Model-based quality management of groundwater resources – catchment area Liedern, Germany

Christine Kübeck, Carsten Hansen, Christoph König, Dorothea Denzig and Wolfgang van Berk

ABSTRACT

Strategies of groundwater protection in agricultural dominated areas are mainly based on a general reduction of the input of nutrients like nitrate. However, preventive measures in different parts of the catchment may provide very different effects on raw water quality. Exemplified on the case study ‘Liedern’ (BEW GmbH Bocholt, Germany) it is shown that hydrogeochemical processes along the flow path and in the well strongly affect the results of agricultural measures in terms of modality and efficiency. Thus, a reduction of fertilization in the vicinity of the well gallery leads to a decrease of nitrate concentration in the raw water. Whereas agricultural measures in the eastern part of the catchment do not influence nitrate, but cause a reduction of the iron concentration and rate of incrustation in the wells after 18 years. In this study we present a management tool that enables assessment of future trends in raw water quality. The tool is based on a reactive transport model which considers land use dynamics as an instrument to influence groundwater/raw water quality. A thermodynamic equilibrium approach is applied for modelling hydrogeochemical processes between aqueous, solid and gaseous phases. Kinetically controlled reactions like the microbial degradation of organic carbon are expressed by multiplicative Michaelis–Menten equations.

Key words | hydrogeochemical modelling, quality management, raw water composition

INTRODUCTION

Freshwater abstracted from groundwater systems is one of the most important water resources used for alimentation, sanitation and industrial processes. As a consequence, a decline in groundwater availability has direct implications on social and economic developments (Custodio 2002). The availability of groundwater for drinking water supply is often characterized by quantity and accessibility. However, in many regions groundwater quality has become an important factor due to environmental pollution (Schot & van der Wal 1992; Spalding & Exner 1995; Karr et al. 2001; McLay et al. 2001). Here, the maintenance of water supply depends on extensive and costly treatment steps. Furthermore, incrustations or the erosion of wells and ductworks often complicate drinking water production (Houben 2005). Still, recent practices of economic resources management are based on water balance calculations but in most do not consider hydrogeochemical processes affecting raw water quality.

This study is focussed on the development of a model-based tool that supports a sustainable quality management of groundwater resources. Exemplified on the catchment area ‘Liedern’ (BEW GmbH Bocholt, Germany) site specific questions and economic needs of the water supplying companies are discussed and transferred into a management tool. This tool is based on a reactive transport model which considers land use dynamics as an instrument to influence raw water quality. A simple user interface enables testing of the effects of time and site specific agricultural measures on future raw water composition for parameters like pH, $E_{H}$, $NO_3^-$, $SO_4^{2-}$, $HCO_3^-$, $Cl^-$, $Fe^{2+}$, $Ca^{2+}$, $Mg^{2+}$ and $Na^+$ concentrations. Thus, the resulting prediction and planning tool serves as a communication platform between complex scientific expertise and economic implications.
METHOD

The management tool is based on a reactive transport model that couples hydrogeochemical and hydraulic processes using a hybrid approach. Groundwater flow and interacting surface water systems are simulated with the program SPRING® (König 2010). Model results of the geohydraulic simulation are transferred into a hydrogeochemical model using the conception of stream tubes (Kübeck et al. 2009). Each stream tube represents a discrete area and a defined volumetric flow rate (recharge, infiltration of surface water) within the catchment. Groundwater flow in the stream tubes is determined by specific retention times and flow paths through the three-dimensional aquifer. The model considers macro-scale dispersion caused by sediment lenses and layers with different hydraulic conductivity. Transverse mixing effects between stream tubes are assumed to be negligible. Along the flow path physical, chemical and biological processes lead to an alteration of groundwater composition. Hydrogeochemical processes between aqueous, solid and gaseous phases are calculated using the program PhreeqC (Parkhurst & Appelo 1999) and the thermodynamic data base water4f (Ball & Nordstrom 1991). Kinetically controlled reactions like the microbial degradation of organic carbon are expressed by multiplicative Michaelis–Menten equation:

$$\mu = \mu_{\text{max}} \cdot \prod \left( \frac{c_i}{K_S + c_i} \right)$$

(1)

where the rate of chemical turnover ($\mu$ [mol/(l·s)]) is calculated as a product of the maximal reaction rate ($\mu_{\text{max}}$ [mol/(l·s)]) and a term that describes the influence of the reactant concentrations ($c_i$ [mol/l]) and the affinity constant ($K_S$ [mol/l]).

Apart from aquifer characteristics like transmissibility and geochemical–mineralogical composition, the occurrence of these processes is triggered by the input of solutes into the groundwater. Numerous studies indicate an exposure of groundwater resources not only to local contamination or infiltrating surface water but mainly due to regional long-term applications of agricultural additives (Strebel et al. 1989; Postma et al. 1991; McLay et al. 2001). Thus, in agriculturally dominated regions shallow groundwater sources often show high nitrate concentrations exceeding the legal limit for drinking water of 11.3 mg nitrate-N per litre in Europe (EU Drinking Water Directive 98/83/EC) and 10 mg nitrate-N per litre in the USA (U.S. EPA 1991) (Andersen & Kristiansen 1984; Böckle et al. 1984; Strebel et al. 1989). Mass balance calculations between nitrogen supply (agricultural additives, fixation of atmospheric nitrogen by leguminous crops and atmospheric precipitation) and the removal of nitrogen from the soil (plant and animal products) provide information about the amount of nitrogen (N-surplus) available for chemical leaching. Field experiments performed by Hatch et al. (2002) demonstrate a direct proportionality between the magnitude of calculated N-surplus and amount of nitrogen leached into the groundwater. Therefore, the documentation of the regional N-surplus enables retracing of the historical development of nitrate concentration in the shallow groundwater.

The input of sulphur, chloride, potassium, calcium, magnesium and a variety of minor elements is linked to the input of nitrogen compounds (Rowell 1994). In agricultural influenced groundwater systems Karr et al. (2001) and Böhlke (2002) could show a correlation between the concentration of nitrate and other nutrients. Thus, the input of solutes into the groundwater is modelled as a function of the N-input using element specific transfer functions (detailed information see Hansen et al. 2010). The N-input, in turn, is determined by regional N-surplus calculations (recent and past N-input) and future land use scenarios (prospective simulations). Physico-chemical parameters like pH, $E_{H}$ and the distribution of species between aqueous, solid and gaseous phases are calculated using an equilibrium approach. In the unsaturated zone the seepage water equilibrates with soil gas ($CO_2(g)$, $O_2(g)$) and solid phases (e.g. $CaCO_3(s)$, iron compounds).

CASE STUDY ‘LIEDERN’ (BEW GMBH BOCHOLT, GERMANY)

Bocholt is located in the agricultural dominated Lower Rhine region, close to the German–Dutch border. Water supply in Bocholt and the surrounding area depends on the extraction of freshwater from quaternary sediments (sand and gravel). In the past drinking water was primarily produced in ‘Liedern’ and a nearby pumping station ‘Mussum’. In 1999 an additional facility was built in Schüttensteiner Wald. Although the application of agricultural additives in all three regions has been very similar, only raw water from ‘Mussum’ shows high nitrate concentrations. In contrast to ‘Mussum’, the pumping station ‘Liedern’ produces raw water with a low nitrate concentration (7–10 mg/l) but high iron and manganese concentrations of about 3.5 and 1 mg/l, respectively. Thus, water supplying companies are particularly concerned whether nitrate concentrations in the raw water from
‘Liedern’ and ‘Schüttensteiner Wald’ may also increase; and if so: how much time is left until nitrate concentration exceeds the legal limitation? What can be done to slow down this development? Another point of interest is related to the formation of incrustations in the wells. The efficiency of freshwater production especially in the pumping station ‘Liedern’ is strongly affected by a fast clogging of wells due to the precipitation of iron hydroxide. An estimation of future incrustation rates may help to assess operational costs on a long-term scale.

**MODEL CONCEPTION**

The pumping station ‘Liedern’ consists of two well galleries each with seven production wells and a total production rate of about 3.8 Mio m³/a. Raw water from the northern and southern gallery is mixed in a collecting pipe (ratio 43.6:56.4). Information about the groundwater flow derives from a steady-state, 2D simulation that represents average flow conditions in the catchment and surrounding area. Depth-related groundwater flow was calculated for the catchment which is about 20 km². The groundwater flow direction is (south-)west, towards the production wells (Figure 1). In the catchment groundwater recharge is 4.2 Mio m³/a. About 1.1 Mio m³/a surface water from the nearby river Aa and 0.35 Mio m³/a lake water infiltrate into the aquifer. A small section of the river Aa in the middle of the catchment and canals in agricultural areas drain the groundwater system (~1.86 Mio m³/a). The catchment area is subdivided into eleven zones (gallery north and south; see Figure 1). Each zone is represented by a stream tube of a specific flow rate, flow time and flow path through the three-dimensional aquifer (Figure 2).

![Figure 1](https://iwaponline.com/wst/article-pdf/66/1/210/442900/210.pdf)  
**Figure 1** | 2D groundwater flow in the catchment area ‘Liedern’ (BEW GmbH, Germany) (grey lines represent groundwater flow paths; dashed lines indicate zones of different flow times).

![Figure 2](https://iwaponline.com/wst/article-pdf/66/1/210/442900/210.pdf)  
**Figure 2** | Flowchart of the hydrogeochemical processes along the profile A–B (see Figure 1) in the aquifer of the northern catchment ‘Liedern’, Germany.
Data of the N-input between 1950 and 2005 are deduced from N-surplus calculations of North-Rhine-Westfalia (UBA 2007). In a first modelling approach surface water quality is assumed to be constant in time. The chemical composition of the surface water used is derived from measurements in 1996. Between 1976 and 2004 about 10% of the grassland was ploughed up. In this process, N-compounds mineralize, and large amounts of nitrate (model assumption: 250 mg/l) are leached into the groundwater. In groundwater-influenced soils the nitrate loaded seepage water reacts with mackinawite (FeS) (and calcite).

The hydrogeochemical model conception of the northern catchment is shown in Figure 2. Groundwater that is recharged in the vicinity of the well gallery (west of Bocholt) flows through the upper part of the aquifer (<10 m below surface). Irregularly distributed peat lenses and drift peats cause high concentrations of dissolved organic carbon (DOC) in the shallow groundwater.

After percolating the upper sediment, groundwater that is recharged in the area of Bocholt and eastern parts of the catchment infiltrates into deeper sediment layers (~10–28 m below surface). This sediment contains pyrite as well as small amounts of calcite and solid organic carbon (OC) (Table 1).

Along the flow path DOC reacts successively with dissolved oxygen and nitrate (Equations (2), (3) and (4)). After depletion of both oxidants, sulphate is used as electron acceptor (Equation (5)). Rate expressions of the kinetically controlled reactions are listed in Table 1. Depending on the pH, the produced CO2(aq) reacts with water to form HCO3− and CO32− ions (Equation (6)).

\[
\begin{align*}
\text{CH}_2\text{O} + \text{O}_2 & \rightarrow \text{CO}_2^{(aq)} + \text{H}_2\text{O} \\
\text{CH}_2\text{O} + 0.8 \text{NO}_3^- + 0.8 \text{H}^+ & \rightarrow \text{CO}_2^{(aq)} + 0.4 \text{N}_2 + 1.4 \text{H}_2\text{O} \\
\text{CH}_2\text{O} + 0.5 \text{NO}_3^- + \text{H}^+ & \rightarrow \text{CO}_2^{(aq)} + 0.5 \text{NH}_4^+ + 0.5 \text{H}_2\text{O} \\
\text{CH}_2\text{O} + 0.5 \text{SO}_4^{2-} + 0.5 \text{H}^+ & \rightarrow \text{CO}_2 + 0.5 \text{HS}^- + \text{H}_2\text{O} \\
\text{CO}_2^{(aq)} + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{Fe}_2\text{S}_3 + 2.8 \text{NO}_3^- + 0.8 \text{H}^+ & \leftrightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 1.4 \text{N}_2 + 0.4 \text{H}_2\text{O} \\
\text{Fe}^{2+} + 0.2 \text{NO}_3^- + 2.4 \text{H}_2\text{O} & \leftrightarrow \text{Fe(OH)}_3(s) + 0.1 \text{N}_2 + 1.8 \text{H}^+
\end{align*}
\]

Nitrate reduction in the deeper sediment is driven by pyrite-S oxidation. In this process, ferrous iron and sulphate are released into the groundwater (Equation (7)). Under oxidizing conditions ferrous iron reacts with nitrate and precipitates as iron hydroxide (Equation (8)).

\[
\begin{align*}
\text{Fe}^{2+} + 0.2 \text{NO}_3^- + 2.4 \text{H}_2\text{O} & \leftrightarrow \text{Fe(OH)}_3(s) + 0.1 \text{N}_2 + 1.8 \text{H}^+
\end{align*}
\]

In the system calcite buffers the pH due to dissolution or precipitation.

| Table 1 | Model parameter (meas. – measurement, mod. – model, \(\mu_{\text{max}}\) – maximal reaction rate, \(\mu\) – calculated chemical turnover based on Michaelis–Menten equation, BF – stream tube influenced by bank filtration, b.s. – depth below surface) |
|---|---|---|---|---|
| Stream tubes: total flow time | Pyrite-S [wt %] | Calcite-C [wt %] |
| <9a | 0 | 0 | 0 | 0.02–0.03 | 0.02 | 0.018–0.027 |
| >9a | Sediment: | | | | | |
| <~ 10 m b.s. | 0 | 0.04 | 0 | 0.01–0.02 | 0.02 | 0.016–0.018 |
| >~ 10 m b.s. | 0.02–0.05 | 0.04 | BF: 0.04 | 0–0.02 | 0.02 | 0.02–0.022 |

**Kinetics: organic bound carbon**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>(\mu_{\text{max}}) [mol/(l·s)]</th>
<th>(\mu) [mol/(l·s)]</th>
<th>References: Monod kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{O}_2^{(aq)})</td>
<td>(1.57 \times 10^{-9})</td>
<td>&lt;(1.27 \times 10^{-9})</td>
<td>Ball &amp; Nordstrom (1994): (\mu = 1.57 \times 10^{-9}) mol/(l·s)</td>
</tr>
<tr>
<td>(\text{NO}_3^-)</td>
<td>(9.8 \times 10^{-10})</td>
<td>&lt;(9.2 \times 10^{-10})</td>
<td>Green et al. (2008): (\mu = 3.5 \times 10^{-13} – 3.5 \times 10^{-9}) mol/(l·s)</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-})</td>
<td>(8 \times 10^{-13})</td>
<td>&lt;(7.28 \times 10^{-13})</td>
<td>Jakobsen &amp; Postma (1994): (\mu = 1 \times 10^{-16} – 2 \times 10^{-10}) mol/(l·s)</td>
</tr>
</tbody>
</table>
MODEL RESULTS

Model results are divided into a retrospective and prospective part. The retrospective simulation enables testing of the plausibility of the underlying reactive transport model by comparing model results with measured raw water composition over a period of 43 years. The model conception (hydrogeochemical and geohydraulic) is considered to be plausible if model results reasonably reproduce measured raw water composition.

As shown in Figure 3, measured HCO$_3^-$ concentration increases between 1960 and 2007 from 150 to 270 mg/l. Sulphate and calcium concentrations increase until the 1990s and decrease slightly afterwards, while magnesium and iron concentrations remain constant. The reactive transport model achieves a good agreement with measured data such as sulphate, calcium, magnesium and iron. Whereas HCO$_3^-$ is problematic as the concentration is influenced by various parameters like soil pH, soil gas composition and the distribution of organic and inorganic carbon compounds. Modelled nitrate concentrations reproduce the observed temporal development; however, overestimate the maximum by 3 mg/l.

Based on the reactive transport model, the management tool enables estimation of the impact of future land use dynamics and to evaluate the effect of agricultural measures on raw water composition (prospective modelling part). In this study we present three N-input scenarios in different parts of the catchment. Concentrations of other nutrients in the shallow groundwater that are linked to the N-input are calculated automatically (see method; model input: Figure 4). Scenario 1 assumes after 2012: a constant N-input, no ploughing up of grassland and the surface water quality remains unchanged. Agricultural measures are planned in scenario 2 and 3 beginning in 2012. Here, the absolute N-input into the groundwater will be reduced by 50% on an area of about 1,000 m$^2$. In scenario 2 measures in the direct vicinity of the wells are modelled; whereas in scenario 3 a reduction of N-input is assumed in the north of Bocholt.

Model results are plotted in Figure 3. In scenario 1 nitrate concentrations increase after 2008 at 10 mg/l and remain stable until 2050, while iron, sulphate and HCO$_3^-$ concentrations decrease slightly. The reduction of the N-input in scenario 2 leads to a decrease of nitrate concentrations after 2014. Here, calcium and HCO$_3^-$ concentrations decrease slightly, but iron and sulphate...
concentrations remain constant. In scenario 3 nitrate concentrations do not change; whereas iron concentrations and the precipitation of iron hydroxide in the wells decrease after 2026.

DISCUSSION AND CONCLUSIONS

The physicochemical composition of groundwater is the result of an interaction between geohydraulic and complex hydrogeochemical processes in the aquifer. The hydrogeochemical processes are triggered by the input of solutes into the groundwater which represents therefore an important influencing factor in groundwater resources management. Variations of flow pattern due to changes in groundwater recharge or infiltration rates of surface water may also influence the chemical composition of raw water but are not presented in this study.

Exemplified on the catchment area ‘Liedern’ (BEW GmbH Bocholt, Germany) it has been shown that hydrogeochemical processes along the flow path and in the wells strongly affect the efficiency of agricultural measures. Model results reveal a strong relation between N-input and HCO$_3^-$ concentrations. The nitrate concentration in the shallow aquifer is mainly influenced by the oxidation of organic carbon compounds. However, nitrate-loaded groundwater reaches the well as detention times in the shallow aquifer are insufficient to provide required nitrate reduction. Agricultural measures in the direct vicinity of the well gallery (scenario 2) cause a reduction of the nitrate concentration in the raw water. This effect, though, is small as the nitrate concentration is influenced by the kinetically controlled DOC degradation. In this context, the spatial distribution and reactivity (DOC leaching) of peat lenses and drift peats are important factors affecting groundwater quality.

In the deeper sediment layer pyrite reacts with groundwater recharged in the eastern section of the catchment area. A reduction of the N-input within this region has little effect on nitrate concentration in the raw water as long as a sufficient amount of pyrite is available. Based on information provided by geochemical–mineralogical analyses of the sediment we do not expect a depletion of pyrite in the deep sediment within the time frame considered by the model. Nevertheless, model scenarios should also be applied to assess the impact of uncertainties in the sediment composition as part of preliminary investigations. Based on this, further analyses of the aquifer system may be planned more purposefully.

The progress of pyrite oxidation front along the flow path depends on the pyrite content and the remaining nitrate in the groundwater after percolating the shallow aquifer. Denitrification coupled to pyrite oxidation leads to an increase of iron and sulphate concentrations in the deep groundwater (scenario 3). After nitrate depletion, sulphate reacts slowly with DOC which may cause a relocation of reductive capacity in the sediment due to pyrite (or mackinawite) precipitation.

In the production wells the iron-loaded, old groundwater mixes up with oxidized groundwater from the shallow aquifer. Consequently, the dissolved ferrous iron reacts with nitrate to form iron hydroxide (Fe(OH)$_3$). The incrustation rate is affected by the amount of ferrous iron released due to ploughing up of grassland and oxidative dissolution of pyrite in the deeper sediment, nitrate concentrations in the shallow groundwater (mixing ratios) and the residence time in the wells.

In summary future raw water quality (in particular nitrate concentration) and incrustation rates in the well gallery ‘Liedern’ depend on a combination of the time and site specific N-input, available DOC and pyrite content in the sediment. The simulation of N-input scenarios enables evaluation of the impact of land use dynamics and agricultural measures as an instrument to influence raw water quality to a certain point.

REFERENCES


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