, The Netherlands
[c] Department of Water Management, Water Resources Section, Faculty of Civil Engineering and Earth Sciences, TU Delft, Stevinweg 1, 2628 CN Delft, The Netherlands
[d] KWR Watercycle Research Institute, PO Box 1072, 3430 BB Nieuwegein, The Netherlands

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SUMMARY

This article describes the post audit and inverse modeling of a 1-D forward reactive transport model. The model simulates the changes in water quality following artificial recharge of pre-treated water from the river Rhine in the Amsterdam Water Supply Dunes using the PHREEQC-2 numerical code. One observation dataset is used for model calibration, and another dataset for validation of model predictions. The total simulation time of the model is 50 years, from 1957 to 2007, with recharge composition varying on a monthly basis and the post audit is performed 26 years after the former model simulation period. The post audit revealed that the original model could reasonably predict conservative transport and kinetic redox reactions (oxygen and nitrate reduction coupled to the oxidation of soil organic carbon), but showed discrepancies in the simulation of cation exchange. Conceptualizations of the former model were inadequate to accurately simulate water quality changes controlled by cation exchange, especially concerning the breakthrough of potassium and magnesium fronts. Changes in conceptualization and model design, including the addition of five flow paths, to a total of six, and the use of parameter estimation software (PEST), resulted in a better model to measurement fit and system representation. No unique parameter set could be found for the model, primarily due to high parameter correlations, and an assessment of the predictive error was made using a calibration constrained Monte-Carlo method, and evaluated against field observations. The predictive error was found to be low for Na^+ and Ca^{2+}, except for greater travel times, while the K^+ and Mg^{2+} error was restricted to the exchange fronts at some of the flow paths. Optimized cation exchange coefficients were relatively high, especially for potassium, but still within the observed range in literature. The exchange coefficient for potassium agrees with strong fixation on illite, a main clay mineral in the area. Optimized CEC values were systematically lower than clay and organic matter contents indicated, possibly reflecting preferential flow of groundwater through the more permeable but less reactive aquifer parts. Whereas the artificial recharge initially acted as an intrusion of relatively saline water triggering Na^+ for Ca^{2+} exchange, further increasing total hardness of the recharged water, the gradual long-term reduction in salinity of the river Rhine since the mid 1970s has shifted to an intrusion of fresher water causing Ca^{2+} for Na^+ exchange. As a result, seasonal and longer term reversal of the initial cation exchange processes was observed adding to the general long-term reduction in total hardness of the recharged Rhine water.

Introduction

Reactive transport modeling (RTM) provides a quantitative interpretation of spatial and temporal changes in water chemistry and deduction of key hydrogeochemical processes and parameters at both aquifer and pore scales. Understanding the chemical interactions between fluids and solids, and among fluids with different physical and chemical characteristics can enable us to predict the evolution of both fluid and solid phases in natural and engineered environments (Steefel et al., 2005). We can acquire this understanding by studying the flow, solute transport and chemical reactions through the application of RTM. More specifically RTMs can be used to determine, for example, the fate of contaminants, the feasibility of remediation strategies, the water quality changes due to artificial recharge for drinking water production, or the chemical reactions triggered by intrusion of foreign water into aquifers. Decision making relies on accurate predictions reflecting our current knowledge, which depends on the quality of both the

* Corresponding author. Present address: Department of Earth Sciences, Uppsala University, Villavägen 16, 752 36 Uppsala, Sweden.

E-mail address: reinert.karlsen@geo.uu.se (R.H. Karlsen).

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numerical code and the conceptual model, and representation of the latter when applying the numerical code. The representation of the system can be improved by gathering data, and employing this data in model calibration and validation. The selection of conceptual models and parameter values is crucial for the predictive capabilities of a model, and one way to improve this selection is by using inverse modeling.

The use of automated inverse models in hydrological modeling has a number of advantages compared to non-automated approaches such as manual trial-and-error calibration. Through the use of inverse modeling the user can gain and assess the quality of and confidence in parameter estimates and model predictions, which again can reveal the quality of model representation of the system. This may further assist in identifying properties of the modeled system and improving future modeling efforts to reduce predictive uncertainties through, for example, data collection strategies targeting uncertain aspects of the model. The term inverse modeling is used for the procedure of acquiring information on the model, and thus the system under investigation, from field observations, and includes parameter estimation (or model calibration) and model identification (Carrera et al., 2005).

Inverse modeling is well established in the domain of groundwater flow and solute transport modeling (GFM/STM). The inverse problem has been discussed (e.g. Poeter and Hill, 1997; Carrera et al., 2005), guidelines have been published (Hill, 1998) and calibration schemes are increasing in complexity and detail, with for example highly parameterized systems (e.g. Tonkin and Doherty, 2005), the use of geostatistical methods (e.g. Gómez-Hernández et al., 1997) and multi-objective calibration (e.g. Cieniawski et al., 1995).

Inverse modeling and predictive analysis in the field of RTM, either coupled with flow models or not, is far less explored in comparison to GFM and STM. Calibration of RTMs is expected to be more challenging than GFM or STM due to the larger number of model parameters often involved and the complex interacting hydrochemical processes occurring. In the recent years published studies applying inverse modeling to RTMs have increased, but few of these studies offer much attention to the inverse process (e.g. van Breukelen et al., 2004; van Breukelen and Griffioen, 2004). Some notable exceptions are briefly listed below. Dai and Samper (2004) presented a formulation of the inverse problem of flow and RTM, and applied this to a synthetic example. They also used their INVERSE-CORE^{2D} code to recalibrate a previously trial-and-error calibrated model of Appelo et al. (1990). This improved the model fit and determined the importance of calcite dissolution in a column study. Dai and Samper (2006) also applied the same methodology to two field cases of reactive transport to estimate parameters, parameter uncertainty and identification of relevant processes. Matott and Rabideau (2008) used the OSTRICH (Matott, 2005) optimization tool in combination with the reactive batch and transport code NIGHTHAWK (Matott and Rabideau, 2010) to evaluate the performance of three inverse search procedures, gradient, global and hybrid methods. The performance of the methods were tested on synthetic batch and transport models simulating nitrate biodegradation, which included complex biochemical processes. They found that the local search procedure using the Levenberg–Marquardt algorithm suffered from local minima and heterogeneous regions of extreme parameter sensitivity and insensitivity. In most of the presented cases, the global and hybrid search techniques resulted in better model fits. Samper et al. (2006) used INVERSE-CORE^{2D} to estimate solute transport parameters in a diffusion and permeation experiment using various tracers. They found that the interpretation of the experiment using the numerical inverse model was superior to the previously applied analytical approach, which failed to account for certain experimental conditions. Samper et al. (2008), also using INVERSE-CORE^{2D}, estimated the diffusion coefficient and initial porewater concentrations in single and dual porosity media with multicomponent reactive transport in a column study. Yang et al. (2008) applied inverse modeling with the microbial and reactive transport code INVERSE-BIOCORE^{2D} to an *in situ* experiment, and illustrated the advantage of the automatic method over the previously applied trial-and-error calibration. They also explored the effect of data noise on parameter estimation error in a synthetic case study using the same model code. However, predictive uncertainty or error analysis of model results was not within the scope of any of these studies.

Uncertainty of model results and predictions may stem from three general sources: parameter uncertainty, scenario/stress uncertainty and model uncertainty (Samper et al., 1990). The latter includes the numerical code, conceptual model and model design. The importance of performing uncertainty analysis on hydrological predictions has been thoroughly discussed and recognized (e.g. Beven and Binley, 1992; Pappenberger and Beven, 2006). Yet, uncertainty analysis, as Pappenberger and Beven (2006) note, is seldom performed in applied modeling for decision making purposes despite a large number of proposed methodologies to perform such analysis. Rigorous predictive uncertainty analyses of GFMs have been performed, exploring different methodologies such as linear and non-linear to evaluate uncertainty (e.g. James et al., 2009; Keating et al., 2010). Uncertainties related to the conceptual model and stresses have been identified as a common problem for the predictive accuracy of GFMs and STMs (Bredehoeft, 2005). For example Troldborg et al. (2007) showed how different conceptualizations in a multi-aquifer field case resulted in large variations in solute transport, in spite of only minor differences in hydraulic head distributions. Bell et al. (2002) used Markov chain Monte-Carlo to assess model uncertainty related to parameter uncertainty in a column transport study. Beyer et al. (2006) performed a model uncertainty assessment of contaminant plume length caused by the estimation of the first-order rate constant using Monte-Carlo in a 2D heterogeneous synthetic flow field. Inverse modeling is a valuable tool in uncertainty analysis, as sensitivity analysis of parameters (including stresses), observations, predictions as well as testing the validity of various conceptualizations can readily be performed. Publicly available and tested inverse modeling software such as UCODE 2005 (Poeter and Hill, 1998) and PEST (Doherty, 2005) include tools for evaluating predictive uncertainty analysis.

To further assess the model performance, a validation step, as for example suggested by Refsgaard and Henriksen (2004), can be performed, where model results are compared to field observations that were not included in the parameter estimation. This step may be difficult to carry out, as data is often sparse and all data is typically used to improve the parameter estimation and predictive capabilities of the model, and none are left available for validation. A stricter form of model validation, a post audit, can be carried out to compare model predictions to field observations. To assure that significant change has occurred in the modeled system, post audits should not be carried out too soon after the previous modeling (Anderson and Woessner, 1992). Post audits can be valuable for our understanding of the model and system, for improving both current model predictions as well as other future modeling tasks. As models are frequently used for predictions and as a tool in decision making, post audits provide valuable information on where our models commonly fail and allow modelers to take action in assessing and reducing uncertainty of model predictions. Since post audits require new field observations, a second inverse modeling step can also be made, possible model errors can be identified and parameter and predictive uncertainties can be reduced.

However, post audits are seldom performed, although their importance and guidelines have been discussed (Anderson and Woessner, 1992). For GFM and STM there is a handful of published