Assessing the reactive transport of inorganic pollutants in groundwater of the Bourtanger Moor area (NW Germany)

G.J. Houben · A. Martiny · N. Bäßler · H.-R. Langguth · W.L. Plüger

Abstract The quality of shallow groundwater in the rural Bourtanger Moor area (NW Germany) has significantly deteriorated because of input of agricultural nutrients and by acid rain. This potentially endangers the local water supply from wells screened in deeper portions of the multi-aquifer system. Several modelling approaches were applied to determine the vertical propagation velocity of the pollutants aluminium, potassium and nitrate. They included distribution of conservative natural tracers, vertically spaced age dating of groundwater, stoichiometric mass balancing of pollutant input and available reactive aquifer material, column experiments and their subsequent reactive transport modelling. The latter method gives the most realistic estimates on reactive transport rates, but requires high efforts.

Keywords Bourtanger Moor · Aluminium · Inorganic pollutants · Nitrate · Reactive transport modelling

Introduction

The rural Bourtanger Moor area is situated in northwestern Germany west of the river Ems and near the small town Haren. The hydrogeological system of the area comprises two aquifers composed of post-glacial outwash material (Fig. 1). The basal aquitard is probably of tertiary age. The aquifers are separated by an clayey interglacial layer of low hydraulic conductivity (see Houben 2000 for a more detailed description). The upper aquifer consists mainly of fine sands. The sandy to gravely lower aquifer, which is used for public water supply, is recharged via leakage through the clayey interglacial aquitard although some hydraulic 'windows' are also present (Fig. 1). Dystric histosols (bog) are the dominant soil type in the western part of the catchment area. Haplic podzols dominate in the eastern part. Most of the podzols are used as agricultural substrate, but smaller parts are wooded. Both soil types have been extensively cultivated by deep ploughing and drainage after World War II.

The Bourtanger Moor area is known for its very intensive agriculture. Additionally, it receives high loads of atmospheric pollutants originating from Dutch and English industrial sites transported by dominantly western winds. Negative effects on shallow groundwater quality are clearly detectable. The pollutants migrate downwards with groundwater replenishing the deeper aquifer. Estimates are needed to predict the time-scale of vertical pollutant transport. All approaches must take into account the hydraulic flow regime as well as the hydrochemical interactions of pollutants with the reactive aquifer material.

Received: 11 May 2001 / Accepted: 1 August 2001

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State of knowledge

The impacts of agricultural activities and acid rain are major contributors to the deterioration of groundwater quality in many areas. Scientific interest into this field began mainly in the early 1980s, but still remains high. Papers on nitrate in groundwater are far too numerous to cite more than a few here. Several processes were identified that attenuate the spreading of nitrate. Obermann (1982) found field evidence for heterotrophic denitrification via organic substances. Autotrophic denitrification via pyrite was first demonstrated from a sandy aquifer at the Fuhrberger Feld (Hannover, Germany) by Kölle (1982) and studied in detail by Böttcher and others (1990) and Frind

DOI. 10.1007/s002540100424

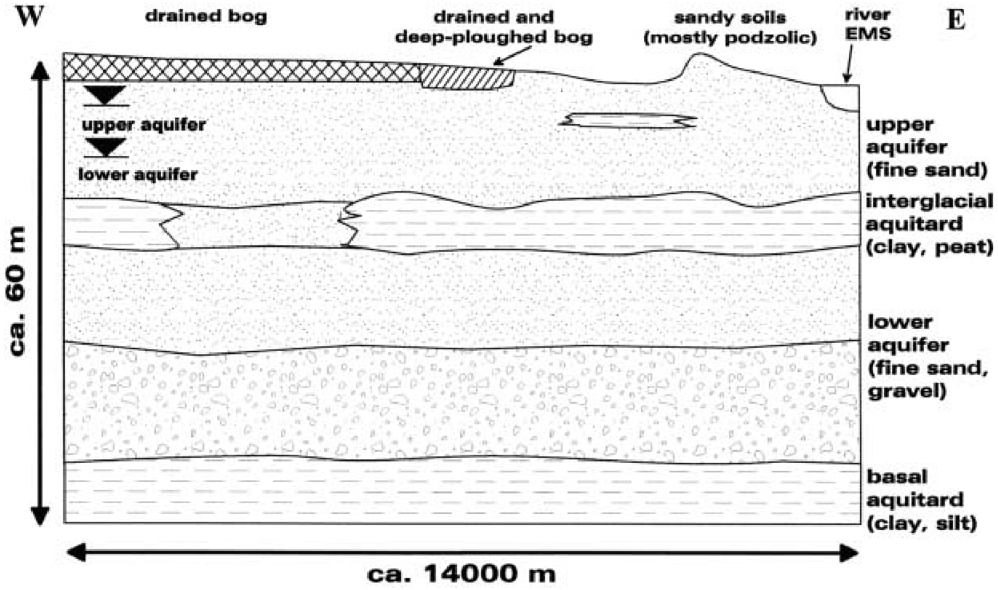

Fig. 1
Simplified hydrogeological section of the Bourtanger Moor aquifer system

and others (1990). It has been found in many other aquifers too (van Beek and others 1989; Postma and others 1991; Houben 2001), including solid rock (Pauwels and others 1998). Kinetic as well as thermodynamic approaches were used to model the movement of the autotrophic denitrification front (Frind and others 1990; Engesgaard and Kipp 1992). The – albeit small -denitrification potential of iron(II) silicates was shown by Postma (1990).

Impacts of acid rain on soils include the destruction of vital soil components such as calcite, clay minerals and aluminium and iron oxides. These reactions and their impact on groundwater were investigated by, e.g. Edmunds and Kinniburgh (1986) and Wilson (1986). Although the acid load of rainwater in Europe has significantly decreased in the last decade the effects in groundwater have to be assessed on a long-term scale because of the long residence times.

Materials and methods

Reactive aquifer components were identified and quantified on fresh core material from several drillings. Drill cores were kept refrigerated and under a nitrogen atmosphere prior to analysis. Pyrite contents were calculated from sulphur measurements using a Leco S-200. Calcite was calculated from measurements of inorganic carbon using a Leco RC 412. The cation exchange capacity was determined using a modified calcium-saturated silver–thiourea method after Pleysier and Juo (1980).

Selected drill cores were used as columns for reactive transport experiments. A peristaltic pump was used for the input water, and pH and specific electrical conductivity in the column outflow were monitored continuously. Samples were taken regularly for hydrochemical analysis. The cation exchange assemblage in the columns was equilibrated before the actual experiments with anaerobic $MgCl_2$ solution. Sodium chloride was added to the input solutions to obtain a more realistic hydrochemical environment. The drill sites were later used to install nested multilevel groundwater samplers with seven to nine individual filters. Additionally, about 40 regular piezometers were available for hydrochemical sampling. Most dissolved cations were measured with ICP-AES (Perkin–Elmer Plasma 400), whereas ion chromatography (Dionex DX 100, salinity detector) was used for most anions and potassium. Chlorofluorocarbons (CFC) were measured by Spurenstofflabor Dr. Oster in Wachenheim (Germany) and tritium (^3H) by Hydroisotop in Schweitenkirchen (Germany).

Hydrogeochemical processes

Pollutant input

Hydrochemical analyses of all available piezometers yielded a strong correlation of groundwater quality with soil type and utilisation. Groundwaters under dystric histosols (bog) show almost no anthropogenic influence. The intensive agriculture on the highly permeable haplic podzols is reflected by nitrate and potassium values that often greatly exceed drinking water limits (Table 1).

The haplic podzol soils are prone to the effects of acid rain because of their low buffering capacities. Minimum pH values for rain as low as pH 3.3 were recorded at the beginning of the 1980s (Fig. 2). Because of stricter emission protection laws, the pH of rain has risen by about one unit until 1997. This is almost exclusively related to the removal of sulphur, whereas nitrogen emissions have remained almost constant.

The probable chemical development from rain to seepage water was calculated after a method described by Appelo and Postma (1996). The processes considered are evaporation and the oxidation of ammonium. The ratio of

Table 1
Range of selected hydrochemical parameters in shallow groundwater of the Bourtanger Moor area (mg/l)

		Nitrate	Potassium	Chloride	Aluminium	pH
Dystric histosols and cultusols (*n*=12)	Minimum	0.1	1.4	16.4	0.02	5.1
	Maximum	3.2	4.7	84.6	0.05	6.9
	Mean	1.8	3.1	32.0	0.03	
Haplic podzols (agriculture) (*n*=19)	Minimum	0.4	3.2	18.0	0.04	4.4
	Maximum	244.4	57.8	97.1	0.64	6.1
	Mean	70.0	17.0	41.2	0.19	
Haplic podzols (forest) (*n*=12)	Minimum	<0.1	<0.1	7.4	0.02	3.5
	Maximum	16.6	6.3	52.0	3.11	5.7
	Mean	3.4	3.0	17.0	0.8	

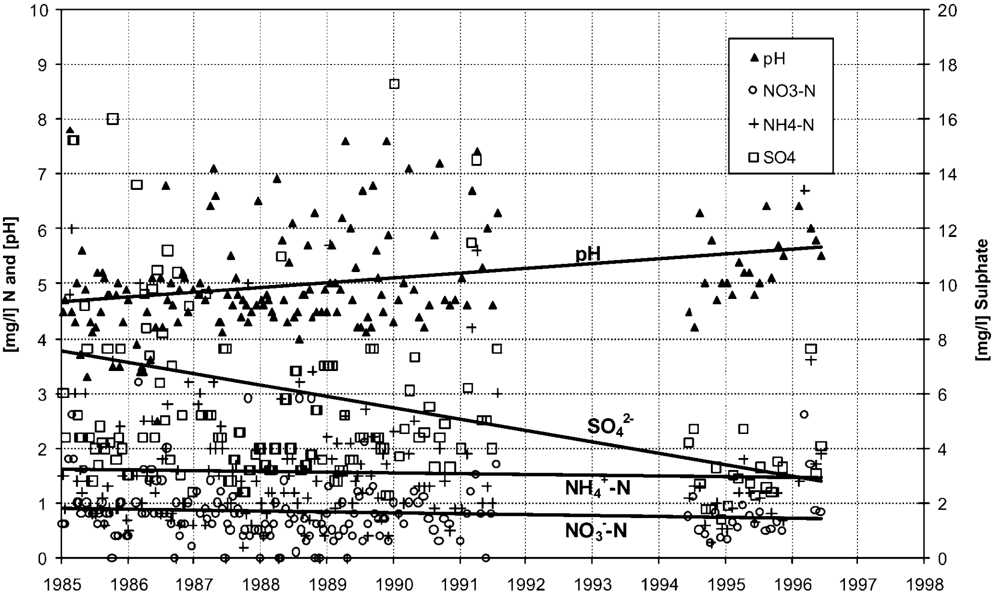

Fig. 2
Development of rainwater hydrochemistry in the Bourtanger Moor area 1985–1997 (after data from Niedersächsisches Landesamt für Ökologie, personal communication)

evaporation to rainfall in the studied area is (540 mm/year)/(710 mm/year)=0.75, so that a fourfold increase in concentrations during evaporation was assumed. It can also be expected that all ammonium becomes oxidised to nitrate during soil percolation, which leads to further acid production (R 1).

$$NH_4^+ + 2O_2 \leftrightarrow NO_3^- + H_2O + 2H^+ \qquad (1)$$

The calculated resulting seepage water has a pH of ≈3 (Table 2). This is reflected by soil pH's on the same scale and the mobilisation of aluminium (Table 1). The agriculturally used podzols fare slightly better because of regular limestone applications by farmers. The measured nitrate concentrations are less than calculated, which is probably caused by some uptake by plants (Tables 1 and 2).

Vertically spaced sampling was used to evaluate the vertical dimension of pollutant distribution. The highest pollutant concentrations could be found in the upper oxic part of the shallow aquifer. No significant concentrations of potassium and nitrate could be found at depths of more than 12 m below the surface (Fig. 3). This is due to attenuating hydrogeochemical reactions with aquifer material.

Attenuation processes

Autotrophic denitrification via pyrite (e.g. Frind and others 1990) was positively identified as the main process that contains nitrate (R2).

Table 2
Calculated evolution of selected hydrochemical parameters from rain to seepage water in the study area

	pH	NO_3^-	NH_4^+	SO_4^{2-}	Cl^-	Unit
Average rain 1985–1991	4.40	2.66	1.93	6.35	3.5	(mg/l)
	4.40	43	107	66	99	(µmol/l)
After evaporation	3.80	172	428	264	396	(µmol/l)
After NH_4^+oxidation	2.99	600	0	264	396	(µmol/l)
	2.99	37.2	0	25.3	14.0	(mg/l)

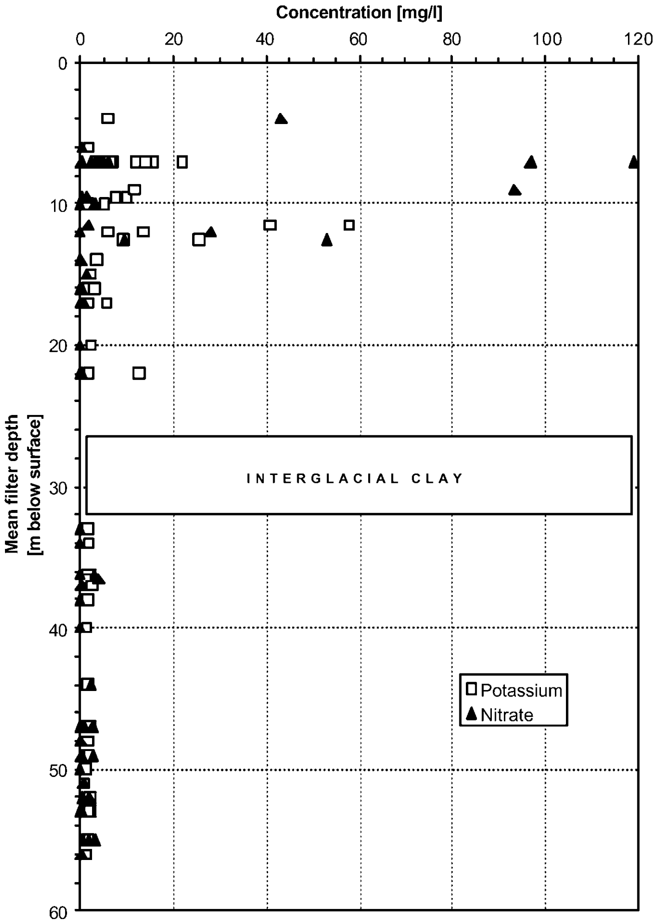

Fig. 3
Vertical distribution of potassium and nitrate in groundwater of the Bourtanger Moor area

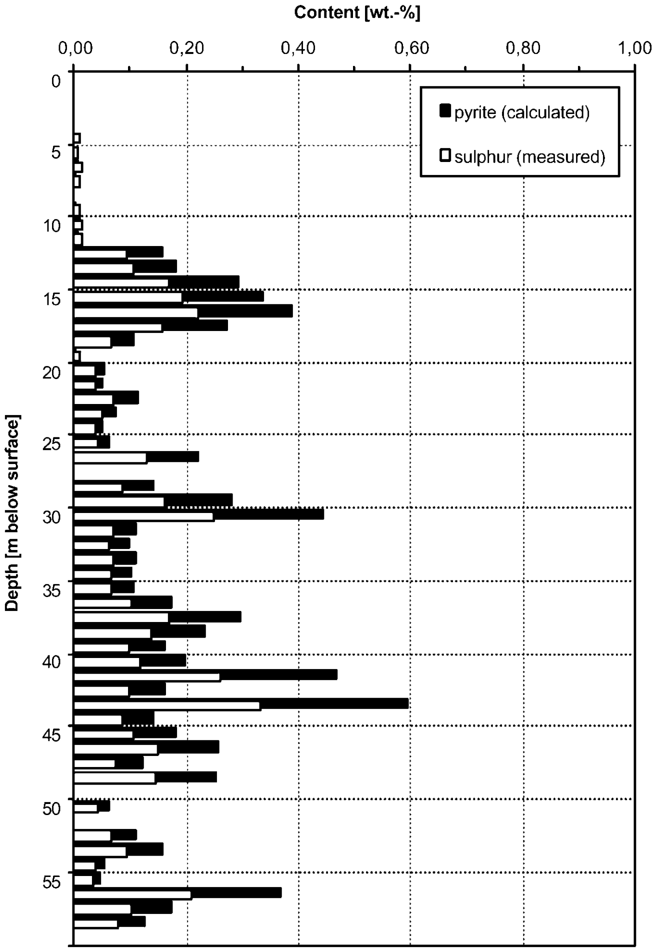

Fig. 4
Vertical distribution of sulphur and pyrite contents in sediment material from one drilling in the study area

$$2FeS_2+6NO_3^-+2H_2O \leftrightarrow 3N_2+4SO_4^{2-}+2H^++2FeOOH \quad (2)$$

The 'disappearance' of nitrate at a depth of ~12 m (Fig. 2) coincides with elevated sulphur contents (Fig. 4). Electron microscopy studies showed that sulphur is mainly present as pyrite. The pyrite contents range between 0.03 and 0.72 wt% for the reduced gravely to clayey sediments (Fig. 3, Table 3). Values for the clayey aquitard are usually higher. Probably not all pyrite present there will be available for reactions because of the low hydraulic conductivity. Pyrite is known to incorporate significant amounts of potentially hazardous trace elements, e.g. Ni, As, which might become mobilised during oxidation. In the case described here, arsenic concentrations in ground water were always well below 10 µg/l. Nickel only exceeded the drinking water limit of 50 µg/l in one filter that was

Table 3
Reactive aquifer material content in sediment material of the Bourtanger Moor area

Formation	Lithology	Cation exchange capacity (CEC)			Pyrite (FeS_2)			Calcite ($CaCO_3$)		
		[mmol(eq) 100 g]			(wt%)			(wt%)		
		Min.	Max.	Mean	Min.	Max.	Mean.	Min.	Max.	Mean
Upper aquifer[a]	Sand	0.6	2.1	1.2	0.00	0.00	0.00	0.01	0.25	0.10
Upper aquifer[b]	Sand	0.8	3.0	1.3	0.04	0.40	0.14	0.05	0.40	0.15
Aquitard	Clay	12.2	19.8	15.5	0.20	0.72	0.24	0.15	7.00	2.00
Lower aquifer	Sand/gravel	0.4	2.5	0.8	0.05	0.44	0.12	0.01	0.95	0.40

[a] Oxic conditions
[b] Reducing conditions

installed in the depth of the expected redox boundary (measured concentration was 60 μg/l).
Cation exchange is the main process of potassium and aluminium retardation. The cation exchange capacity (CEC) of the sandy sediments is in the range of 0.4–3.0 mmol(eq)/l00 g with a mean around 1.0 mmol(eq)/l00 g. Illite is the main provider of exchange sites. The interglacial clays have much higher CEC's of 12–20 mmol(eq)/100 g (Fig. 5, Table 3). This is due to the additional presence of interstratified illite–smectite type clay minerals.

Assessing the velocity of vertical pollutant spreading

Non-reactive vertical transport

The flow velocity of groundwater can be used as a constraint on the maximal propagation rate of dissolved pollutants because pollutants should not flow faster than water. Multilevel samplers were used for vertically spaced determinations of groundwater mean residence time ('age') and the distribution of non-reactive groundwater constituents.

Non-reactive tracers

Chloride was selected as the most useful non-reactive natural tracer. Elevated chloride concentrations are not restricted to the upper part of the shallow aquifer (Fig. 6). Water derived from agricultural areas has obviously reached the deeper aquifer in some parts. The concentrations often exceed local natural background values of about 25 mg/l for tritium-'free' waters (Fig. 5). Elevated chloride concentrations stem from anthropogenic activities including fertiliser and road salt application. Because the cultivation of the Bourtanger Moor area commenced at the beginning of the 1950s this is a good time-mark for the start of input. In 1998, elevated chloride was found at maximum depths of about 47 m (Fig. 6). Assuming that the input began in 1950 this gives a vertical propagation velocity of 47 m/48 year≈1 m/year.

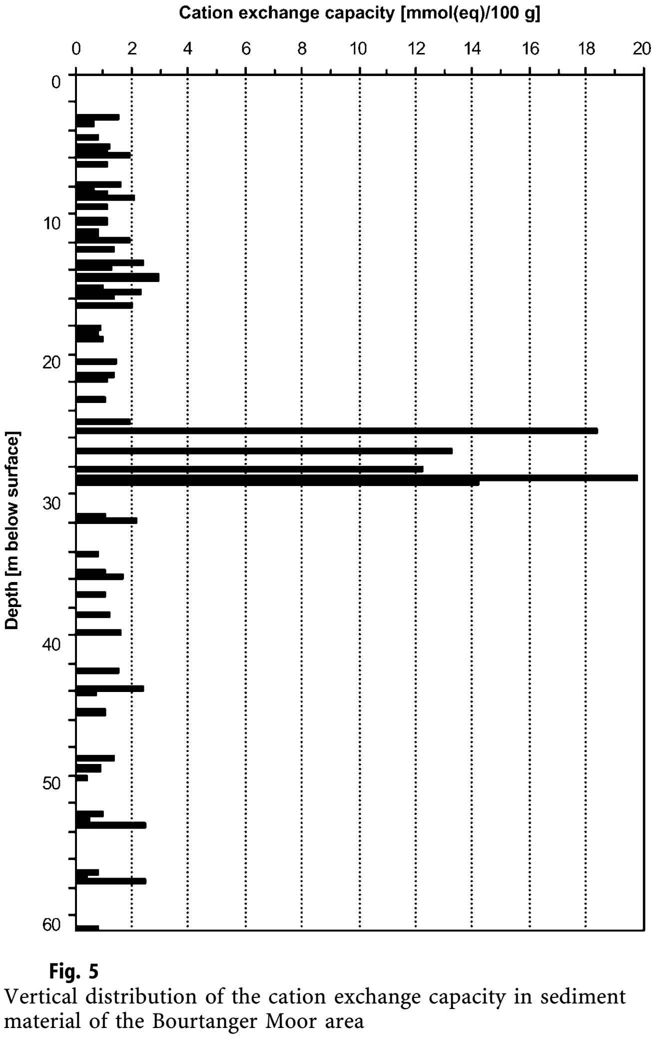

Fig. 5
Vertical distribution of the cation exchange capacity in sediment material of the Bourtanger Moor area

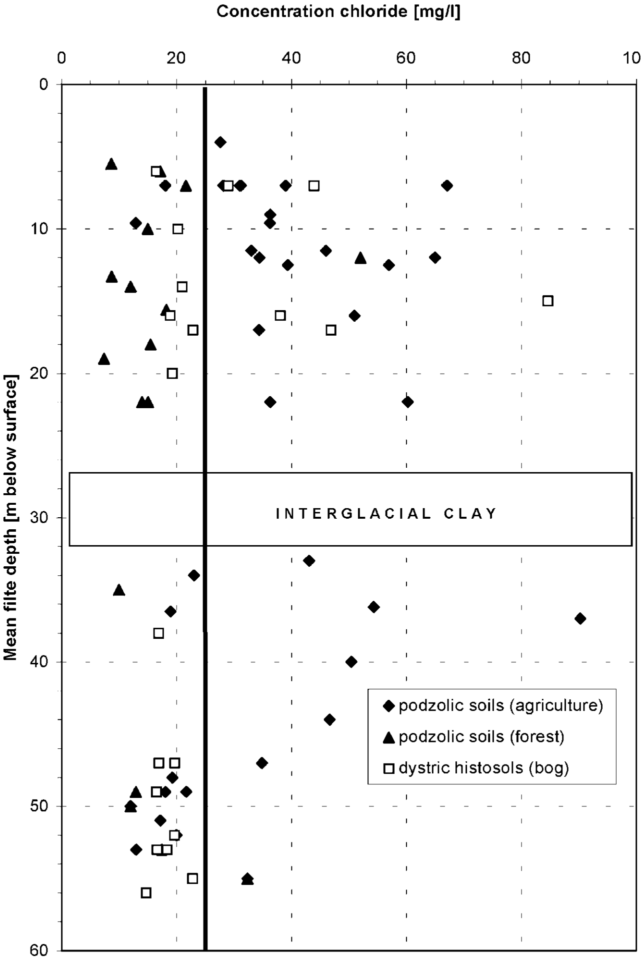

Fig. 6
Vertical distribution of chloride in groundwater of the Bourtanger Moor area. The *solid vertical line* indicates the maximum chloride concentration of tritium-'free' old groundwater (natural background)

Age dating

Dating methods included tritium (^3H) and chlorofluorocarbons (CFC). For the latter, F11, F12 and F113 were determined. For a detailed description of the CFC method, see, e.g. Busenberg and Plummer (1992). Groundwater below bog histosols was not considered for CFC-dating because CFCs are known to degrade under reducing hydrochemical conditions.

The average vertical flow velocity calculated from CFC measurements is, again, about 1 m/year indicated by the solid line given in Fig. 7. The interglacial clay seems to have no effect on the age distribution. Obviously some 'windows' provide preferred vertical flow paths. With $v_{vertical}$=1 m/year and assuming a porosity of 25% the annual recharge rate should be 250 mm/year, a value that is reasonable for sandy soils of NW Germany. The somewhat lower recharge rates for forested soils are also visible in Fig. 7: residence times at shallow depths are slightly higher. The results from CFC-dating were in good accordance with results from tritium dating (Houben 2001).

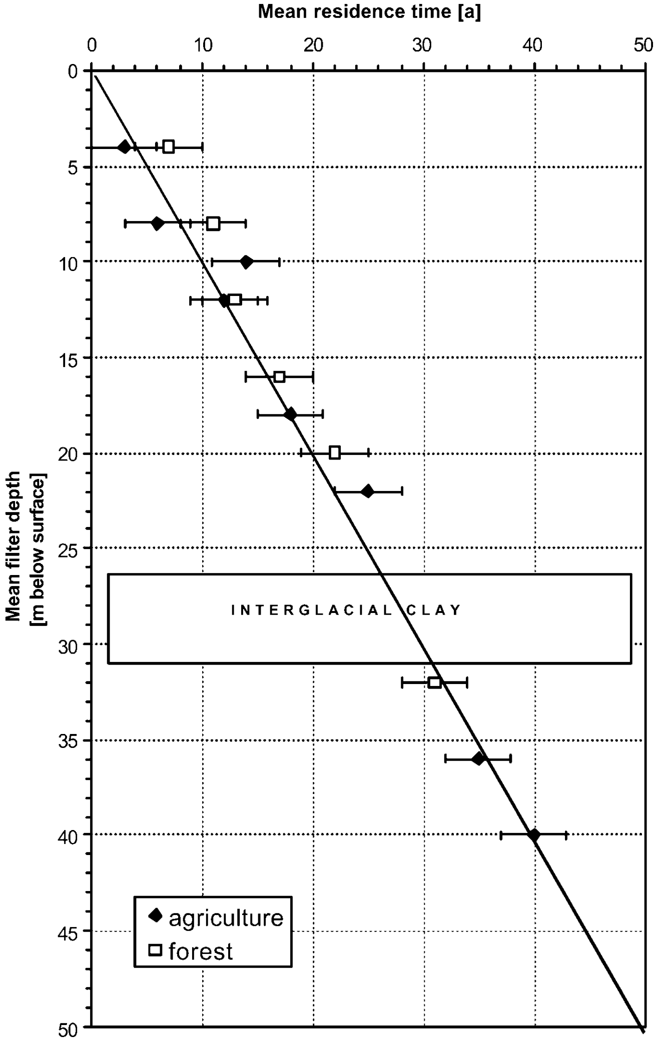

Fig. 7
Groundwater mean residence times (*'age'*) under haplic podzols of the Bourtanger Moor as a measure of vertical flow velocity (based on CFC dating). The *solid line* indicates a vertical flow velocity of 1 m/year

The values of 1 m/year for vertical flow velocity and 250 mm/year for annual recharge only apply to the haplic podzols. Dystric histosols allow only very little groundwater recharge. Residence times of groundwater found underneath are, therefore, much higher. Both chloride and tritium values are subsequently much lower.

Reactive transport

Stoichiometric mass balance calculations

A simple approach of modelling the vertical propagation of reactive contaminants is based on stoichiometric mass balance calculations (e.g. Postma and others 1991). Using the known stoichiometry of the attenuation reaction, the front velocity can be calculated by dividing the annual contaminant input by the amount of available reactive aquifer material. Input is calculated from average concentrations in groundwater (Table 1) and the annual recharge rate. The amount of reactive aquifer material can be determined from mineralogical and geochemical data. Mass balance approaches for nitrate, aluminium and potassium gave front velocities of a few centimetres per year (e.g. Fig. 8, Table 4).

The simplistic model concept allows rapid assessment of a variety of hydrochemical situations, whilst only requiring a spreadsheet computer program. On the other hand, it cannot take into account hydraulic dispersion and can thus only simulate sharp reaction fronts. Effects of pH, temperature, competitive reactions and kinetic inhibitions cannot be included. This limits the practical application especially for cation exchange, which is usually influenced by the interactions of several different cations.

Column experiments and reactive transport modelling

Column experiments were performed to study the reactive spreading of Al^{3+}, K^+ and NO_3^-. Breakthrough curves for the cations Mg^{2+}, Na^+, K^+ and Al^{3+} were successfully

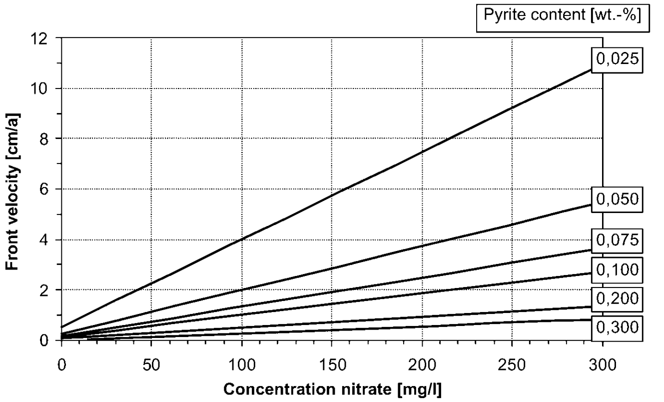

Fig. 8
Stoichiometric mass balance calculations of the vertical propagation velocity of nitrate in groundwater. Note that the offset of the lines at the *y*-axis is caused by pyrite oxidation by dissolved oxygen

Table 4
Model results: time required for a vertical reactive transport of 1 m according to different model approaches. *1* First arrival; *2* exceeds drinking water limits; *3* breakthrough of input concentration

Input		Reactive material		Mass balance	1D transport model		
(mmol/l)		[mmol(eq)/100 g], (wt%)			1	2	3
				(a)		(a)	
Al^{3+}	0.5	CEC	1.00	50	36	37	60
K^+	1.0	CEC	1.00	75	10	30	70
NO_3^-	2.0	FeS_2	0.05	42	32	35	35

modelled using the computer model PHREEQC-2 (Parkhurst and Appelo 1999). The equilibrium constant from PHREEQC-2's database for the sorption of K^+ had to be altered from logK=0.7 to logK=1.4. This is caused by the main bearer of CEC in the actual sediment, illite, which has a fivefold higher affinity for K^+ than the standard exchange site of PHREEQC-2.

Both sorption and desorption experiments were performed. The latter showed that sorbed K^+ and Al^{3+} can be almost completely de-sorbed (Fig. 8) and will thus present a long-term problem even after a potential halt on input. De-sorbed aluminium will extend the acidification of groundwater (Fig. 9).

Average front velocities for aluminium from column experiments are in reasonable accordance to the results from stoichiometric mass balance calculations (Table 4). Deviations are caused by the dispersive spreading of the contaminant front, which cannot be considered in the mass balance approach.

For potassium, there are severe deviations between the mass balance and the reactive transport models (Table 4). They are caused by limitations of the mass balance approach which does not consider the competition of different cations for exchange positions. Potassium has only a medium sorption affinity and competes with other common cations such as Na^+, Mg^{2+} and Ca^{2+}. This problem does not affect Al^{3+} because the sorption affinity for Al^{3+} is among the highest of all cations common in the hydrogeosphere.

Autotrophic denitrification only affected a minor proportion of the nitrate pumped through the columns. The flow velocity in the experiments was higher than in nature, so that most nitrate left the column without reacting to pyrite. The reaction is obviously kinetically controlled. A kinetic model approach was used to successfully simulate the measured results. These results were similar to those from stoichiometric mass balancing (Table 4). The incomplete denitrification in the columns at high flow velocities hides an important implication for the real world: denitrification may not be complete in zones of steep hydraulic gradients and high flow velocities, such as in the vicinity of wells.

Conclusions

In order to realistically evaluate the natural attenuation potential of the Bourtanger Moor area detailed studies of both hydrochemistry and sediment geochemistry were performed. The hydrochemical survey had to include the third (vertical) dimension. This made the delineation of the current depth of the reaction fronts possible. Fresh drill cores were needed to investigate type, amount and distribution of reactive aquifer material. Carefully selected data were incorporated into model approaches. The non-reactive vertical transport velocity of groundwater is about 1 m/year under podzolic soils whereas the vertical reactive propagation velocity of the pollutants considered is in the

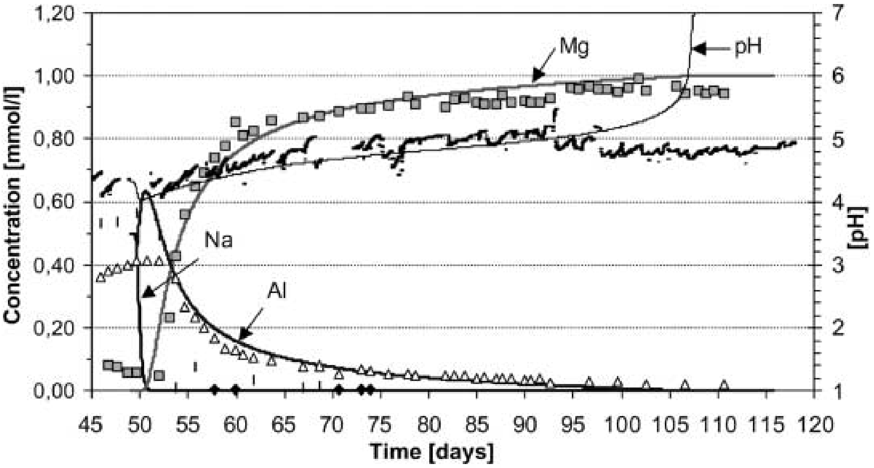

Fig. 9
Measured and modelled breakthrough curves of a column experiment on aluminium desorption (model parameters: column length: 0.25 m; flow rate: 30 ml/h; dispersivity: 0.01 m; input solution: 1.0 mmol/l $MgCl_2$; CEC: 0.33 mmol(eq)/100 g; temperature: 20 °C)

range of a few centimetres per year. Care has to be taken because all models are only approximations of nature:

- Conservative tracers and vertically spaced age dating of groundwater give only a constraint on the maximum velocity of vertical pollutant transport.
- Stoichiometric mass balance models cannot address hydraulic dispersion and fail when competitive or kinetic reactions need to be considered.
- Column experiments and subsequent 1D reactive transport models give the most realistic results, but require a lot of experimental and analytical work as well as computational time.
- The interpretation of models and experiments must take into account the large spatial and temporal variations of pollutant input and reactive aquifer material distribution.

The vertical distance from the present pollutant fronts to the top of the well screens is more than 20 m. With the calculated vertical propagation velocities being in the range of a few centimetres per year there is no immediate danger for the public water supply in the Bourtanger Moor area.

Acknowledgements This work was made possible through the aid of the Trink-und Abwasserverband Bourtanger Moor.

Appendix

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TITLE model on desorption of aluminium in column (PHREEQC-2)
EQUILIBRIUM_PHASES
Gibbsite 0.0
SOLUTION 0   # de-sorbing 1 mmol/l MgCl2 solution
units mol/l
pe 14 O2(g) –0.68
pH 7 charge
Mg 0.0010
Cl 0.0020
SOLUTION 1–25   # Al(NO3)3 solution inside column before de-sorption
pH 7 charge
pe 14 O2(g) –0.68
Na 0.0005
Al 0.0004
N(5) 0.0017 as NO3
END
EXCHANGE 1–25   # cation exchange capacity
X 0.021
–equil 1
SELECTED_OUTPUT
-file Al1_3.prn
USER_PUNCH
-headings Tage Na Al Mg Cl N(5)
10 punch total_time/(24*3600*100000)
20 punch tot(“Na”)/100, tot(“Al”)/100, tot(“Mg”)/100, tot(“Cl”)/100, tot(“N(5)”)/100
TRANSPORT   # defines parameters for 1D-transport model
–cells 25   # number of cells
–lengths 0.01   # length of individual cells [m]
–shifts 2000   # number of transport steps
–time 2880   # duration of time step (sec) (≅ 30 ml/h)
–flow_direction forward
–boundary_conditions flux   # boundary conditions
–dispersivities 0.010   # dispersivity [m]
–correct_disp true
–punch 25   # only outflow at end of column is considered (cell 25)
–punch_frequency 1
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References

Appelo CAJ, Postma D (1996) Geochemistry, groundwater and pollution. Balkema, Rotterdam

Böttcher J, Strebel O, Voerkelius S, Schmidt H-L (1990) Using isotope fractionation of nitrate–nitrogen and nitrate–oxygen for evaluation of microbial denitrification in a sandy aquifer. J Hydrol 114:413–425

Busenberg E, Plummer LN (1992) Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: the alluvium and terrace system of central Oklahoma. Water Resour Res 28(9):2257–2283

Edmunds WM, Kinniburgh DG (1986) The susceptibility of UK groundwaters to acidic deposition. J Geol Soc 143:707–720

Engesgaard P, Kipp KL (1992) A geochemical transport model for redox-controlled movement of mineral fronts in ground water flow systems: a case of nitrate removal by oxidation of pyrite. Water Resour Res 28(10):2829–2843

Frind E, Duynisveld WHM, Strebel O, Boettcher J (1990) Modeling of multicomponent transport with microbial transformation in groundwater: the Fuhrberg case. Water Resour Res 26(8):1707–1719

Houben G (2000) Modellansätze zur Prognose der langfristigen Entwicklung der Grundwasserqualität – Fallbeispiel Bourtanger Moor (Model approaches for predicting the long-term development of groundwater quality – the Bourtanger Moor case). Aachener Geowissenschaftl. Beiträge 36, Aachen

Houben G (2001) Natural attenuation of common agricultural and atmospherical pollutants: reactive transport of nitrate, potassium and aluminium in sandy sediments of northwestern Germany. Proc 3rd Int Conf Groundwater Quality 2001, Sheffield

Kölle W (1982) Auswirkungen der Nitratbelastung in einem reduzierendem Grundwasserleiter (effects of nitrate pollution in a reducing aquifer). DVGW-Schriften 31:109–126

Obermann P (1982) Hydrochemische/hydromechanische Untersuchungen zum Stoffhaushalt von Grundwasser bei landwirtschaftlicher Nutzung (hydrochemical/hydromechanical investigations of the chemical balance of groundwater in agricultural areas). Besondere Mitteilungen zum deutschen gewässerkundlichen Jahrbuch 42, Düsseldorf

Parkhurst D, Appelo CAJ (1999) User’s guide to PHREEQC (version 2) – a computer program for speciation, reaction path, 1D-transport and inverse geochemical calculations. USGS, Lakewood

Pauwels H, Kloppmann W, Foucher JC, Martelat A, Fritsche V (1998) Field tracer test for denitrification in a pyrite-bearing schist. Appl Geochem 13:767–778

Pleysier JL, Juo ASR (1980) A single-extraction method using silver–thiourea for measuring exchangeable cations and effective CEC in soils with variable charges. Soil Sci 129(4):205–211

Postma D (1990) Kinetics of nitrate reduction by detrital Fe(II)-silicates. Geochim Cosmochim Acta 54:903–908

Postma D, Boesen C, Kristiansen H, Larsen F (1991) Nitrate reduction in an unconfined aquifer: water chemistry, reduction processes and geochemical modeling. Water Resour Res 278:2027–2045

van Beek CGEM, Hettinga FAM, Straatman R (1989) The effect of manure spreading and acid deposition upon groundwater quality at Vierlingsbeek, the Netherlands. IAHS Publ 185:155–162

Wilson MJ (1986) Mineral weathering processes in podzolic soils on granitic materials and their implications for surface water acidification. J Geol Soc 143:669–697