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FACTORS AFFECTING DENITRIFICATION DURING INFILTRATION OF RIVER WATER INTO A SAND AND GRAVEL AQUIFER IN SAXONY, GERMANY

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Abstract—River infiltration into a sand and gravel aquifer was investigated to assess the importance of denitrification in maintaining low-NO_3^- groundwater supplies. Samples from the River Elbe and groundwater sampling points along a section of the aquifer were analysed for dissolved organic carbon, major ions and the $^{15}N/^{14}N$ isotopic ratio of dissolved NO_3^-. Input of NO_3^- to the aquifer is influenced by seasonal, temperature-dependent denitrification in the river bed sediments. Along an upper flowpath in the aquifer from the River Elbe to a sampling point at a distance of 55 m, the median NO_3^- concentration decreased by 4.8 mg litre^{-1} and the $\delta^{15}N$ composition increased by +9.0‰, consistent with denitrification. Similar isotopic enrichment was demonstrated in a laboratory column experiment with a reduction in NO_3^- of 10.5 mg litre^{-1} for an increase in $\delta^{15}N$ of +9.8‰, yielding an isotopic enrichment factor of −14.6‰. A mass balance for denitrification shows that oxidizable organic carbon required for denitrification is derived from both the infiltrating river water and solid organic matter fixed in the river bed sediments and aquifer material. © 1998 Elsevier Science Ltd. All rights reserved

Key words—River Elbe, river infiltration, nitrogen isotopes, denitrification, nitrate pollution

NOMENCLATURE

C = concentration at time t (mg litre^{-1})
C_0 = concentration at time $t = 0$ (mg litre^{-1})
DOC = dissolved organic carbon
DOM = dissolved organic matter
i.d. = inner diameter
K = hydraulic conductivity (m s^{-1})
n = number of samples
R_{spl} = $^{15}N/^{14}N$ ratio of the sample
R_{std} = $^{15}N/^{14}N$ ratio of air
SP = sampling point
SOC = solid organic carbon
$\delta^{15}N$ = $^{15}N/^{14}N$ isotopic ratio of dissolved NO_3^- at time t (‰)
$\delta^{15}N_0$ = $^{15}N/^{14}N$ isotopic ratio of dissolved NO_3^- at time $t = 0$
$\delta^{34}S$ = $^{34}S/^{32}S$ isotopic ratio of dissolved SO_4^{2-}
ϵ = isotope enrichment factor

INTRODUCTION

The rivers Danube, Elbe and Rhine sustain important supplies of raw water from river bank infiltration schemes. In Saxony, a region in eastern Germany, 18% of raw water production is based on river-bank infiltration, and waterworks along the River Elbe supply 1.5 million people. Given this dependence, the geological material comprising the zone of infiltration is of importance in the removal of river-borne pollutants. The River Elbe is polluted by industrial and municipal wastewater as well as diffuse inputs from superficial runoff. However, since 1990 an improvement in water quality has occurred with the decline in industry following German reunification (Grischek *et al.*, 1995). In the 1970 s and 1980 s the dissolved organic carbon (DOC) concentration of the River Elbe exceeded 8 mg litre^{-1} with maximum values of up to 20 mg litre^{-1} due to wastewater input. The closure of paper mills in Saxony has greatly reduced the load of organic compounds such as lignin-sulphonic acids and chlorinated hydrocarbons.

To sustain pumped raw water quality, processes in the zone of river-water infiltration must be understood and their long-term potential evaluated. In general, long flowpaths and travel times between infiltrating river water and production boreholes have a beneficial effect on the elimination of NO_3^- and organic compounds, although anoxic groundwater conditions can have an undesirable effect (for example, dissolution of manganese and iron oxides, and ammonification). In the context of achieving low NO_3^- concentrations in drinking water, denitrification is considered a key process.

A highly productive river-bank infiltration scheme is found on the River Elbe near Torgau in Saxony (Fig. 1). The capacity of the Torgau aquifer amounts to 3.2×10^5 m^{3}d^{-1}. In 1991 a research pro-

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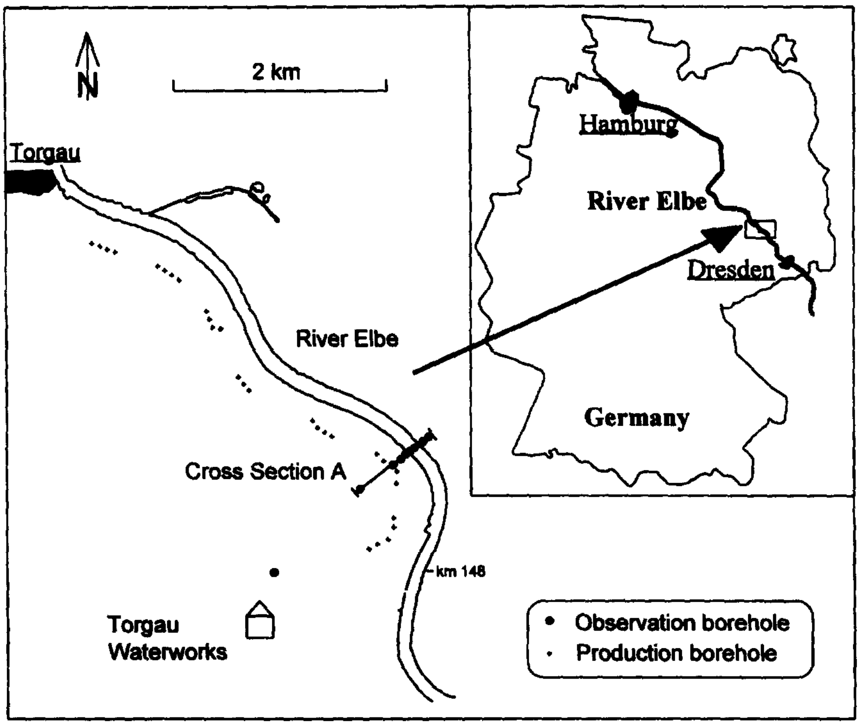

Fig. 1. Location of the study area in the River Elbe basin near Torgau. Details of cross-section A are shown in Fig. 2.

gramme was initiated to investigate the hydrogeology of the Torgau aquifer, focussing on groundwater flow behaviour, mixing processes and transport of dissolved constituents. This paper presents the results of field monitoring between 1993 and 1996 along a section of the Torgau aquifer, together with the results of a laboratory column experiment. This work aimed to investigate denitrification within the river bed sediments and aquifer material. Application of the technique of nitrogen isotope tracing was additionally incorporated with the objective of identifying sources of NO_3^- and to provide further evidence of denitrification.

^{15}N isotope tracing and denitrification

Sources of NO_3^- in natural waters may be identified by comparison of the nitrogen isotope ratio of dissolved NO_3^- with that of potential sources (Heaton, 1986; Kaplan and Magaritz, 1986; Wilson *et al.*, 1994). Sources of NO_3^- and their typical range of $\delta^{15}N$ composition, include the following: nitrified soil organic nitrogen (+4 to +9 ‰); nitrogenous fertilizers (–4 to +4 ‰); and animal and sewage wastes (> +10 ‰). These ranges incorporate the majority of values associated with each source, although site-specific conditions may cause the ranges to overlap. Also, isotopic fractionation by denitrification can alter the original isotope ratios, typically resulting in a depletion of the heavier isotope in the reaction products, and an enrichment in the residual NO_3^-.

Denitrification is observed to proceed at reduced O_2 levels via a number of microbially mediated steps, the end product of which is normally N_2 (Korom, 1992). The denitrification process has often been treated as a single-step, unidirectional reaction so that changes in the isotopic composition of NO_3^- can be modelled using a Rayleigh fractionation model (Mariotti *et al.*, 1988; Fustec *et al.*, 1991). Under favourable hydrochemical conditions, the isotopic enrichment of NO_3^- with a decreasing NO_3^- concentration can be predicted by the classical Rayleigh equation, as follows:

$$\delta^{15}N = \delta^{15}N_0 + \epsilon \ln(C/C_0) \qquad (1)$$

where $\delta^{15}N$ represents the isotopic composition of reactive NO_3^- at time t, with concentration, C; and $\delta^{15}N_0$ represents the isotopic composition of unreacted NO_3^- at time $t = 0$, with concentration C_0. Different values for the isotope enrichment factor (ϵ) result, depending on specific site conditions such as substrate composition, concentration and microbial availability of the electron donor, temperature, denitrification rate, type of bacterium involved and growth conditions (Böttcher *et al.*, 1990).

SITE HYDROGEOLOGY

The site near Torgau, 247 km from the source of the River Elbe, is situated within a large basin which is 4 km wide and 9 km long. The basin is

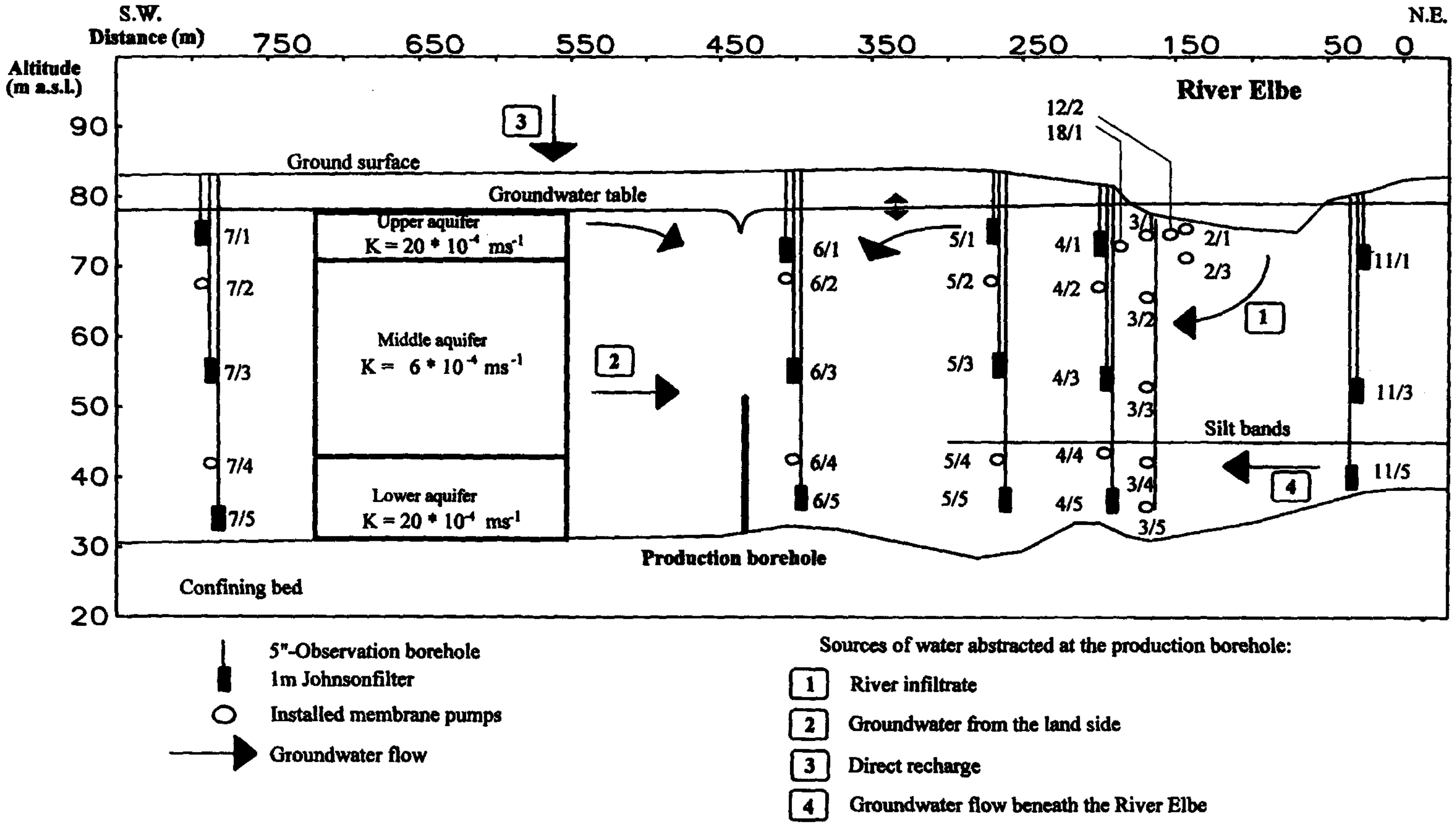

Fig. 2. Cross-section A (for line of section, see Fig. 1) showing the general hydrogeological situation and position of sampling points. K is hydraulic conductivity.

filled with Pleistocene deposits to a depth of 10–55 m that comprise interfingered glaciofluviatile sediments ranging from fine sand and silt to medium sand and gravel. The deposits are overlain by Holocene river gravels (5–8 m thick) and meadow loam (2 m thick). The Torgau aquifer can be described as a three-layer system. The middle layer is formed by medium sand with a hydraulic conductivity of about 6×10^{-4} m s^{-1}. The upper and lower layers are formed by coarse sand to gravel, with a hydraulic conductivity of about 2×10^{-3} m s^{-1}. Along the line of cross-section A (Fig. 2), silt bands, less than 0.5 m thick, form an almost continuous boundary between the middle and the lower aquifer layers and promote leaky aquifer conditions (Grischek *et al.*, 1995; Nestler *et al.*, 1996).

The contribution of the upper aquifer layer to groundwater flow depends on the water level in the River Elbe, which is in direct hydraulic contact with the aquifer. Groundwater abstraction from adjacent boreholes has induced river-bank infiltration and reversed natural flow conditions within the aquifer.

The mean discharge of the River Elbe at Torgau is 340 m^3 s^{-1}. Land use in the 200-m-wide strip of land between the river and the production borehole is predominantly grassland, temporarily used for sheep pasture. Land use in the remaining catchment area is dominated by arable agriculture.

METHODOLOGY

Groundwater sampling

For this study, groundwater samples were taken from cross-section A (Fig. 2) at an interval of 2 weeks. Groundwater was either obtained using *in situ* membrane pumps or using a mobile submersible pump lowered into 125 mm diameter observation boreholes. Membrane pumps were also used to sample from directly below the bed of the River Elbe (Nestler *et al.*, 1993). Samples were collected in polyethylene bottles prior to immediate analysis of NO_3^-. Water samples for analysis of $\delta^{15}N$ composition were taken from the River Elbe and groundwater sampling points on various occasions in April, June and November 1995. All samples were stored in polyethylene bottles, with 0.01 M $HgCl_2$ added to inhibit biological degradation of the samples prior to analysis.

Analytical methods

In the field, well-head measurements included temperature, pH, alkalinity and O_2. In the laboratory, analyses included DOC, major ions, Fe^{2+}, Mn^{2+}, NH_4^+, NO_3^- and NO_2^-. In general, analyses were carried out according to German guidelines and DIN methods. Prior to analysis, water samples were filtered through a 0.45-μm cellulose-acetate filter. NO_3^- was determined using an ion chromatograph (model 690, Metrohm GmbH, Herisau, Switzerland) with a SC-04 Hamilton PRP-X100 column (Hamilton GB Ltd, Carnforth, U.K.), giving an estimated detection limit of 0.2 mg litre^{-1}. Samples for DOC analysis were preserved by adding concentrated H_2PO_4 to pH < 2, stored at 4°C, and analysed with a Dohrmann Carbon Analyser (model DC190, Rosemount GmbH, Hanau, Germany).

Preparation of samples for analysis of $\delta^{15}N$ of dissolved NO_3^- followed the method of Feast and Dennis (1996). A distillation procedure was used to convert dissolved NO_3^- into $(NH_4)_2SO_4$, followed by combustion to produce N_2. Once purified, the $\delta^{15}N$ of the N_2 produced was measured on a VG Isogas Sira II isotope-ratio mass spectrometer (Micromass, Manchester, UK). The method is reliable and yields a precision better than ± 0.2 ‰, with compositions measured and reported relative to purified air according to the accepted isotope terminology: $\delta^{15}N = (R_{spl}/R_{std}) - 1)1000$, where $R_{spl} = {}^{15}N/{}^{14}N$ ratio of the sample and $R_{std} = {}^{15}N/{}^{14}N$ ratio of air. Results are given in deviations of parts per thousand (‰).

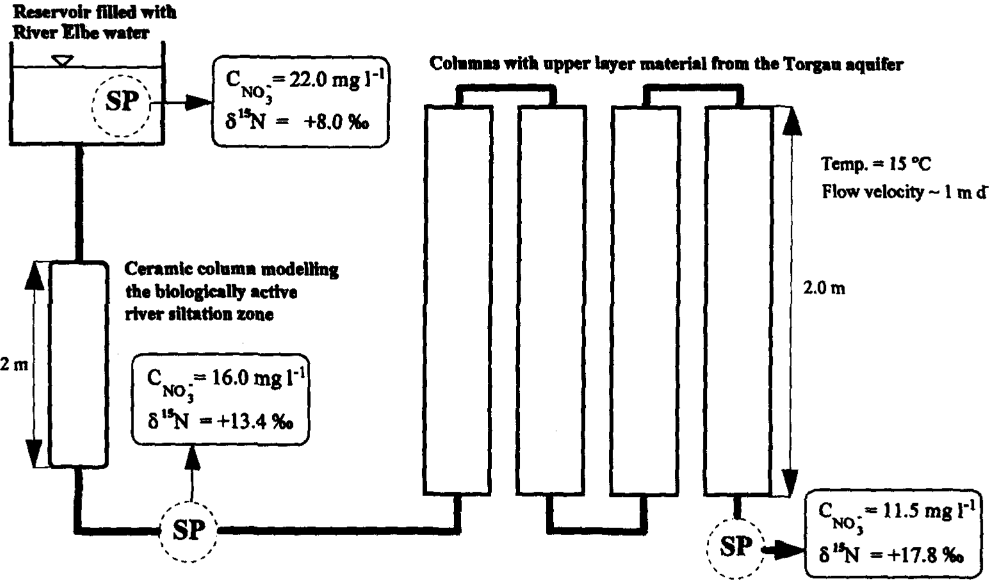

Fig. 3. Set-up of laboratory column experiment to investigate denitrification in river-bed sediments from the River Elbe and material from the upper layer of the Torgau aquifer. Concentration of NO_3^- ($C_{NO_3^-}$) and nitrogen isotopic composition ($\delta^{15}N$) of dissolved NO_3^- for three sampling points (SP) are shown at 10 days after the start of the experiment.

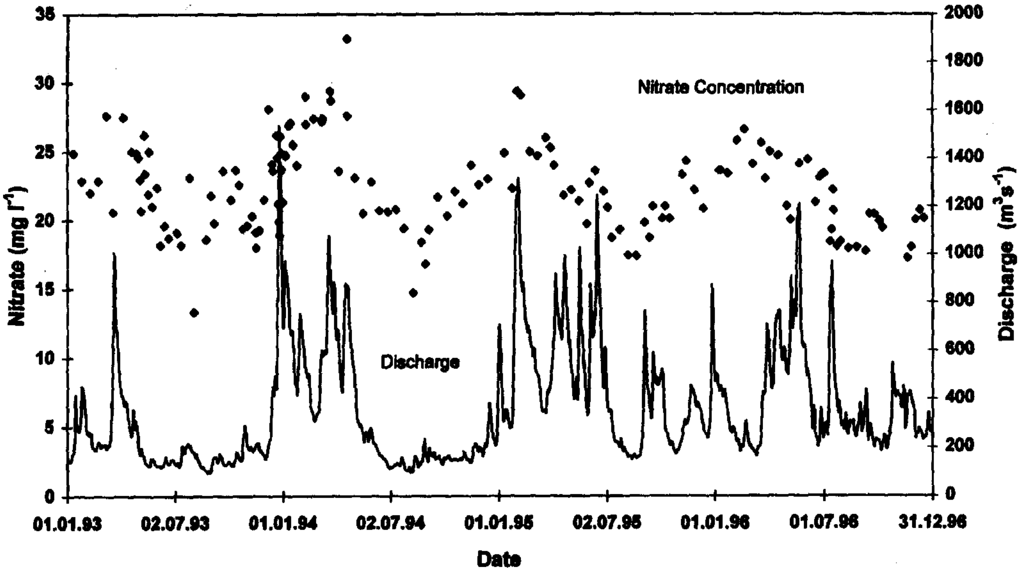

Fig. 4. Record of discharge (Torgau station) and NO_3^- concentration of the River Elbe (Jan. 1993 to Dec. 1996).

Laboratory column experiment

A laboratory column experiment was designed to model river-bank infiltration processes (Fig. 3). Four columns, 2 m in length (i.d. = 74 mm), were filled with cored material from the upper layer of the aquifer at the Torgau site, and sieved to a less than 1 mm size-fraction. The columns were coupled with a ceramic column, 0.42 m in length (i.d. = 87 mm), filled with material from the bed of the River Elbe. Prior to the start of the experiment, the ceramic column was rinsed continuously for 4 months with water from the River Elbe (at a flow velocity of about 1 m d^{-1}) to allow natural infiltration conditions to become established. Following conditioning, the column experiment was conducted at a controlled temperature of 15°C with samples taken every 2 weeks from the three sampling points shown in Fig. 3 and analysed for the determinands described above.

RESULTS

River Elbe water quality

Input of NO_3^- to the River Elbe is from both agricultural fertilizers and wastewater discharges. Between January 1993 and December 1996, the median NO_3^- concentration was 22.2 mg litre^{-1} ($n = 150$). Figure 4 shows the temporal variation in NO_3^- during this 4-year period, with maximum and minimum values occurring in winter and summer, respectively. The NO_3^- concentration depends more on seasonal biological uptake of nitrogen by plants than on the river discharge. In 1995 the median temperature of the river water was 13.6°C, ranging

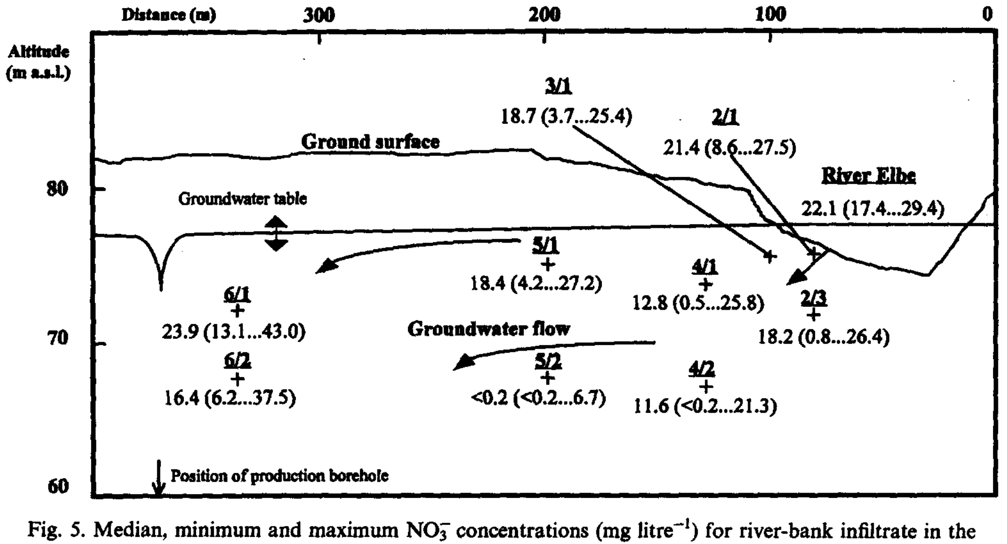

Fig. 5. Median, minimum and maximum NO_3^- concentrations (mg litre^{-1}) for river-bank infiltrate in the upper layer of the Torgau aquifer (Jan.–Dec. 1995). The minimum and maximum NO_3^- values are shown within parentheses.

from –0.5 to 24.1°C ($n = 28$). The median O_2 concentration was 10.2 mg $litre^{-1}$ ($n = 28$); and the pH of the river water ranged from 7.0 to 8.5, with higher values in summer.

River bank infiltrate quality

Figure 5 and Table 1 give the median NO_3^- concentrations along cross-section A for the sampling period January to December 1995. The data given in Fig. 5 are for sampling depths 1 and 2 covering a distance of 300 m from the river. This region of the aquifer represents infiltrated river water that does not mix with groundwater from other sources (Grischek *et al.*, 1995). However, sampling points 5/1, 6/1 and 6/2 were temporarily influenced by a local NO_3^- source in 1995, thought to be contributed by recharge from the soil surface in an area of former sheep pasture and manure application. This source is of minor significance compared with the quantity of water induced by river-bank infiltration. Groundwater at sampling depth 1, near the groundwater table, has O_2 and NO_3^- concentrations dependent on water level, and can be influenced by additional $NO3_3^-$ recharge from the soil surface. High NO_3^- concentrations are detected some weeks after high water level (following flooding in the river) when the normally 6 m-thick unsaturated zone is flushed-out.

The infiltrating river water experiences O_2 consumption within the first decimetres of the river-bed sediments through the processes of nitrification and decay of organic matter, although data from sampling point (SP) 2/1 show that denitrification can begin in the river bed during the summer months (see Fig. 6). This seasonal reduction of NO_3^- over a short distance can be significant, but at other times the NO_3^- concentration in the river bed is higher than in the river water. The sustained low NO_3^- concentrations measured in SP 2/1 between July and November 1994 are the result of the slow exfiltration of groundwater to the River Elbe during a period of interrupted abstraction from the production borehole. Since November 1994, the pumping rate of the production borehole has increased by two-thirds, decreasing the residence time of river infiltrate in the aquifer. The effect of this change at SP 2/1 together with the high water level of the river has been to maintain NO_3^- concentrations above zero in the following summer 1995. From September to November 1996 water abstraction was stopped, resulting in low NO_3^- concentrations at SP 2/1 due to low groundwater flow and exfiltration.

The middle and lower aquifer layers, represented by sampling depths 3, 4 and 5, show very low NO_3^- concentrations. Old water present in the lower layer, beneath the silt bands, and which flows to the production borehole, has no NO_3^- and a low DOC concentration. In the middle layer the infiltrating water is mixed with groundwater flowing from the east, beneath the River Elbe, and has an elevated Cl^- concentration (Table 1).

$\delta^{15}N$ composition of river-bank infiltrate

During the three periods of sampling in 1995, the $\delta^{15}N$ composition of dissolved NO_3^- in river water ranged between +7 and +13‰ (median value

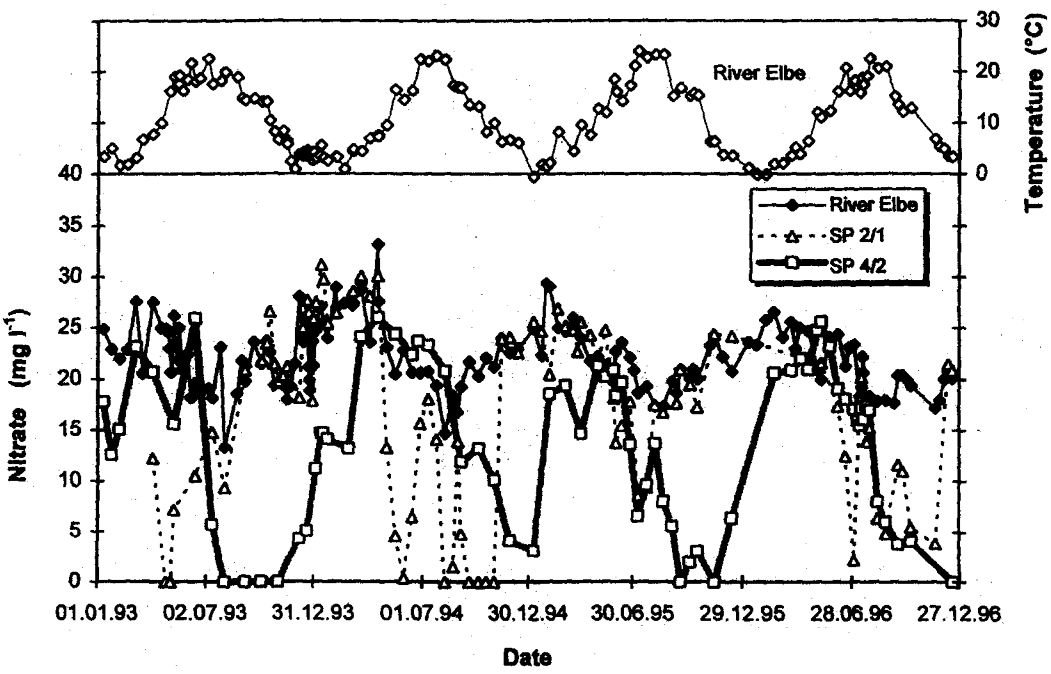

Fig. 6. Temperature and NO_3^- concentration of River Elbe water, and NO_3^- concentration at sampling points (SP) 2/1 and 4/2 in the upper layer of the Torgau aquifer (Jan. 1993 to Dec. 1996).

Table 1. Median, minimum and maximum concentrations of selected field and laboratory analyses for the River Elbe and the upper and middle layers of the Torgau aquifer in 1995[a]

Sampling point	n	NO_3^- (mg litre^{-1})	NH_4^+ (mg litre^{-1})	NO_2^- (mg litre^{-1})	O_2 (mg litre^{-1})	DOC[b] (mg litre^{-1})	pH	Alkalinity (meq litre^{-1})	SO_4^{2-} (mg litre^{-1})	Fe^{2+} (mg litre^{-1})	Mn^{2+} (mg litre^{-1})	Cl^- (mg litre^{-1})
Elbe	31	22.1 (17.4...29.4)	0.40 (0.09...0.6)	0.19 (0.04...0.36)	10.2 (7.5...12.4)	5.3[c] (4.4...8.7)[c]	7.35 (6.95...8.54)	1.50 (1.10...1.93)	84.2 (76.6...108)	0.08 (0.04...0.2)	0.11 (0.02...0.33)	25.6 (21.0...37.2)
2/1	25	21.4 (8.6...27.5)	0.10 (0.03...0.2)	0.09 (0.00...0.65)	0.6 (0.0...5.8)	4.2 (3.3...4.9)	6.93 (6.68...7.44)	1.46 (1.09...1.96)	84.7 (76.6...107)	0.0 (0.0...0.52)	0.0 (0.0...0.25)	25.2 (20.4...35.3)
2/3	25	18.2 (0.8...25.3)	0.10 (0.04...0.3)	0.09 (0.00...0.44)	— —	4.0 (3.5...4.5)	7.01 (6.68...7.30)	1.36 (1.16...1.71)	89.0 (77.7...105)	0.06 (0.0...0.4)	0.05 (0.0...0.17)	23.8 (20.0...38.9)
3/1	8	18.0 (3.7...25.4)	0.09 (0.05...0.12)	0.08 (0.00...0.38)	— —	4.5 (3.7...4.9)	6.89 (6.24...7.07)	1.44 (1.37...1.69)	87.2 (75.4...101)	0.04 (0.02...0.08)	0.05 (0.0...0.08)	26.7 (20.3...35.4)
3/3	16	<0.2 (<0.2...6.0)	0.30 (0.18...0.4)	0.01 (0.00...0.01)	0.0 (0.0...0.8)	2.7 (1.8...3.4)	6.83 (6.67...7.21)	1.59 (1.29...1.75)	115.0 (101...273)	1.70 (1.4...3.4)	0.11 (0.07...0.18)	31.0 (26.5...58.4)
4/1	20	12.8 (0.5...25.8)	0.10 (0.05...0.19)	0.04 (0.00...0.63)	0.2 (0.0...10.0)	4.0 (3.4...4.9)	6.71 (6.28...7.11)	1.52 (1.15...1.90)	82.7 (76.3...125)	0.0 (0.0...0.04)	0.0 (0.0...0.03)	24.3 (18.3...36.0)
4/2	20	11.6 (<0.2...21.3)	0.07 (0.05...0.2)	0.05 (0.00...0.41)	— —	3.3 (3.0...4.2)	6.95 (6.49...7.37)	1.50 (1.20...1.73)	92.2 (80.3...120)	0.0 (0.0...0.12)	0.12 (0.07...0.20)	25.0 (21.3...39.3)
4/3	12	<0.2 (<0.2...1.1)	0.30 (0.08...0.4)	0.00 —	0.0 0.0...0.3)	2.9 (2.4...3.2)	6.74 (6.61...6.92)	1.38 (1.23...1.50)	115.0 (105...202)	5.30 (4.0...8.0)	0.47 (0.28...0.68)	29.9 (26.3...45.3)
5/1	20	18.4 (4.2...27.2)	0.06 (0.03...0.12)	0.00 (0.00...0.01)	4.3 (1.2...8.4)	2.8 (2.5...3.4)	6.58 (6.08...6.96)	1.55 (1.16...1.75)	90.0 (77.3...120)	0.0 (0.0...0.04)	0.0 (0.0...0.09)	23.5 (18.1...33.9)
5/2	19	<0.2 (<0.2...6.7)	0.07 (0.04...0.11)	0.00 (0.00...0.17)	0.6 (0.0...1.3)	2.9 (2.8...3.2)	7.13 (6.08...7.56)	1.65 (1.40...1.85)	105.0 (88.6...118)	0.08 (0.0...0.44)	0.02 (0.0...0.11)	27.6 (20.8...34.8)
5/3	12	<0.2 (<0.2...0.7)	0.30 (0.2...0.5)	0.00 (0.00...0.01)	0.0 (0.0...0.2)	2.9 (2.5...3.1)	6.69 (6.46...7.00)	1.14 (1.05...1.39)	116.0 (106...145)	11.2 (8.0...13.6)	0.75 (0.57...0.94)	31.7 (26.4...36.2)
6/1	19	23.9 (13.1...43.0)	0.06 (0.03...0.15)	0.00 (0.00...0.01)	1.9 (0.0...4.0)	2.5 (2.3...3.1)	6.66 (6.11...6.80)	1.41 (1.25...1.68)	95.8 (83.0...109)	0.0 (0.0...0.24)	0.0 (0.0...0.09)	26.2 (23.0...35.1)
6/2	20	16.4 (6.2...37.5)	0.06 (0.03...0.3)	0.01 (0.00...0.05)	0.5 (0.0...1.2)	2.4 (2.2...2.7)	6.72 (6.10...6.86)	1.39 (1.28...1.61)	103.5 (87.7...136)	0.0 (0.0...0.02)	0.07 (0.02...0.18)	26.8 (22.8...38.4)
6/3	14	<0.2 (<0.2...0.8)	0.07 (0.05...0.13)	0.00 (0.00...0.01)	0.0 (0.0...0.3)	2.8 (2.3...3.1)	6.86 (6.43...7.03)	1.62 (1.38...1.62)	108.0 (92.8...121)	0.15 (0.08...0.32)	0.07 (0.02...0.11)	26.2 (19.6...32.3)
Borehole	17	3.1 (0.4...6.2)	0.30 (0.08...0.5)	0.00 —	0.2 (0.0...0.5)	2.2 (2.1...2.3)	6.52 (6.03...6.75)	1.88 (0.85...1.27)	165.0 (142...189)	13.0 (11.0...16.4)	0.69 (0.57...0.85)	35.0 (31.2...37.4)

[a] Data within parentheses represent the minimum and maximum of measured parameters.
[b] DOC is dissolved organic carbon.
[c] n = 240.

Table 2. Median, minimum and maximum concentrations of NO_3^- and $\delta^{15}N$ compositions in the River Elbe and upper layer of the Torgau aquifer for various times in 1995

		NO_3^- concentration			$\delta^{15}N$ composition		
Sampling point (see Fig. 2)	n	min (mg litre^{-1})	max (mg litre^{-1})	median (mg litre^{-1})	min (‰)	max (‰)	median (‰)
Elbe	6	17.4	24.0	23.2	7.1	13.1	8.6
2/1	6	13.8	24.4	17.3	10.3	15.6	12.4
2/3	2	17.7	18.3	18.0	11.9	17.0	14.4
4/1	3	13.0	21.9	17.1	8.8	14.7	10.7
4/2	3	13.6	19.7	18.4	13.3	24.3	17.6
12/2	1	—	—	27.3	—	—	7.4
18/1	1	—	—	5.3	—	—	25.6

+ 8.6‰), with a NO_3^- concentration between 17.4 and 24.0 mg litre^{-1} (median value 23.2 mg litre^{-1}) (Table 2). The $\delta^{15}N$ composition of river-bank infiltrate demonstrated an enrichment with distance from the river, while the NO_3^- concentration showed an apparent decrease (compare median values for River Elbe water—$NO_3^- = 23.2$ mg litre^{-1} and $\delta^{15}N$ = + 8.6‰—with SP 4/2—$NO_3^- = 18.4$ mg litre^{-1} and $\delta^{15}N$ = + 17.6‰). A single, relatively depleted $\delta^{15}N$ value of + 9.4‰, and lowered NO_3^- concentration of 1.4 mg litre^{-1}, for SP 3/3 in the middle aquifer layer is the result of mixing of the infiltrating water with groundwater from the opposite side of the river. Sampling point 18/1 is situated in a local low-flow region of the aquifer and shows lower nitrate concentrations and a higher $\delta^{15}N$ value. Sampling point 4/1 is fed from overlying layers with higher conductivity and reacts much faster to changes in river water-quality than SP 18/1.

Changes in the water quality of the River Elbe influence the chemical composition of groundwater at the observation boreholes. The measured NO_3^- and $\delta^{15}N$ values vary considerably at different sampling dates at each of the sampling points listed in Table 2 (a range of 10.6 mg litre^{-1} for NO_3^- is observed at SP 2/1, and a range of + 11‰ is observed for $\delta^{15}N$ at SP 4/2). The NO_3^- data shown in Table 1 for the whole of 1995 show a wider range of concentrations than for the sub-set of values corresponding to the times of $\delta^{15}N$ measurements. It is likely, therefore, that the compositional range of $\delta^{15}N$ would also be greater, although the relative trend of $\delta^{15}N$ enrichment with distance from the river is not thought to change.

Laboratory column experiment

Figure 3 shows the NO_3^- concentration and $\delta^{15}N$ composition of dissolved NO_3^- 10 days after the start of the experiment for samples of river water in the supply reservoir, and at the outlets from the column containing river-bed material and the four columns containing aquifer material. The NO_3^- concentration of river water decreased from 22.0 to 11.5 mg litre^{-1} between the supply reservoir and the outlet from the fourth packed column, while the $\delta^{15}N$ composition increased from + 8.0‰ to + 17.8‰. The DOC concentration of the River Elbe water decreased by 0.2 mg litre^{-1} within the ceramic column and by a further 0.4 mg litre^{-1} along the 8 m flowpath of the four packed columns, consistent with a denitrification reaction. The O_2 concentration reduced to < 0.5 mg litre^{-1} at the outlet from the ceramic column. The NH_4^+ concentration was 0.08 mg litre^{-1} following the ceramic column and < 0.02 mg litre^{-1} at the outlet from the fourth packed column. No changes in Cl^- and SO_4^{2-} concentrations were detected along the entire flowpath of the columns.

A cross-plot of $\delta^{15}N$ against $\ln(NO_3^-)$ for the three column experiment samples (see Fig. 7) shows that the observed denitrification conforms to the Rayleigh equation (equation 1, with an isotope enrichment factor (ϵ) of −14.6‰. Neglecting NH_4^+, the calculated denitrification rates for water flowing

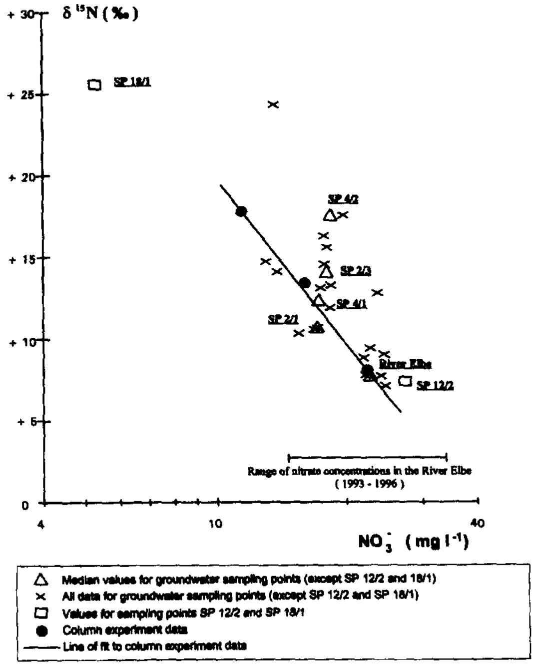

Fig. 7. Cross-plot of the results of $\delta^{15}N$ composition of dissolved NO_3^- versus NO_3^- concentration of samples from the laboratory column experiment and groundwater samples from the upper layer of the Torgau aquifer. Data are for various times in 1995. The isotopic enrichment factor, ϵ (equation 1), for the line of fit to the column experiment data is −14.6‰.

through the river-bed sediments and aquifer material contained in the columns are 3.2 and 0.1 mg-N litre^{-1}d^{-1}, respectively.

DISCUSSION

At Torgau, the absence of high NO_3^- concentrations in the River Elbe during periods of low discharge suggests that sources of NO_3^- from direct discharges of wastewater are of minor influence, and that the main source is from diffuse runoff. The river water has a median $\delta^{15}N$ composition of +8.6‰, towards the upper end of the range of values associated with nitrified soil organic nitrogen. Seasonal variations in NO_3^- concentration are similar to those observed in the River Ythan (MacDonald *et al.*, 1995). Lower NO_3^- concentrations are observed in river water during the late summer months when NO_3^- is accumulated, compared to the late autumn and winter when NO_3^- is lost from the soil.

For groundwater samples, the NO_3^- concentration of the river infiltrate depends strongly on the temperature in the River Elbe. During summer months, denitrification reduces the NO_3^- concentration to zero in the river bed (see SP 2/1, Fig. 6). In comparison, SP 4/2 shows a lagged response to this decrease in NO_3^-. The travel time between these two points (separated by 55 m and estimated from inspection of Cl^- concentration peaks and hydraulic calculations) is between 50 and 80 days depending on river-water level. In winter months, sampling points 2/1 and 2/3, when compared with river water, have temporarily increased NO_3^- concentrations by up to 4 mg litre^{-1}. This increase coincides with a decrease in NH_4^+ concentration by up to 0.5 mg litre^{-1} in the infiltrating water and is a result of nitrification within the first decimetres of infiltration. Otherwise, the low NH_4^+ concentration in the region near the river bed is relatively stable throughout the year as a result of oxidizing conditions maintained in the River Elbe.

Major chemical changes in the river infiltration zone can be modelled using mass-balance calculations as long as chemical conditions are assumed to be at steady-state, i.e. invariant over the time interval of a given time series. This assumption is contradicted by processes such as diurnal photosynthetic activity that alter the chemical characteristics of river water, and seasonal cycles of flooding and low flow that influence the physical and chemical characteristics at the river–aquifer interface. To overcome these difficulties, median values for NO_3^-, NH_4^+, O_2 and DOC concentrations for 1995 data given in Table 1 are discussed here in relation to the flowpath from the River Elbe to sampling points 2/1–4/2 in the upper aquifer layer. If it is assumed that the decrease in NO_3^-, O_2 and DOC in the zone of infiltration is due to microbially mediated degradation of dissolved organic matter (DOM), then a mass-balance calculation can be undertaken using the simplified equations given by Von Gunten *et al.* (1991): Oxygen respiration:

$$\mathrm{DOM} + 138O_2 \rightarrow 106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \qquad (2)$$

Heterotrophic denitrification

$$\mathrm{DOM} + 94.4NO_3^- + 92.4H^+ \rightarrow 106CO_2 + 55.2N_2 + HPO_4^{2-} + 177.2H_2O \qquad (3)$$

where DOM is $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$.

Examining the river water composition, it is evident that NO_3^- produced by nitrification of NH_4^+ should be included in the mass balance. Beginning with the siltation zone (River Elbe to SP 2/1), 0.3 mg litre^{-1} of NH_4^+ are nitrified and 1.1 mg litre^{-1} of O_2 are consumed, according to the equation given by Jacobs *et al.* (1988):

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + H_2O + NO_3^- \qquad (4)$$

The nitrification of NH_4^+ results in an additional 1.0 mg litre^{-1} of NO_3^-. Assuming negligible O_2 at SP 2/1, the remaining 9.1 mg litre^{-1} of O_2 in the siltation zone are respired, according to the stoichiometry of equation 2, for an oxidation of 2.6 mg litre^{-1} of organic carbon, and produces a further 2.0 mg litre^{-1} of NO_3^-. With reference to equation 3, the decrease in NO_3^- (22.1–21.4 + 1.0 + 2.0 = 3.7 mg litre^{-1}) in the river-bed sediments requires the oxidation of a further 0.8 mg litre^{-1} of organic carbon. The calculated organic carbon demand of 3.4 mg litre^{-1} compares with an observed decrease in DOC of 1.1 mg litre^{-1}. Within the aquifer (between sampling points 2/1–4/2) the decrease in NO_3^- is 9.8 mg litre^{-1}, and the calculated organic carbon demand for denitrification is 2.1 mg litre^{-1}, compared with an observed decrease in DOC of 0.9 mg litre^{-1}. Therefore, the total organic carbon demand between the River Elbe and SP 4/2 is 5.5 mg litre^{-1}.

The above calculations show an apparent discrepancy between the total demand for organic carbon and the amount of DOC oxidized. This suggests that there is an additional supply of organic carbon. Additional sources are particles of >0.45 μm size fraction contained in river water and the available solid organic carbon (SOC). Guderitz *et al.* (1993) found about 1.5 mg litre^{-1} particulate organic carbon (>0.45 μm) in River Elbe water in 1991–1992. Lawrence and Foster (1986), Trudell *et al.* (1986) and Starr and Gillham (1993) all considered that SOC in an aquifer, although present in seemingly small amounts, is a potential oxidizable source of carbon. In the present study, the mean SOC content of aquifer material was 0.015% by dry weight, size-fraction <2 mm, including reworked brown coal fragments. The SOC content of river-bed material was 0.04%–0.5% by dry weight. It is likely, therefore, that a portion of this SOC is involved in the denitrification process. The degradability of the small amount of brown coal fragments (which are potential e^- donors, Postma *et al.*, 1991) found in the aquifer is assumed to be low, in that over geologic time the SOC remaining in a formation is not very labile (Korom, 1992). Prior to 1990 and the improvement in river-water quality, the river infiltrate contained a high organic carbon content and probably contributed a pool of organic carbon within the river-bed sediments and aquifer material. It is this component of organic carbon that is additionally available as a source of oxidizable matter.

The mean total NO_3^- reduction of 10.5 mg litre^{-1} between the River Elbe and SP 4/2 (a distance of about 55 m) compares with other alluvial aquifers where reductions of up to 14.9 mg litre^{-1} over a distance of 100 m (River Glatt, Switzerland; Jacobs *et al.*, 1988) and up to 3.1 mg litre^{-1} over a distance of 50 m (River Lot, France; Bourg and Bertin, 1993) are reported. Between sampling points 2/1 and 4/2, and for a travel time of 60 days, the calculated denitrification rate is approximately 0.04 mg-N litre^{-1} d^{-1}, at least an order of magnitude less than the rate obtained from the laboratory column experiment.

Autotrophic denitrification involving reduced inorganic species such as Mn^{2+}, Fe^{2+} and HS^- serving as e^- donors can be important in aquifers containing large quantities of these species (Korom, 1992). The SO_4^{2-} concentration is observed to increase by 8.0 mg litre^{-1} along the upper flowpath (Table 1). However, sulphidic minerals such as pyrite were undetected from XRD analyses of river-bed sediments and aquifer material. Mallen *et al.* (1997) reported a decrease in the sulphur isotopic composition ($\delta^{34}S$) of dissolved SO_4^{2-} and an increase in SO_4^{2-} concentration between sampling points 2/1 and 4/2 in September 1995. The sulphur isotope results were interpreted as evidence for autotrophic denitrification in the absence of oxygen for pyrite weathering. Therefore, although NO_3^- and SO_4^{2-} concentrations measured in this study do not respond in a similar manner, it is possible that autotrophic denitrification occurs where NO_3^- is introduced into sulphate-reducing zones within the upper aquifer layer. In the middle aquifer layer concentrations of Mn^{2+}, Fe^{2+} and SO_4^{2-} are elevated (Table 1) indicating that autotrophic denitrification may be more significant with increasing residence time in the aquifer.

At Torgau, the $\delta^{15}N$ composition of dissolved NO_3^- becomes enriched in ^{15}N relative to the River Elbe, increasing from a median value of +8.6‰ in the river water to +17.6‰ at SP 4/2. Derivation of an isotopic enrichment factor (ϵ) using equation 1 for the field data is not straightforward, in that a constant initial substrate concentration (C_0) for the variable river water NO_3^- input is not a realistic assumption. For the Cape Cod sand and gravel aquifer (USA), Smith *et al.* (1991) found an isotopic enrichment factor of −13.9‰, similar to the value derived in the present study for the laboratory column experiment ($\epsilon = -14.6‰$). If median values for $\delta^{15}N$ composition and NO_3^- concentration are compared in Fig. 7, an upper flowpath represented by the River Elbe and sampling points 2/1-12/2-18/1-4/1 (see Fig. 2), which is entirely composed of river infiltrate, is in general agreement with the line of fit to the column experiment data, and further corroborates the conclusion that microbial denitrification is occurring in the zone of river-water infiltration.

CONCLUSIONS

The following conclusions are drawn regarding the factors affecting denitrification of infiltrated river water.

1. The input of NO_3^- to the aquifer from the River Elbe is determined by seasonal effects, principally river-water temperature that controls denitrification in the biologically active siltation zone, and decreased agricultural runoff of NO_3^- during the summer months.
2. Denitrification is observed in the upper layer of the aquifer, as demonstrated by an enrichment of the $\delta^{15}N$ composition of residual NO_3^- contained in groundwater. An isotopic enrichment factor of −14.6‰ conforming to Rayleigh fractionation, and determined for a laboratory column experiment, appears typical for granular aquifer material under anaerobic conditions.
3. A mass balance for the infiltrating river water reveals that the source of oxidizable organic carbon to support denitrification is not only DOC in the infiltrating water but also SOC fixed in the river bed and aquifer materials and probably contributed by former river inputs.
4. The calculated denitrification rate of 0.04 mg-N litre^{-1}d^{-1} from the field results is less than the range obtained from the column experiment (0.1–3.2 mg-N litre^{-1} d^{-1}). Also, the isotopic enrichment observed for the field data does not exactly conform to a Rayleigh fractionation process. It is concluded that changing physical and chemical conditions in the river limit the establishment of optimum denitrification conditions in the aquifer.
5. At present there is effective denitrification along the infiltration flowpath from the river to the production borehole. In future, and with continued high groundwater abstraction rates, the available SOC reservoir may become a limiting factor in sustaining denitrification. Protection of the biologically active siltation zone against the destructive effects of flooding and higher currents

from navigation is also necessary to maintain denitrification of infiltrated river water.

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REFERENCES

Böttcher J., Strebel O., Voerkelius S. and 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,** 413–424.

Bourg A. C. and Bertin C. (1993) Biogeochemical processes during infiltration of river water into an alluvial aquifer. *Environ. Sci. Technol.* **27,** 661–666.

Feast N. A. and Dennis P. F. (1996) A comparison of methods for nitrogen isotope analysis of groundwater. *Chem. Geol. (Isotope Geoscience Section)* **129,** 167–171.

Fustec E., Mariotti A., Grillo X. and Sajus J. (1991) Nitrate removal by denitrification in alluvial ground water: role of a former channel. *J. Hydrol.* **123,** 337–354.

Grischek T., Dehnert J., Nestler W., Neitzel P. and Trettin R. (1995) Groundwater flow and quality in an alluvial aquifer recharged from river bank infiltration, Torgau Basin, Germany. In *Geomorphology and Groundwater* (Edited by Brown A. G.), pp. 21–35. John Wiley.

Guderitz T., Schmidt W. and Brauch H-J. (1993) Organic compounds in the upper River Elbe and their impact on quality of bankfilter water. *Vom Wass.* **81,** 315–326.

Heaton T. H. E. (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem Geol. (Isotope Geoscience Section)* **59,** 87–102.

Jacobs L. A., Von Gunten H. R., Keil R. and Kuslys M. (1988) Geochemical changes along a river-groundwater infiltration flow path: Glattfelden, Switzerland. *Geochim. Cosmochim. Acta* **52,** 2693–2706.

Kaplan N. and Magaritz M. (1986) A nitrogen-isotope study of the sources of nitrate contamination in groundwater of the Pleistocene coastal plain aquifer, Israel. *Wat. Res.* **20,** 131–135.

Korom S. F. (1992) Natural denitrification in the saturated zone: a review. *Wat. Resour. Res.* **28,** 1657–1668.

Lawrence A. R. and Foster S. S. D. (1986) Denitrification in a limestone aquifer in relation to the security of low-nitrate groundwater supplies. *J. Inst. Wat. Engng Sci.* **40,** 159–172.

MacDonald A. M., Edwards A. C., Pugh K. B. and Balls P. W. (1995) Soluble nitrogen and phosphorus in the river Ythan system, UK: annual and seasonal trends. *Wat. Res.* **29,** 837–846.

Mallen G., Geyer S., Strauch G., Trettin R., Gehre M. and Grischek T. (1997) Contribution from carbon and sulphur isotopes to the evaluation of biogeochemical processes in groundwater systems controlled by river bank filtration—an example from the Torgau aquifer (Saxony, Germany). Int. Symp. Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere (Edited by Murphy, P.). IAEA-SM-349/32. In press.

Mariotti A., Landreau A. and Simon B. (1988) ^{15}N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. *Geochim. Cosmochim. Acta* **52,** 1869–1878.

Nestler W., Kritzner W., Grischek T. and Dehnert J. (1993) Das Beschaffenheitsüberwachungssystem für das Uferfiltrat der Sächsischen Elbe; Konzeption und Erfahrungen bei Entwurf, Bau und Betrieb (The monitoring system for the water quality of bank-filtered water of the Elbe in Saxony). *Wass. Boden* **9,** 707–728.

Nestler W., Dehnert J., Neitzel P., Grischek T. and Nitzsche I. (1996) Untersuchungen zur Unterströmung der Elbe (Investigations on groundwater flow beneath the Elbe river). *Wass. Boden* **5,** 53–58.

Postma D., Boesen C., Kristiansen H. and Larsen F. (1991) Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modelling. *Wat. Resour. Res.* **27,** 2027–2045.

Smith R. L., Howes B. L. and Duff J. H. (1991) Denitrification in nitrate contaminated groundwater: occurrence in steep vertical geochemical gradients. *Geochim. Cosmochim. Acta* **55,** 1815–1825.

Starr R. C. and Gillham R. W. (1993) Denitrification and organic carbon availability in two aquifers. *Ground Wat.* **31,** 934–947.

Trudell M. R., Gillham R. W. and Cherry J. A. (1986) An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *J. Hydrol.* **83,** 251–268.

Von Gunten H. R., Karametaxas G., Krähendühl U., Kuslys M., Giovanoli R., Hoehn E. and Keil R. (1991) Seasonal biogeochemical cycles in riverborne groundwater. *Geochim. Cosmochim. Acta* **55,** 3597–3609.

Wilson G. B., Andrews J. N. and Bath A. H. (1994) The nitrogen isotope composition of groundwater nitrates from the East Midlands Triassic sandstone aquifer, England. *J. Hydrol.* **157,** 35–46.