

# Raw water quality prognosis

## Hydrogeochemical modelling of raw water quality – a planning and forecasting tool

Nitrate, denitrification, hydrogeochemical modelling, PHREEQC, raw water prediction

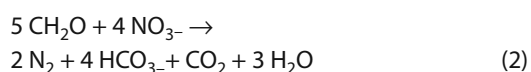
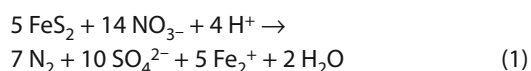
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*Nitrate pollution of groundwater due to excessive application of fertilizers and manure in agriculture is an increasing problem in many countries and displays a major threat to drinking water supply. Ensuring future drinking water supply requires a sustainable management of water resources regarding both quantity and quality. As illustrated by the case study of the Rasseln Waterworks (Moenchengladbach, Germany) a reactive transport model has been developed. The model calculates the development of ground- and raw water quality for each of the three aquifers used for drinking water production under consideration of all relevant hydrogeochemical and geo-hydraulic processes as well as temporal changes in fertilizer and manure application on arable land. Monitored trends in raw water quality can be retraced retrospectively. For predefined scenarios of nitrate input long-term forecasts of raw water quality are calculated. Thus, this model is an appropriate tool to test the efficiency of agricultural measures on raw water quality development.*

### 1. Introduction

For decades nitrogen fertilizers are used intensively, to increase agricultural productivity. In many cases, nitrate concentrations in shallow aquifers exceed the maximum allowable concentration for nitrate of 50 mg/L accordingly to national, EU and WHO drinking water standards [1–8].

Deeper horizons of shallow aquifers as well as deeper aquifers are often virtually free of nitrate either because nitrate contaminated groundwater have not expanded so far or because nitrate had been removed by reduction along the flow path. To ensure drinking water supply in catchment areas with elevated nitrate concentrations ground water abstraction is often transferred to deeper aquifers. Nevertheless, it cannot be excluded that this “escape to deeper aquifers” is only a mid-term solution. Although retarded by denitrification coupled to the oxidation of pyrite (1) and/or organic carbon (2) nitrate may reach the abstraction wells some day.



In the view of a supposable long lasting nitrate input to shallow aquifers and with a special emphasis on the finite nature of any subsurface potential of denitrification, water distribution companies need a planning and forecasting tool to ensure drinking water supply. Such a tool could be used to develop and to evaluate long term

protection strategies for groundwater bodies regarding long term effects on raw water quality. Also economic aspects of groundwater protection measures could be evaluated. Moreover, a comprehensive evaluation of water resources should not only be focussed on a single critical parameter like nitrate but also on ground- and raw water quality as a whole.

Funded by the RWE Energy AG and the RWE Aqua GmbH a planning and management tool focused on raw water quality prognosis has been developed. As illustrated by the case study of the “Rasseln Waterworks” the tool is based upon a reactive transport model using PHREEQC-2 [9, 10]. The model calculates the development of ground- and raw water quality (pH, concentrations of nitrate, sulphate, iron, calcium, magnesium, chloride and total inorganic carbon) for all aquifers in the catchment area used for drinking water production under consideration of all relevant hydrogeochemical and geo-hydraulic processes. Comparing measured and modelled data, causes for long-term trends in raw water quality can be retraced retrospectively. For predefined future scenarios of nitrate input long-term forecasts of raw water quality can be calculated.

### 2. Area under investigation

The catchment area “Rasseln” is situated north-west of the city of Moenchengladbach, in the western part of the Lower-Rhenish Bay (**Fig. 1**). The “Rasseln Waterworks” annually abstract up to 2.5 million m<sup>3</sup> groundwater from up to three aquifers since mid-1950s. Due to increasing nitrate concentrations groundwater abstrac-

tion from the first aquifer had been successively transferred to underlain aquifers (Fig. 2). The catchment area and its surroundings are well investigated and a topic of scientific and technical literature [e.g.: 11–16]. Published and unpublished geo-hydraulic and geochemical data were evaluated and used for modelling.

The first aquifer (Rhein-Hauptterrasse: Pleistocen, Reuver Kies: Pliocene) and the second aquifer (Hauptkiesserie: Pliocene) consist of well permeable ( $k_f: 1 \times 10^{-3} - 5 \times 10^{-4} \text{ m/s}$ ) fluvial sands and gravels. They are separated by a low permeable layer of Pliocene clay (Reuver Ton). Sediments of the first aquifer show nearly no potential for denitrification. Also the second aquifer shows only a small potential for denitrification which is bound to interstratified clay- and silt lenses passed by groundwater flow. The third aquifer (Neurather Sand: Miocene) consists of marine fine grained sands with a lower permeability of about  $3 \times 10^{-5} \text{ m/s}$  and fine-spread contents of pyrite ( $\text{FeS}_2$ ) and organic carbon (OC). Both solid phases represent the reductive capacity of the aquifer that can be used for denitrification. For modelling a mean sulphide content of 0.44% S by wt ( $\sim 0.825\%$  pyrite by wt) and a mean OC reaction rate of  $2 \times 10^{-3} \text{ mmol C / (L a)}$  is assumed (3<sup>rd</sup> aquifer).

The mean recharge area of the well field covers an area of 6.8 km<sup>2</sup>, consisting of farmland (68%), forest (13%) and settlements (16%). Fertilization and liming of farmlands causes intensive inputs of nutrients and other dissolved substances into the groundwater. Raw water from the upper aquifers shows high concentrations of nitrate (1<sup>st</sup> aquifer: 75–90 mg/L, 2<sup>nd</sup> aquifer: 85–125 mg/L) as well as enhanced concentrations of sulphate, chloride, calcium and magnesium.

Since mid-1980s increasing abstraction of groundwater from the third aquifer causes an enhanced flow from the upper aquifers into the deeper systems. At the beginning raw water from the third aquifer is virtually free of nitrate and shows only minor concentrations of sulphate, iron and chloride (Fig. 3). Since mid-1990s the concentrations of sulphate, iron and chloride increase. These increases can be explained by an increasing admixture of groundwater from the upper aquifers which are rich in chloride and nitrate and a subsequent denitrification along the remaining flow path within the third aquifer. As a consequence of ongoing denitrification the reductive capacity of the aquifer decreases continuously. The crucial question is how raw water quality will develop. And if a break through of nitrate to the wells in the third aquifer is a risk in the next decades.

### 3. Reactive transport modelling

#### 3.1 Model conceptualization and time variant input data

The reactive transport model is based on a conceptual model that integrates information about site-specific geology, groundwater hydraulics and hydrochemistry.

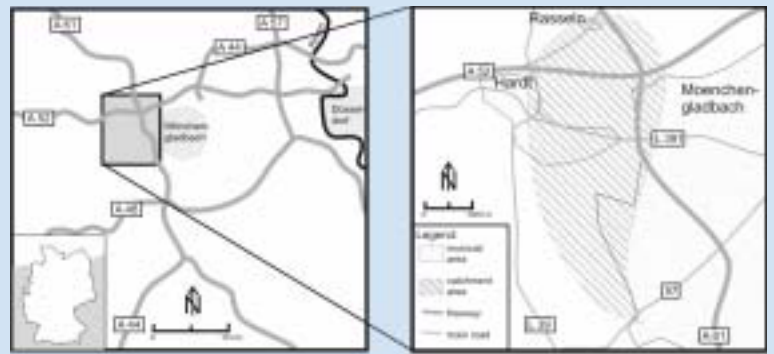


Fig. 1. Location of the catchment area.

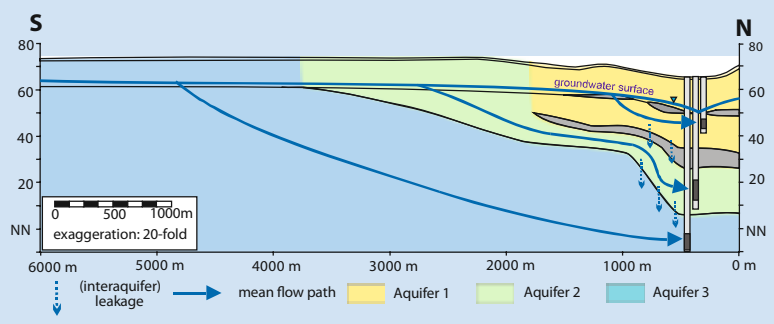


Fig. 2. Schematic cross section of the catchment area.

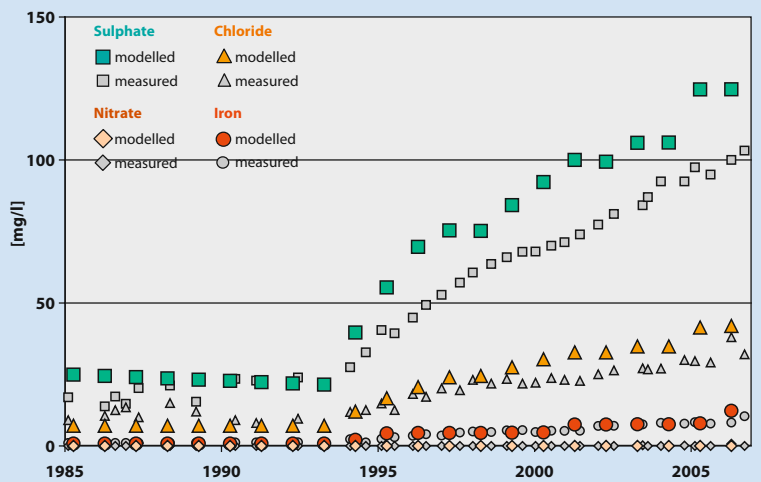
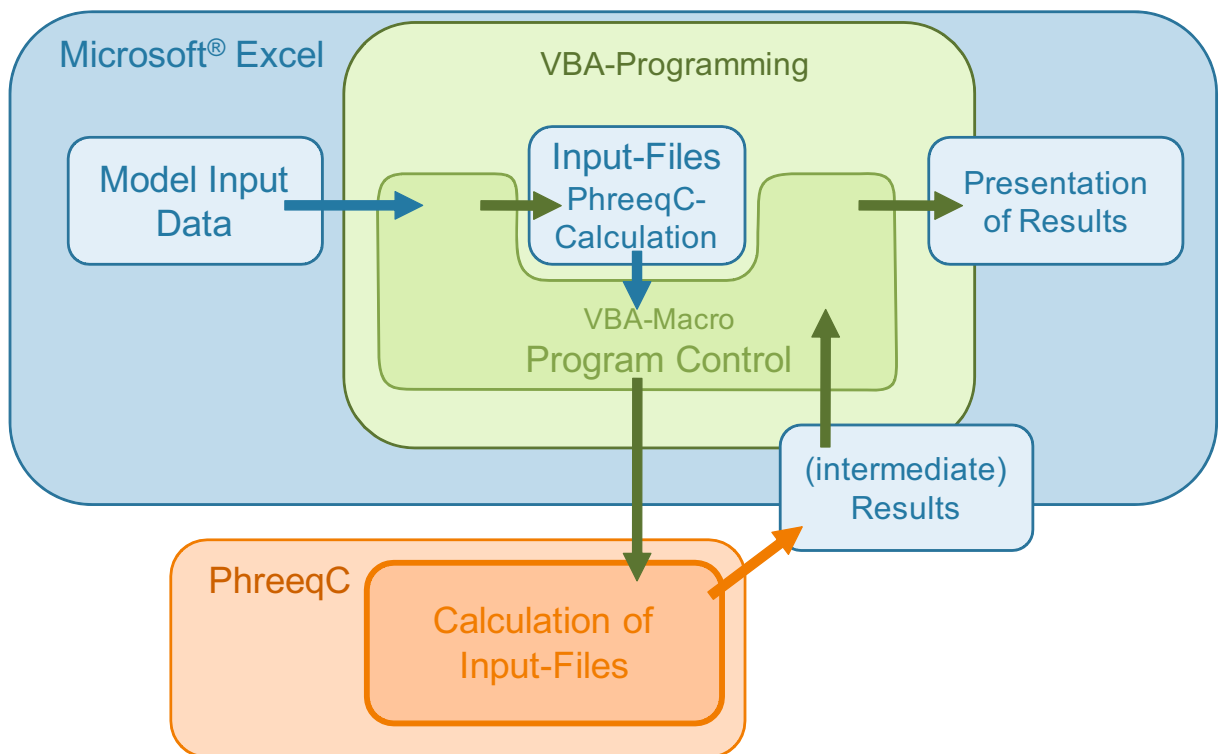


Fig. 3. Retrospective modelling 3<sup>rd</sup> aquifer: Comparison of modelled and measured raw water quality for selected parameters (sulphate, chloride, nitrate, iron).

Extracted raw water is composed of several groundwater partial flows, each with a different provenience and a different chemical alteration caused by hydro-geochemical processes along the flow paths (Fig. 2). Hydraulic flow path characteristics and the mixing fractions of groundwater from different flow paths are

Fig. 4. Data input and software structure.



derived from the water balance and basic hydrogeological and geo-hydraulic assumptions (ground water contour maps, results of pumping tests etc.).

For modelling purposes, existing time series of nutrient application to farmland by fertilizer and livestock manure were evaluated. Current nutrient concentrations in surface-near groundwater were determined in water samples taken from direct-push soundings. Comparing these concentrations with time-equivalent nutrient application data, substance-specific leaching factors were determined. On this basis nutrient application time-series were transferred to input functions of nutrients into the groundwater.

### 3.2 Model design

The complex groundwater flow system of the catchment area will be essentially simplified to benefit a comprehensive hydrogeochemical model using the software-code PHREEQC-2 [9]. Based upon the conceptualization the reactive transport model calculates the development of aqueous solutions along different model stream tubes – from infiltration of precipitation and the passage of the unsaturated zone to the traverse of different geochemical zones in an aquifer and the abstraction of the raw water. Each model stream tube represents a mean flow path of an aquifer (Fig. 2) and reflects varying input functions and geochemical conditions.

Water quality along flow paths is computed as a sequence of local equilibrium states and irreversible reactions within the model stream tubes. Based on equilibrium chemistry of aqueous solutions including

minerals and gases, equilibrium calculations are coupled with irreversible reactions to implement rates of kinetically driven reactions of solid bound, non-mobile organic carbon (OC). Each model stream tube is defined by a series of cells (1-D column). In every time step of reactive transport calculations water and dissolved species are shifted from one cell to the next cell. Afterwards irreversible reactions and chemical equilibria are calculated. For every cell and time step the resulting composition of the aqueous solution and the composition of the solid phase assemblages are saved and can be activated in the next step. Chemical properties of aquifer sediments, e. g. available stocks of reactive phases like pyrite, partial pressures (only in the unsaturated zone) as well as turnover rates of OC are attributed to each cell. For each model stream tube a time-step for advective transport is specified. At the beginning of a flow path, sub-stream tubes are used to model land-use specific input functions. Corresponding to areal proportions and specific recharge rates aqueous solutions from land-use specific sub-stream-tubes are mixed. The resulting solution flows in a single model stream tube and represents at the end of the flow path the abstracted raw water from a single aquifer. To model the development of the water quality in the second and the third aquifer, a synchronously mixing of groundwater volume flows from the upper aquifer is considered. Modelled raw water composition for each aquifer (characterized by eight parameters: pH, concentrations of nitrate, sulphate, iron, calcium, magnesium, chloride and total inorganic carbon) can be directly compared with time-corresponding measured data.

In a first step the model is used to retrace the measured development of raw water quality (retrospective modelling). If measured raw water quality can be retraced adequately for all aquifers and all parameters the model can be used as a tool for raw water quality prognosis.

### 3.3 Software structure

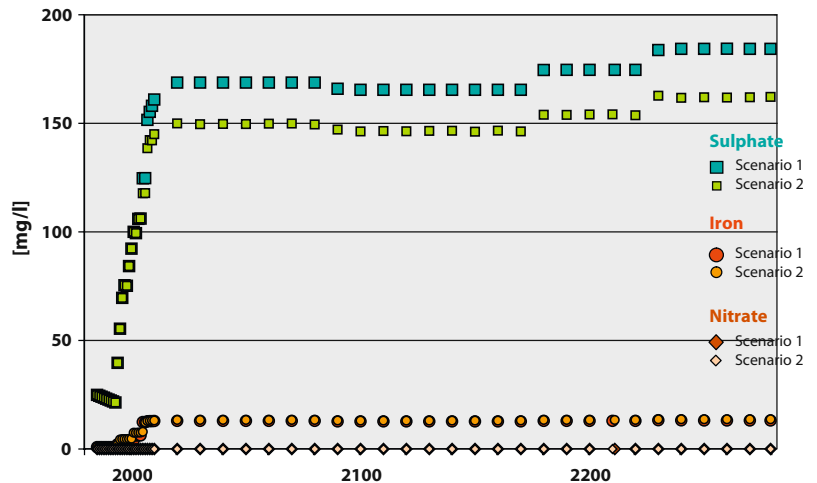
The reactive transport model consists of an input file for the free hydro-geochemical modelling software PHREEQC-2. The input file contains all site specific geochemical and geo-hydraulic data to model the development of ground- and raw water quality for a certain period of time. To make the model more user-friendly, PHREEQC-2 modelling is embedded into a Microsoft Excel environment. Excel spreadsheets and diagrams are used for data management (pre-processing) as well as for the presentation of results (post-processing). The input file is generated automatically from tabulated data by a program control, coded in VBA (visual basic for applications). Afterwards PHREEQC-2 is activated and the model results will be transferred automatically to Excel. Software tools used for pre-processing, modelling and post-processing are shown in **Fig. 4**.

## 4. Modelling results

**Fig. 3** shows the match between calculated raw water concentrations for nitrate, sulphate, chloride and iron within the time period 1985–2007 and measured data for the third aquifer, which is the most interesting one. Chloride acts as a conservative tracer, whose concentration is not altered by degradation or sorption processes. Thus, the match of the chloride concentrations retraces the increasing admixture of nitrate bearing groundwater from the upper aquifers and confirms the geo-hydraulic model. Nitrate is completely degraded by denitrification coupled to pyrite oxidation (1). This results in the observed increases of sulphate and ferrous iron. Both increases are well-reproduced by the model. Denitrification coupled to OC (2) is of less importance. Besides the parameters shown in **Fig. 3**, all other parameters (pH, Ca, Mg, total inorganic carbon) achieve sufficient matches with measured data, also for the upper aquifers.

Based on this, a long term forecast has been calculated for two scenarios. In the first scenario a constant nitrate input on the current level is assumed (mean nitrate concentration in recharged groundwater 2007: approx. 75 mg/L). For the second scenario a constant nitrate input less 25% with respect to current level is accounted. Pre-set modelled time period in both scenarios is 300 years each. Results are shown in **Fig. 5**.

In both scenarios sulphate and iron concentrations will increase until the end of the 2010s and remain on their levels until the end of the forecast period. Compared with the results of the first scenario sulphate con-



**Fig. 5.** Results of two long-term prognoses of raw water quality abstracted from the 3rd aquifer for selected parameters (sulphate, iron and nitrate). Scenario 1: constant nitrate input on the current level (2007), Scenario 2: constant nitrate input but less 25% with respect to current level (2007).

centrations in the second scenario are slightly diminished (1st scenario: 170 mg/L, 2nd scenario: 150 mg/L). Modelled iron concentrations do not differ noticeable. The reductive capacity of the aquifer is sufficient to reduce nitrate completely. Modeling results indicate that within the next decades a nitrate breakthrough to the wells in the third aquifer is no matter of concern if flow conditions remain constant.

## 5. Conclusion

The case study "Rasseln Waterworks" has shown, that also for a complex hydrogeological and hydrogeochemical system with several interacting aquifers and a time-variant input of nutrients a reactive transport model can be developed. The model reproduces the previous raw water quality (retrospective modeling). For predefined future scenarios of nitrate input long-term forecasts of raw water quality can be calculated. Thus, such type of model is an appropriate tool to test the efficiency of agricultural measures on raw water quality development.

## Literature

- [1] Strebel, O., Duynisveld, W. H. M. and Boettcher, J.: Nitrate pollution of Groundwater in Western Europe. *Agriculture, Ecosystems and Environments* 26 (1989), p. 189–214.
- [2] Van Beek, C. G. E. M., Boukes, H., van Rijsbergen and D. Straatman, R.: The threat to the Netherlands waterworks by nitrate in the abstracted groundwater as demonstrated on the well field Vierlingsbeek. *Water Supply* 6 (1988), p. 313–318.
- [3] Tesoriero, A. J., Liebscher, H. and Cox, S. E.: Mechanisms and rate of denitrification in an agricultural watershed: Electron and mass balance along ground water flow paths. *Water Resources Research* 36 (2000), p. 1545–1559.

- [4] *Spalding, R.F. and Exner, M.E.*: Occurrence of nitrate in groundwater – a review. *J. Env. Qual.* 22 (1993), p. 392–402.
- [5] *Boelke, J.K., Wanty, R., Tuttle, M., Delin, G. and Landon, M.*: Denitrification in the recharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. *Water Resources Research* 38 (2002) No. 7, p. 1–23.
- [6] COUNCIL DIRECTIVE 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC).
- [7] COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.
- [8] WHO: Guidelines for Drinking-water Quality – Third Edition incorporating the first and second addenda, Vol. 1, Recommendations, World Health Organization, Geneva 2008.
- [9] *Parkhurst, D.L. and Appelo, C.A.J.*: User's guide to PHREEQC (Version 2) – a computer program for speciation, batch reaction, one dimensional transport and inverse geochemical calculation, US Geological Survey, Water-Resource Investigations Report p. 99–4259 (1999).
- [10] *Van Berk, W. and Hansen, C.*: Hydrogeochemische Stoffflussmodelle – Leitfaden zur Modellierung der Beschaffenheit von Grund- und Rohwässern. 226 p., Springer 2006.
- [11] *Cremer, N.*: Schwermetalle im Grundwasser Nordrhein-Westfalens unter besonderer Berücksichtigung des Nickels in tieferen Grundwasserleitern der Niederrheinischen Bucht, Bes. Mitt. Dt. Gewässerkundl. Jahrb., 60, 178 p. Doctoral Thesis Ruhr-Universität Bochum, 2002.
- [12] *Bergmann, A.*: Hydrogeochemische Untersuchungen anoxischer Redoxprozesse in tiefen Porengrundwasserleitern der Niederrheinischen Bucht im Umfeld des Tagebaus Garzweiler I. Bochumer Geologische und Geotechnische Arbeiten, 51, 167 p. Doctoral Thesis Ruhr-Universität Bochum, 1999.
- [13] AHU AG: Planungsunterlagen zur Festsetzung eines Wasserschutzgebietes für das Wasserwerk Rasseln der Stadtwerke Mönchengladbach GmbH – Teil A: Hydrogeologisches Gutachten, unpublished report, 1996.
- [14] *Wisotzky, F. and Mäurer, D.*: Untersuchungen zur Entwicklung der zukünftigen Rohwasserqualität im Wasserwerk Rasseln, unpublished report Ruhr-Universität Bochum und NiederrheinWasser GmbH, 2006.
- [15] *Mäurer, D. und Wisotzky, F.*: Prognose zur Entwicklung der Nitrat- und Sulfatkonzentration in einem tiefen Grundwasserleiter durch hydrogeochemische Untersuchungen. *Grundwasser* 13 (2008) p. 208–219.
- [16] *Wisotzky, F.*: Untersuchungen zur Pyritoxidation in Sedimenten des Rheinischen Braunkohlereviere und deren Auswirkungen auf die Chemie des Grundwassers. Besondere Mitteilungen zum Dtsch. Gewässerkl. Jb., 58 (1994), 153 p.

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