Natural attenuation of common agricultural and atmospheric pollutants: reactive transport of nitrate, potassium and aluminium in sandy sediments of northwestern Germany

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Abstract Groundwater under haplic podzol soils of the rural Bourtanger Moor area (northwest Germany) suffers from deteriorating quality. Effects of intensive agriculture are visible in elevated nitrate (up to 250 mg l⁻¹) and potassium (up to 60 mg l⁻¹) concentrations. Heavy deposition of acid rain has lead to low soil and groundwater pH (pH 2.75 and 3.4, respectively) and elevated aluminium concentrations of up to 3.1 mg l⁻¹ because of low soil buffering capacity. Natural attenuation processes are responsible for confinement of the pollutants to the upper parts of the water column. Cation exchange and autotrophic denitrification are the main processes. Hydrochemical as well as geochemical data were integrated into different models to estimate the vertical propagation velocity of the contaminants. Model approaches include groundwater age determinations, stoichiometric mass balance, and numerical reactive transport models.

Key words: acid rain; agriculture; aluminium; autotrophic denitrification; Bourtanger Moor, Germany; cation exchange; hydrogeochemical modelling; natural attenuation; nitrate; podzols; potassium

INTRODUCTION

The causes and effects of deteriorating groundwater quality in the Bourtanger Moor area of northwestern Germany were studied from several perspectives. A hydrochemical survey delineated the spatial distribution of pollutants in three dimensions. Geochemical and mineralogical studies allowed the identification and quantification of reactive aquifer constituents that attenuate pollutant spreading. Hydrochemical as well as geochemical data were integrated into stoichiometric mass balance and numerical reactive transport models to predict the time scale of vertical pollutant transport. Column experiments were performed to test the numerical models.

HYDROGEOLOGICAL SETTING OF THE STUDIED AREA

Geology and hydrology

The Bourtanger Moor area comprises two main aquifers composed of sandy post-glacial outwash. They are separated by a clayey interglacial layer of low hydraulic

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Conductivity. The lower aquifer is used for drinking water production. It is recharged via leakage through the aquitard.

Cultivated dystric histosols (bog) are the dominant soil type in the western part of the catchment whilst cultivated haplic podzols prevail in the eastern part. Most of the podzolic soils are used as agricultural substrate. Smaller parts are forested.

Hydrochemistry

The podzolic soils are highly permeable and have low denitrification capacities. The shallow groundwater below shows distinctive influences of anthropogenic activities. Due to the intensive application of manure and fertilizers nutrient concentrations often greatly exceed drinking water limits (Table 1). The dystric histosols (bog) are mainly used as pastures and thus receive much less nutrients. Additionally they have a notable denitrification capacity. Groundwater under bog soils is therefore much less polluted.

Because of their low buffering capacities the haplic podzol soils are also vulnerable to the effects of acid rain. Minimum pH values for rain were recorded in the mid-1980s (Fig. 1). As a result of stricter emission protection laws the pH of rain has risen about one unit till 1997. The increase is mostly due to the removal of sulphur whilst nitrogen emissions have remained at a high level.

Due to evaporation and the oxidation of ammonium as water moves through the soil, the resulting seepage water is even more acidic than the rain. Soil pHs were commonly found to be around pH 3 with minimum values at pH 2.75. Hydrogeochemical equilibrium modelling using the model PHREEQC-2 (Parkhurst & Appelo, 1999) showed that buffering of the acid through the soil mineral gibbsite (Al(OH)₃) is compensated by strong mobilization of aluminium below pH 4 (Fig. 2).

Geochemistry

Reactive aquifer components responsible for natural attenuation processes were identified and quantified on fresh drill core material (Table 2).

Table 1 Average pollutant concentrations (mg l⁻¹) in groundwater of the Bourtanger Moor area.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Land use</th>
<th>Aluminium:</th>
<th>Potassium:</th>
<th>Nitrate:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
<td>mean</td>
</tr>
<tr>
<td>Haplic podzols</td>
<td>Forest</td>
<td>0.02</td>
<td>3.11</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Agriculture</td>
<td>0.04</td>
<td>0.64</td>
<td>0.19</td>
</tr>
<tr>
<td>Dystric histosols</td>
<td>Cultivated, grassland</td>
<td>0.02</td>
<td>0.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 2 Average amount of reactive aquifer material in sediments of the Bourtanger Moor area.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Lithology</th>
<th>CEC (mmol(eq) 100 g)</th>
<th>Pyrite (FeS₂) (wt %)</th>
<th>Calcite (CaCO₃) (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
<td>mean</td>
</tr>
<tr>
<td>Upper aquifer*</td>
<td>Sand</td>
<td>0.5</td>
<td>3.0</td>
<td>1.0</td>
</tr>
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<td>Upper aquifer*</td>
<td>Sand</td>
<td>0.5</td>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Aquitard</td>
<td>Clay</td>
<td>10.0</td>
<td>18.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Lower aquifer</td>
<td>Sand</td>
<td>0.4</td>
<td>2.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* Oxic, † Reducing
Geochemistry

Reactive aquifer components responsible for natural attenuation processes were identified and quantified on fresh drill core material (Table 2).

All pollutants "disappear" at rather sharp reaction fronts located in the upper aquifer. The propagation of aluminium and potassium is retarded by cation exchange reactions. Illite is the most abundant exchanger mineral. Due to its high affinity for sorption, aluminium can be found in groundwater only after it has almost completely "filled" the cation exchanger assemblage.

Chemical interactions with pyrite (FeS₂) are responsible for the attenuation of nitrate. This process—called autotrophic denitrification—was described for northwestern Germany by Frind et al. (1990).
MODELLING OF POLLUANT MIGRATION

Mean residence time of groundwater

Pollutants cannot flow faster than groundwater itself. Vertical flow velocities are thus a first constraint on their maximal propagation velocity. Vertically spaced determinations of groundwater mean residence times were performed on several multilevel samplers. Dating tools included tritium and chlorofluorocarbons (CFC). The measured average vertical flow velocity of groundwater is about 1 m year\(^{-1}\). Tritium "ages" were determined by backward extrapolation of measured tritium values using the decay rate. Therefore the points of intersection between the decay curves and an input curve from a nearby rainwater isotope station were determined. They give the year of infiltration. The results were in good to reasonable accordance with the CFC data (Fig. 3). CFC ages were determined by matching measured concentrations with input curves.

![Fig. 3 Groundwater mean residence times in the Bourtanger Moor area determined from backward extrapolation of tritium measured in 1999 vs the input curve of IAEA-station 0628001 Groningen (NL). Ages from CFC-dating given as comparison.](image)

Mass balance approaches

The hydrochemical and geochemical data obtained were integrated into stoichiometric mass balance models (e.g. Postma et al., 1991). The propagation velocity of any pollutant can be calculated by dividing its input flux (concentration times recharge) by the amount of reactive aquifer material using the known stoichiometry of the reaction. Mass balance approaches for nitrate, aluminium and potassium yielded vertical front velocities of a few centimetres per year (e.g. Fig. 4). The model set up is easy and requires only minimal computation time. Hydraulic dispersion, temperature effects, competitive reactions and kinetic inhibitions were not included here although methods
to include mass balancing into advective–reactive models do exist (Schweich et al., 1993). The practical application of the model presented here is thus limited to reactions that are only marginally affected by these constraints.

**Column experiments and reactive transport models**

Column experiments were performed using undisturbed drill cores. Sorption and desorption of Mg$^{2+}$, Na$^+$, K$^+$ and Al$^{3+}$ were successfully modelled in one-dimensional reactive transport approaches using PHREEQC-2 (e.g. Fig. 5).

There are severe deviations between the mass balance and the reactive transport models for potassium. The former predicts a much quicker breakthrough than the
latter. This is due to limitations of the mass balance concept. It cannot address the competition of different cations for exchange positions. Whilst potassium has only a medium affinity for sorption, this problem hardly affects \( \text{Al}^{3+} \) due to its high sorption affinity. Average front velocities for aluminium from both model types were thus in reasonable accordance with each other. The remaining deviations could—at least in part—be due to the hydraulic dispersion of the contaminant front, which is not considered in the mass balance approach.

The flow velocity applied in the column experiments was higher than in nature so that most nitrate left the column without reacting with pyrite. A kinetic model approach had to be used to simulate the obviously kinetically controlled reaction.

CONCLUSIONS

In order to realistically evaluate the natural attenuation potential of the Bourtanger Moor area detailed studies of both hydrochemistry and geochemistry were necessary. The hydrochemical survey had to include the vertical dimension. This made the delineation of the current depth of reaction fronts possible. Fresh drill cores are essential to investigate the type, distribution and amount of reactive aquifer material. Only carefully selected data could be incorporated into model approaches. Models showed that the vertical propagation velocity of all pollutants is in the range of a few centimetres per year. Care has to be taken since all models are only approximations of nature:

- Vertically spaced age dating of groundwater provides only a limit to the maximum velocity of vertical pollutant transport.
- Stoichiometric mass balance models are simple to construct but cannot address hydraulic dispersion and fail when competitive reactions need to be considered.
- Column experiments and subsequent use of one-dimensional reactive transport models give the most realistic results but require a lot of experimental and analytical work and computational time.
- Interpretation of models must take into account the large spatial and temporal variations of pollutant input and reactive aquifer material distribution.

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