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Water quality dynamics and hydrology in nitrate loaded riparian zones in the Netherlands

Mariet Hefting [a,*], Boudewijn Beltman [a], Derek Karssenberg [b], Karin Rebel [a], Mirjam van Riessen [b], Maarten Spijker [b]

[a] *Department of Geobiology, Faculty of Biology, Utrecht University, PO Box 80084, 3508 TB Utrecht, The Netherlands*
[b] *The Netherlands Centre for Geo-ecological Research (ICG), Faculty of Geographical Sciences, Utrecht University, PO Box 80115, 3508 TC Utrecht, The Netherlands*

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Riparian zones reduced nitrate from agricultural lands.

Abstract

Riparian zones are known to function as buffers, reducing non-point source pollution from agricultural land to streams. In the Netherlands, riparian zones are subject to high nitrogen inputs. We combined hydrological, chemical and soil profile data with groundwater modelling to evaluate whether chronically N loaded riparian zones were still mitigating diffuse nitrate fluxes. Hydraulic parameters and water quality were monitored over 2 years in 50 piezometres in a forested and grassland riparian zone. Average nitrate loadings were high in the forested zone with 87 g NO_3^--N m^{-2} y^{-1} and significantly lower in the grassland zone with 15 g NO_3^--N m^{-2} y^{-1}. Groundwater from a second aquifer diluted the nitrate loaded agricultural runoff. Biological N removal however occurred in both riparian zones, the grassland zone removed about 63% of the incoming nitrate load, whereas in the forested zone clear symptoms of saturation were visible and only 38% of the nitrate load was removed.

Keywords: Nitrate removal; Groundwater; Dilution; N-saturation; Riparian wetlands

1. Introduction

Research of riparian zones in agricultural catchments with high nitrate concentrations in subsurface runoff has often shown a substantial decrease in nitrate concentrations within the riparian zone (Lowrance et al., 1984; Peterjohn and Correll, 1984; Pinay and Decamps, 1988; Simmons et al., 1992; Hill et al., 2000; Dhondt et al., 2002). Natural processes such as vegetation uptake, denitrification and microbial immobilization have been demonstrated to be important in the removal of nitrate from shallow groundwater in riparian zones (Groffman et al., 1996; Haycock and Pinay, 1993; Martin et al., 1999). These results have led to the conclusion that riparian zones are crucial to the control of non-point source pollution of surface waters in agricultural environments.

However, flows of groundwater from a semi-confined aquifer with low nitrate concentrations and surface water in the near stream (hyporheic) zone may significantly contribute to the decrease in nitrate concentrations in the shallow groundwater through dilution or mixing (Vought et al., 1994; Altman and Parizek, 1995; Pinay et al., 1998). The relative contribution of groundwater

* Corresponding author. Tel.: +31 302 537 441; fax: +31 302 518 366.
E-mail address: m.m.hefting@bio.uu.nl (M. Hefting).

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from a semi-confined aquifer to the water and solute budgets in riparian zones is largely dependent on the geological setting, and can be substantial in glacial terrain due to the scaled and folded deposits in the moraine (Roulet, 1990).

Another factor that needs to be considered is that flow patterns within riparian zones with heterogeneous sediments may be complex and create spatial differences in both residence time and material encountered by the groundwater travelling within the riparian zone (Gold et al., 1998; Devito et al., 2000). Preferential flow paths may occur as a result of local differences in permeability of the soil and these may conduct substantial quantities of water and decrease the overall residence time of water in the buffer zone. A second example of the importance of the hydrological flow paths in nitrate removal is bypass flow, when nitrate-rich groundwater passes underneath the riparian buffer zone. The nitrate-rich groundwater then short-circuits the biologically active topsoil and reaches the stream without any improvement in water quality (Phillips et al., 1993; Wigington et al., 2003). Thus, knowledge of groundwater flow paths and physical water mixing is essential for a correct evaluation of the N mitigation by riparian buffers (Nelson et al., 1995).

Besides these hydrological processes, the intensity of nitrate loading is another key factor influencing the removal efficiency of riparian zones (Hanson et al., 1994; Willems et al., 1997). In the Netherlands, the rate of fertilizer application is high (200–400 kg N ha^{-1} y^{-1}) as are the losses to the groundwater (Oenema and Roest, 1997). Consequently, riparian ecosystems in Dutch agricultural watersheds have been subject to prolonged nitrogen enrichment with high loading rates compared to other riparian ecosystems in Europe (Sabater et al., 2003; Hefting et al., 2005). This increased nitrogen availability has resulted in increased nitrogen cycling rates and possibly reduced N retention (Hanson et al., 1994). Over time, the chronic N inputs may even cause saturation of buffer zones and consequently loss of their beneficial function on water quality improvement. Sabater et al. (2003) found a negative relation between nitrate loading and riparian zone removal efficiency over a wide range of riparian sites in Europe. In this study we examined two N loaded Dutch riparian buffer zones in detail.

Our aims were to determine the effect of groundwater pathways, both in horizontal and vertical direction, on measured changes in nitrate concentration within the riparian zone with special attention to the possible occurrence of N saturation effects along these pathways.

In this research the following step-wise approach was pursued:

1. determination of the groundwater flow paths at a regional and local scale using equi-potential contours of measured hydraulic heads and the groundwater flow model MODFLOW (McDonald and Harbaugh, 1984);
2. investigation of changes in groundwater nitrate concentrations along flow paths by monitoring water quality on a monthly basis;
3. determination of the mixing of water from different sources along flow paths within the riparian zone on the basis of chemical signatures, especially chloride concentrations;
4. calculation of the contribution of dilution removal processes to the groundwater nitrate decrease along flow paths;
5. analyse the effect of N loading on the N removal capacity along flow paths.

2. Materials and methods

2.1. Site descriptions

The study was conducted in two riparian buffer zones; a forest on the Hazelbekke stream (Hefting and De Klein, 1998) and a grassland zone on the Ribbert stream (Hefting et al., 2003). Both riparian zones were located along first-order streams, in the Eastern part of the Netherlands (51°25′ N, 6°51′ E). The vegetation of the forested zone mainly consisted of alder (*Alnus glutinosa* L. Gaertn.) and nettle (*Urtica dioica* L.). The grassland vegetation consisted of reed-grass (*Glyceria maxima* Hartm. Holmb) and nettle (*U. dioica*). Both riparian zones border intensively managed arable land planted with maize, with high manure and fertilizer application rates, approximately 200–400 kg N ha^{-1} $year^{-1}$, resulting in high concentrations of NO_3^- in the groundwater below the agricultural field (>30 mg NO_3^-–N l^{-1}). Lateral nitrate influx rates to the buffer zones were high, with approximately 630 g N m^{-2} y^{-1} into the forested buffer and 270 g N m^{-2} y^{-1} into the grassland buffer in 1999 (Sabater et al., 2003).

The geological substratum of the study area consists of glacial till with a variable composition mostly of sediments with low conductivity covered by a thin layer (0–4 m) of aeolien sand, fluvioglacial sediments and Quaternary peat layers (Van den Berg and Den Otter, 1993). The first-order streams at the buffer zones have narrow streambeds (0.5–1.5 m) positioned in valleys of 20–50 m width, created by the erosive force of the melting water. Soils in the buffer zones are classified as entisols and histosols (USDA; http://www.usda.gov) and are characterized by high groundwater levels throughout the year. In the adjacent agricultural fields water table depth varies from 0.4 m to more than 1.2 m below the soil surface.

2.2. Lithology

To obtain insight into the groundwater flow paths in the complex glacial terrain, we carried out a detailed study of the lithology. Over 110 drillings with depth ranging from 1.2 to 5.0 m were performed using hand auger equipment (Eijkelkamp, The Netherlands). On a regional scale 70 auger holes were divided over 8 transects, and 20 additional drillings were performed both in the forested and grassland riparian zone. Distinct layers found in the drillings were mapped and grouped according to the texture class. Additional information was used from a study using georadar in the same area (Van der Aa et al., 1999) and a hydrological field study (Hendriks et al., 1996). Information on hydraulic conductivities (K) of the different texture classes was obtained from the unsaturated soil hydraulic database (UNSODA; http://www.ussl.ars.usda.gov/models/unsoda.htm). Pumping tests were performed in the field to verify data from the database. Field measurements were in the same order of magnitude although high spatial variability was observed.

2.3. Groundwater monitoring

A grid of dipwell piezometers (5 transects with at least 3 wells, at approximately 10 m intervals) was installed in both study sites over an elevational gradient (slope 10%) from the agricultural fields towards the stream (Fig. 1). Dipwell piezometers (1–3 m) were installed into the phreatic groundwater on top of the Tertiary clay layer and tubes were perforated along the whole length. Additional standpipe piezometers with short filters were installed below (and into) the semi-confined clay layers, to monitor water quality in the second aquifer (depth >5 m) and determine the possible existence of bypass flow underneath the riparian soils. This will hereafter be called the "deep groundwater". Groundwater levels were recorded fortnightly from spring 1998 to mid-November 2000 and seasonally to July 2001. Groundwater flux along flow paths was estimated using Darcy's formula.

The lithological surveys and water table elevations (Figs. 1, 2) revealed a more complex hydrological system in the grassland riparian zone compared to the forested system. On the basis of these results we decided to study the groundwater flow pattern of the grassland zone in more detail. In the forested zone, groundwater flow paths were determined from equi-potential contours of hydraulic heads in the piezometers (Fig. 1).

2.4. Groundwater modelling for the grassland riparian zone

A spatial database was constructed for groundwater flow modelling with MODFLOW (McDonald and Harbaugh, 1984). Digitized land use maps were based on topographical maps (scale 1:10,000) and field observations. Daily precipitation data were used from the grassland zone in 1999 and from a KNMI weather station at Tubbergen (at a distance of 5 km). Evapotranspiration data were used from the regional (Twente) weather station at a distance of approximately 20 km (Dutch Royal Meteorological Institute). The digital elevation model for this study area was based on elevation data measured on a 5×5 m grid using laser altimetry (data from Ministry RWS).

We first created a regional groundwater model in MODFLOW (McDonald and Harbaugh, 1984) to calculate the boundary conditions (fixed head) for the local model. The size of the regional model was 2 by 1 km with grid cells of 10×10 m, and 5 layers. To study the groundwater flow paths in the riparian zone, a local model was built, which was only 60×110 m, using a grid size of 1×1 m and 5 layers. Both forward and backward particle tracking was performed with PMPath (Chiang and Kinzelbach, 1994–1996) which uses the algorithm described by Pollock (1988), from each piezometer filter location in the grassland zone to interpret groundwater flow paths. In the particle tracking algorithm, dispersion and diffusion are not taken into account. Therefore we assumed that, besides the piezometers that were directly linked by simulated flowlines, also neighbouring piezometers were influenced by the passing groundwater flow, only in cases when the filter depth coincided with the depth of the flow paths.

2.5. Water quality measurement

Groundwater was sampled monthly from June 1998 to February 2000, and seasonally from May 2000 to July 2001, using a peristaltic pump. Piezometers were emptied prior to water sampling to remove the standing water. Water samples for cation and DOC analyses were collected in glass flasks and acidified in the field (0.1 ml 37% HNO_3 in 10 ml) to prevent precipitation of iron. Water samples for pH, conductivity and anion analyses were transported in PVC flasks. Additional surface water samples were taken mid-stream at a fixed position.

Water samples were transported to the laboratory at 4 °C. Measurements of pH (WTW pH 540 GLP) and conductivity (WTW LF 539) were made upon arrival in the laboratory. Water samples were filtered using glass fibre filters (Schleicher and Schuell, GF 52) and analysed within 24 h of sampling for NO_3^-, NH_4^+, SO_4^{2-}, Cl^-, Ca^{2+}, and Mg^{2+} using a continuous flow autoanalyser (SKALAR SA-40, Breda, The Netherlands). Chloride was measured to detect possible dilution, considering chloride as a conservative tracer (Altman and Parizak, 1995; Cey et al., 1999; Clément et al., 2002). Additional measurements on Na^+, K^+, and HCO_3^- were performed at an irregular basis to characterize the chemical signatures of the water. Groundwater DOC and organic

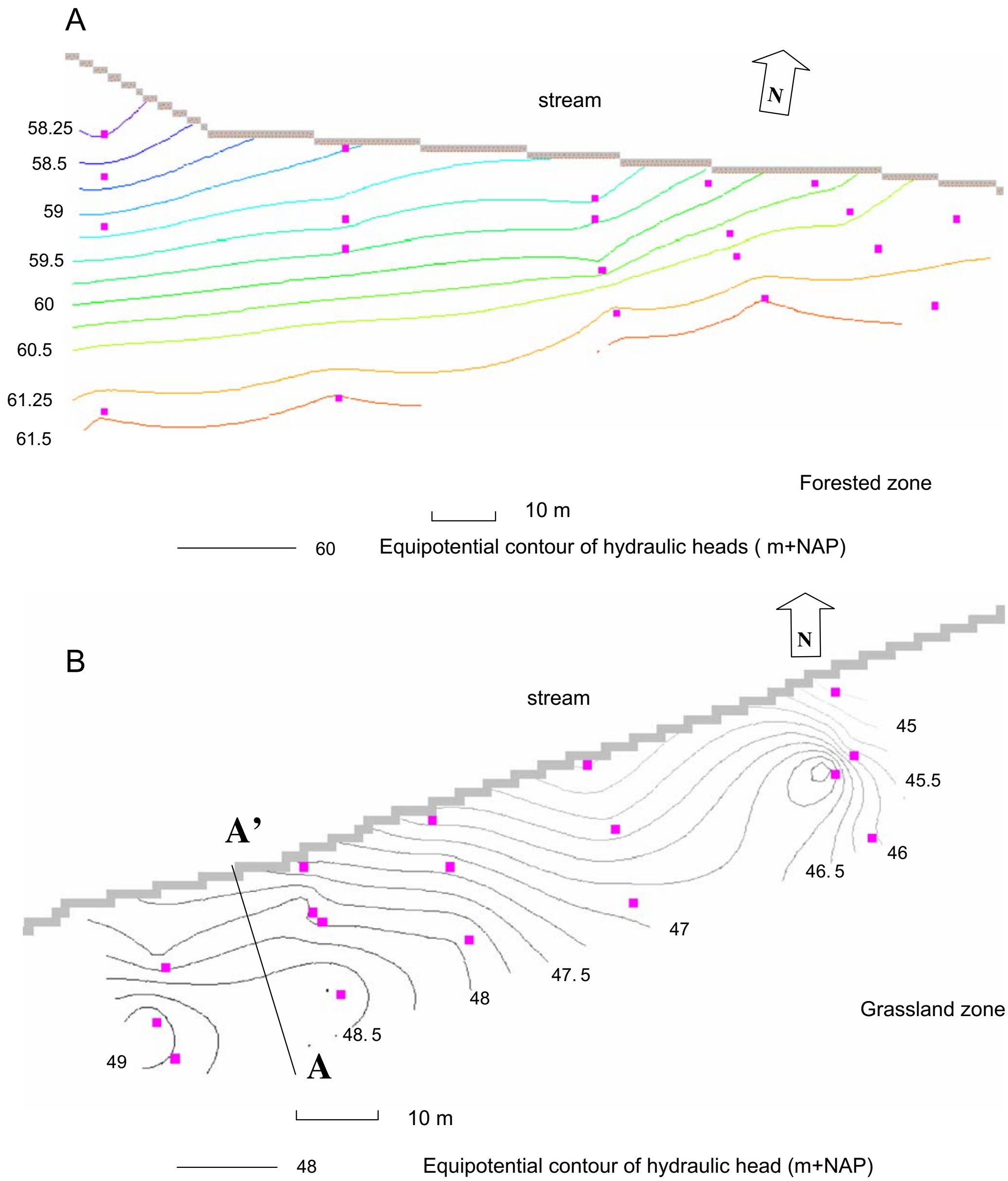

Fig. 1. Average annual phreatic water table elevation contours and piezometer locations within the forested (A) and grassland (B) riparian zone.

N contents were determined to study possible organic N losses (Prior and Johnes, 1999).

2.6. Statistical analysis

Water quality data were tested for normality and homogeneity of variance. If data did not meet the requirements they were log transformed before statistical analysis.

Variables were tested using Student *t*-tests, regression analysis, ANOVA, repeated measures analysis of variance and Tukey post hoc tests, using SPSS 8.0 for Windows (SPSS, 1997, Chicago, IL, USA).

3. Results

3.1. Groundwater table

Fluctuations in groundwater levels were rather similar between the two study sites (Fig. 3). Close to the stream and in the middle of the riparian zones the water table remained close to the soil surface (−15 cm to 0 cm) and hardly fluctuated during the year. Water tables at the field border were always well below the soil surface (> 40 cm) and showed a clear seasonal variation. However, only a weak relation could be found with precipitation data, indicating a more regional groundwater flow system (Altman and Parizak, 1995; Caissie

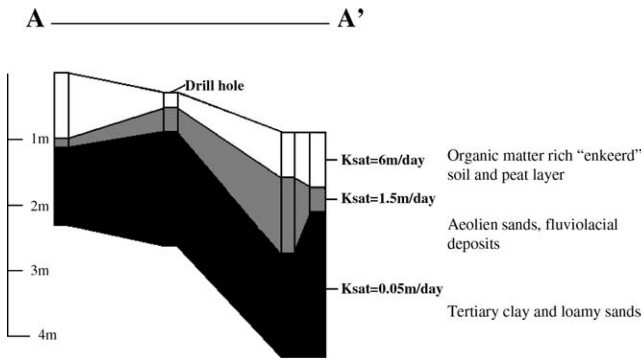

Fig. 2. Cross-section of the grassland riparian zone showing the three main formations encountered in the detailed lithological study.

et al., 1996). Differences in hydraulic heads between the field border and the middle of the riparian zone were significantly different during summer and winter periods, resulting in significantly higher water fluxes through the riparian zones in winter periods (Fig. 2, paired-sample t-test, $p = 0.002$).

3.2. Lithology

The glacial history of the area has resulted in a complex lithology with many discontinuous folded and fractured layers. The major layers are shown in Fig. 2. Tertiary clay layers and loamy sand layers containing glauconite were encountered at depths varying from 1 m close to the stream to 4 m below the agricultural fields. Saturated hydraulic conductivities of these layers varied between 0.05 m d^{-1} and 10^{-6} m d^{-1}. On top of the semi-confined tertiary material, mixed fluvioglacial deposits and aolien sands were found with saturated hydraulic conductivities of about 0.5–1.5 m d^{-1}. The soil consists of 1 m thick organic matter rich loamy sands (enkeerdgronden) on the higher grounds and Quaternary peat layers in the riparian zones with depth varying between 0.2 and 1 m with saturated conductivities of 5.0–6.0 m d^{-1}and 0.35–0.5 m d^{-1} respectively (Hendriks et al., 1996).

3.3. Groundwater flow paths

Results from the local model of the grassland zone showed that water infiltrating in the agricultural fields directly adjacent to the stream valley was transported, as subsurface flow, through the grassland zone towards the stream. However, groundwater flow patterns appeared to be complex (Fig. 4a). Based upon the piezometer grid, we distinguished four flow paths sections (Fig. 4b) which

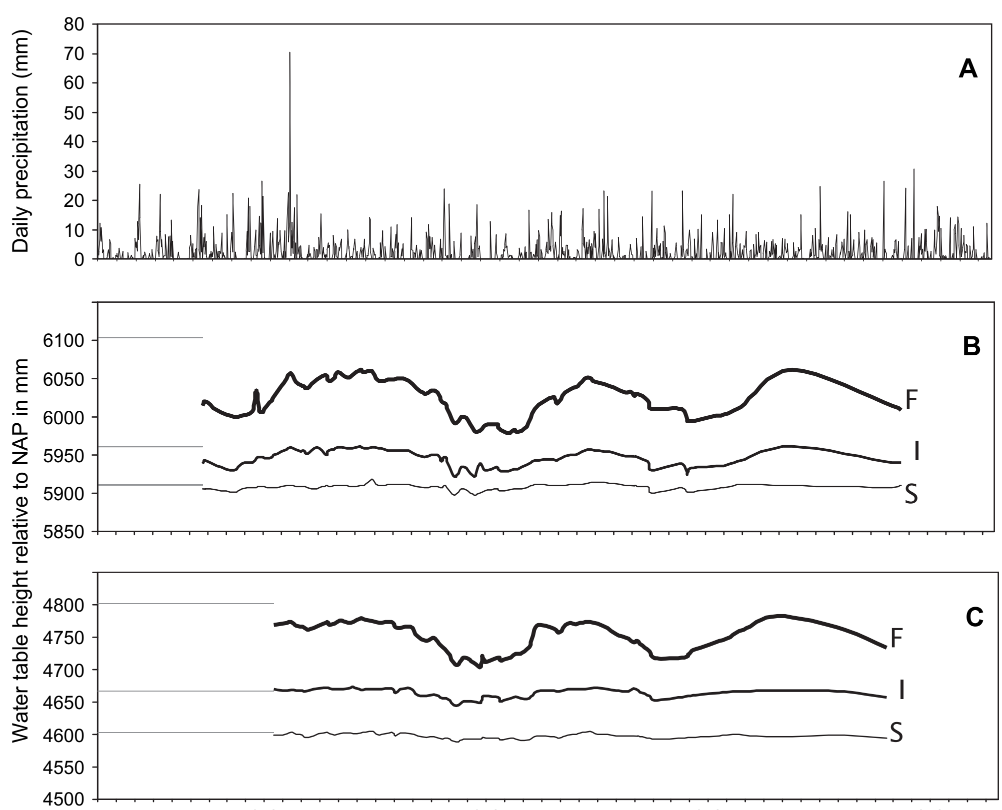

Fig. 3. Precipitation in mm (A) and water table elevation (referred to NAP, Amsterdam Ordnance datum in cm) from January 1998 to July 2001 in strips parallel to the stream in the forested (B) and grassland (C) riparian zone. Water table data are averages of two weekly recordings in 5–12 dipwell piezometers per strip, i.e. field (F), intermediate (I) and near stream (S). Dotted lines indicate the height of the soil surface.

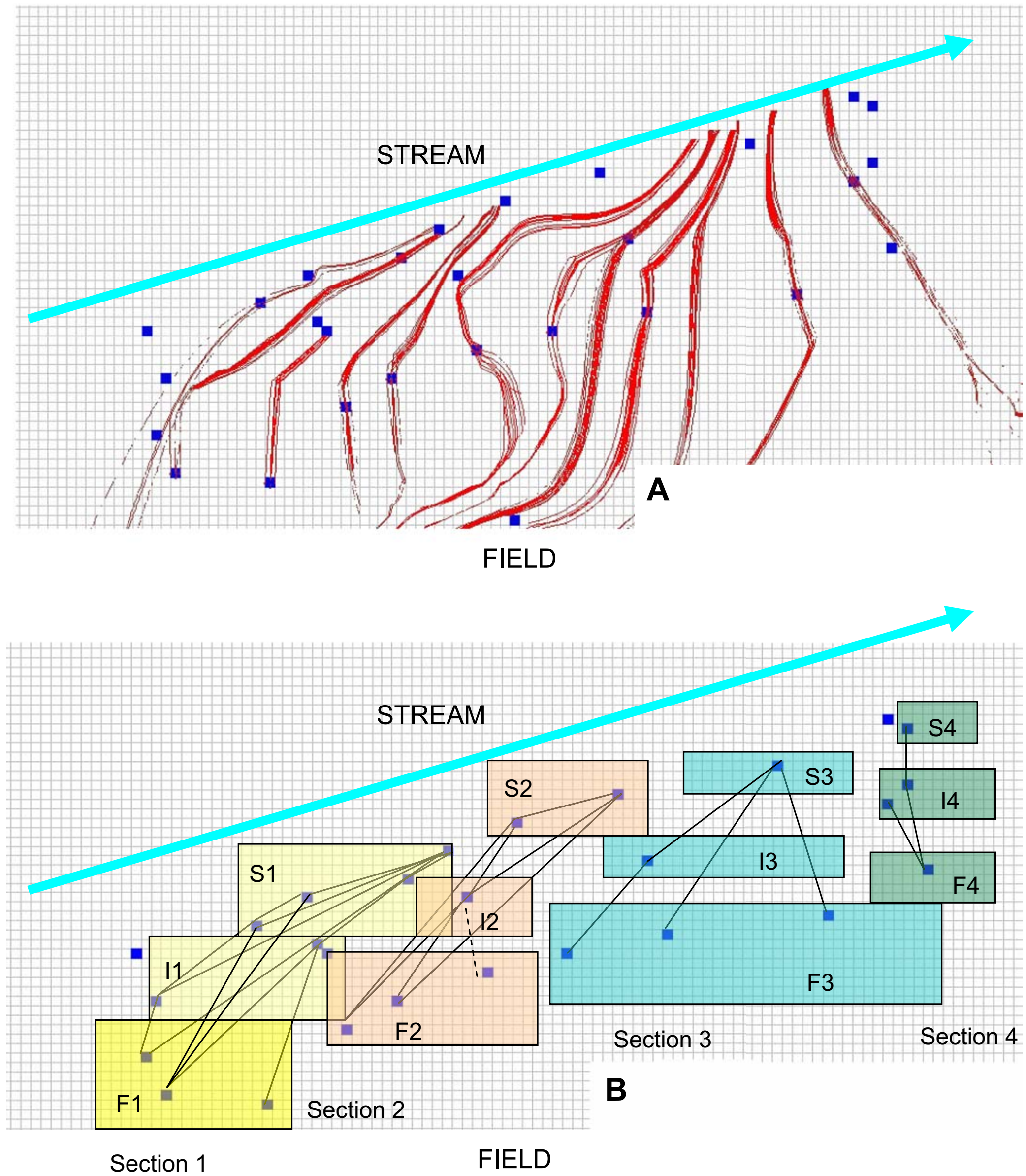

Fig. 4. The overall result of a virtual tracing experiment using particle tracking in PMPath (A). showing four sections of connected piezometers. Each section has groups of piezometers in three strips parallel to the stream, i.e. field border (F), intermediate (I) and near stream (S).

were determined by particle tracking connecting piezometer locations in three dimensions. To cope with the complex flow pattern, we grouped piezometer observations along the observed flow paths in three groups (Fig. 4b), i.e. field (F), intermediate (I) and near stream (S).

Determination of piezometric surfaces within the forested riparian zone (Fig. 1) revealed that the dominant flow path was perpendicular to the stream. Five flow path sections were identified and the piezometers were also clustered in three groups.

3.4. Nitrogen inflow

Mean monthly groundwater nitrate concentrations over the study period were significantly higher in the field border of the forested zone (average 35 mg NO_3^--N l^{-1}, median 36 mg NO_3^--N l^{-1}), compared to the field border in the grassland zone (average 11 mg NO_3^--N l^{-1} median 8 mg NO_3^--N l^{-1}) (repeated measures $F = 10.613$, $p = 0.012$) (Fig. 5). NH_4^+ concentrations in the shallow groundwater were low in both riparian zones with mean concentrations below 0.4 mg N l^{-1}. No significant seasonal variation was measured in the mean nitrate concentration at the field boundaries, and no direct response of nitrate concentrations to agricultural practice in the adjacent farmlands (e.g. manure application, ploughing, harvesting) was observed. However, inflow nitrate concentrations at the field border were significantly higher in 1998 compared to 1999–2000, due to extremely wet weather conditions in 1998.

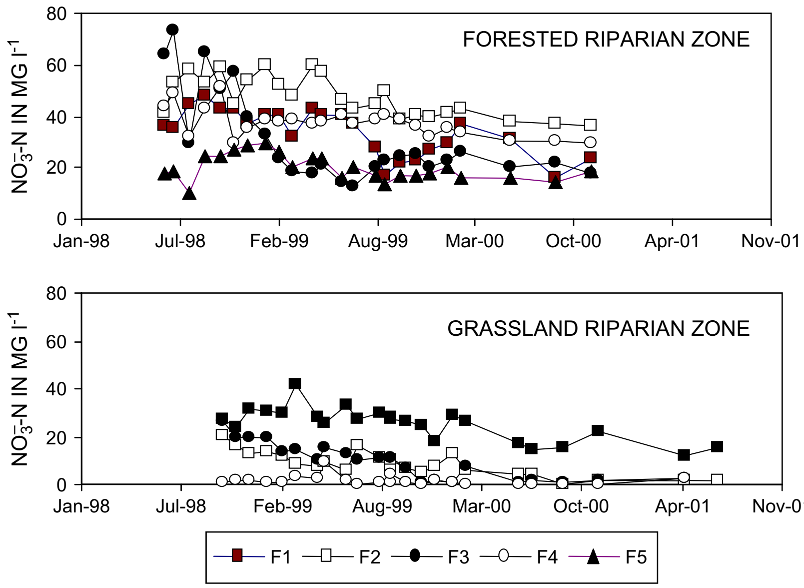

Fig. 5. Nitrate-N inflow concentrations at the field border (F) over the study period in the forested and grassland buffer zone. Five groups ($n=2$) of piezometers at the field border were analysed in the forested zone (F1–F5) and four main groups ($n=2$–3) of piezometers were analysed at the field border of the grassland zone (F1–F4) (see Fig. 4).

Furthermore, nitrate concentration input to the grassland zone decreased significantly over the period January 1999 to July 2001 (ANOVA, $F=73.510$, $p=0.04$). This was caused by a 12 m unfertilized zone in the agricultural field on the upland edge of the riparian zone fenced off in spring 1999. Moreover, nitrate concentrations in the field border of the grassland zone were significantly higher at the "upstream" field border piezometers compared to "downstream" field border piezometers (ANOVA, $F=60.697$, $p<0.0001$, Fig. 6A–C.). In the forested zone no systematic difference in inflow concentrations could be observed in the flow direction of the stream. Nitrate concentrations at the field border were, however, significantly different between the transects (ANOVA, $F=26.353$, $p<0.0001$, Fig. 6A–C).

3.5. Nitrogen concentrations along flow paths

A decrease in nitrate concentration was observed along flow paths in both areas (Fig. 6A,B). Such a decrease also occurred in periods with lower nitrate inflow concentrations (Fig. 6C). Nitrate concentrations were significantly lower in the near-stream strips compared to the field border strips (Table 1). In contrast to the low nitrate concentrations observed at the stream border of the grassland zone, the mean nitrate concentration in the stream border of the forested buffer zone showed a strong spatial variation with a range of concentrations between 0.5 and 45 mg N l^{-1}. The higher nitrate concentrations were strongly correlated to lower pH values (Fig. 7, $R^2=0.754$, $p<0.001$).

To separate the contribution of dilution and biological removal processes responsible for the decrease in nitrate, chloride was used as a conservative tracer. We observed a significant increase of chloride concentration with decreasing nitrate from the field border to the stream (Table 1). This strong increase of 20–150% was not likely to be caused by evapotranspiration in the riparian zone, because increases were too high and no seasonal differences were observed in chloride concentrations. Moreover, differences in other macro ionic compounds, expressed in STIFF diagrams (Beltman and Rouwenhorst, 1991; Freeze and Cherry, 1979) and pH indicated that there was a change in groundwater composition down the flow paths, most probably caused by dilution with deep groundwater in both study sites (Fig. 8, Table 1).

The correction based on chloride concentrations revealed that the nitrate dynamics in both riparian zones was significantly affected by dilution with deep groundwater. In the grassland zone an average dilution of 65% and in the forested zone an average dilution of 47% was calculated. Large spatial differences in dilution occurred in both sites, although no significant differences were observed in dilution rates between summer and winter (paired sample t-test, $p=0.67$ and $p=0.96$ for the forested and grassland riparian zone). In the forested site a slightly different type of deep groundwater was encountered in the upstream part of the area.

A considerable "real" nitrate removal along most of the flow paths still exists after correction of the nitrate concentrations for dilution (Fig. 6D–F). In the forested zone and grassland zone respectively 6–77% and 28–99% of the inflowing nitrate was removed. The decrease of

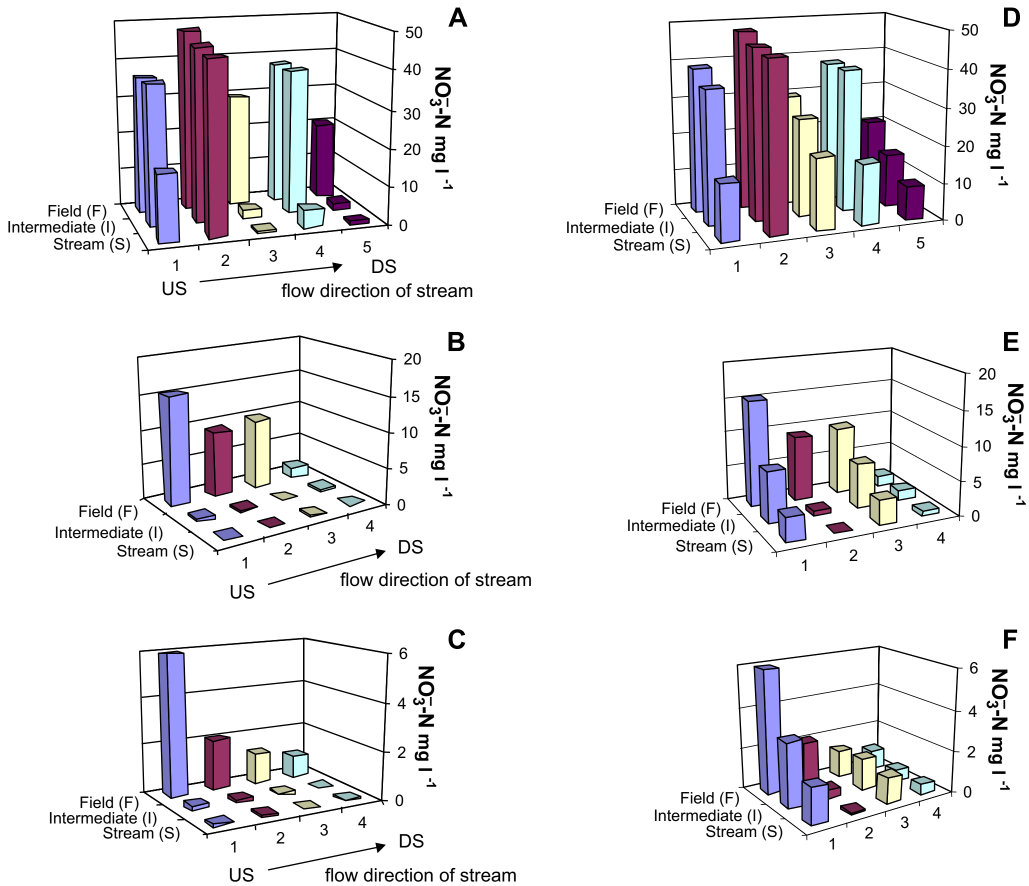

Fig. 6. Average nitrate-N concentrations observed along flow paths June 1998–February 2000 in the forested riparian zone (A) and in the grassland riparian zone (B). Average nitrate concentrations observed along flow paths in the grassland riparian zone from July 2000–July 2001 with significant lower nitrate inflow concentrations (C). US, upstream and DS down stream location of the flow paths (parallel to the stream). Average nitrate-N concentrations corrected for dilution with deep groundwater using chloride concentration in the forested riparian zone (D) and in the grassland riparian zone (E). Average corrected nitrate concentrations observed along flow paths in the grassland riparian zone from July 2000–July 2001 with significant lower nitrate inflow concentrations (F).

Table 1
Average macro ionic composition of the groundwater in strips parallel to the stream

	Field border	Intermediate	Near stream	Surface water	"Deep" groundwater
Forested riparian zone					
NO_3^-N	34.78 (1.99)	21.48 (3.02)	11.47 (2.43)	6.42 (1.72)	0.83 (0.35)
Cl^-	21.6 (1.5)	31.3 (1.9)	31.5 (1.2)	19.1 (2.3)	38.3 (2.1)
SO_4^{2-}	81.1 (6.2)	158.7 (13.0)	151.8 (11.1)	64.9 (6.5)	201.3 (23.3)
Ca^{2+}	56.4 (3.0)	94.6 (8.0)	98.6 (5.5)	93.4 (29.2)	121.0 (17.8)
pH	5.00 (0.12)	5.65 (0.2)	6.66 (0.12)	7.24 (0.22)	6.98 (0.17)
EC	534 (21)	691 (25)	635 (20)	406 (27)	748 (83)
N	198	141	144	21	44
# l	9	5	5	1	2
Grassland riparian zone					
NO_3^-N	15.29 (3.6)	0.12 (0.03)	0.11 (0.05)	3.05 (1.91)	0.31 (0.21)
Cl^-	21.1 (1.3)	30.1 (2.3)	33.6 (2.2)	31.8 (3.2)	41.4 (5.6)
SO_4^{2-}	88.0 (7.3)	86.6 (4.7)	85.9 (3.5)	50.3 (7.0)	103.4 (7.0)
Ca^{2+}	49.5 (3.5)	69.8 (4.8)	82.2 (7.9)	66.7 (19.3)	72.5 (8.3)
pH	6.28 (0.16)	7.28 (0.07)	7.39 (0.07)	7.31 (0.10)	7.32 (0.07)
EC	368 (12)	426 (18)	426 (10)	440 (15)	462 (13)
N	160	150	132	21	23
# l	12	7	5	1	3

Standard errors are given in parentheses. *N*, number of observations; # l, number of piezometer locations.

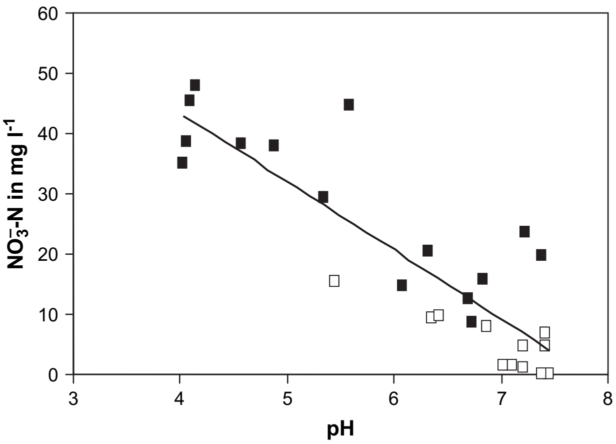

Fig. 7. Relationship between the nitrate concentration and the pH. Open symbols indicate the grassland riparian zone, filled symbols indicate the forested riparian zone.

nitrate was not reciprocated by an increase in ammonium concentration. Moreover, dissolved organic N concentrations in the groundwater were often below the detection limit of 0.5 mg l^{-1}.

Mean nitrate loading rates and removal rates were calculated using the corrected concentrations, the hydraulic conductivity of 0.5 m day^{-1} (assuming a homogeneous, isotropic soil) and the hydrological gradient between strips (F and I and I and S, respectively, Fig. 4) in each flow path using Darcy's formula. Absolute nitrate removal rates (ANR) (expressed as the difference between the input and output nitrate loading in relation to the lengths of the flow paths in the riparian zone) were mainly positive, ranging from 1 to 20 g NO_3^--N per metre flow path per year. Values close to zero removal were found along flow paths connecting the intermediate (I) and near stream (S) strips of the grassland zone with extremely low N inputs but also at the extreme other side in some highly loaded flow paths in the forested zone (Fig. 9, flow path 2). Average ANR rates were higher in the forested zone compared to the grassland zone (independent sample *t*-test, $p = 0.015$).

A spatial pattern of nitrate removal was visible; the upper edge of the grassland riparian zone showed the highest ANR (ANOVA $F = 5.161$, $n = 16$, $p = 0.042$), whereas in the forested zone the highest ANR was located between the intermediate (I) and the near-stream (S) strip; although not significant (ANOVA $F = 3.893$, $n = 10$, $p = 0.084$).

Nitrate removal rates were significantly correlated with nitrate loading (Fig. 9A). In the grassland zone a positive relation was found between the ANR and N load ($R^2 = 0.761$, $p < 0.0001$) whereas higher nitrate loading in the forested zone did not result in higher ANR.

Nitrogen removal efficiencies (NRE) expressed as % m^{-1} were not significantly different between the forested and grassland riparian zones with average values of 1.9 and 2.7% m^{-1} respectively. The NRE showed a negative relation with nitrate loading in the forested zone ($R^2 = 0.634$, $p = 0.011$, Fig. 9B). In the grassland zone no clear relation was observed between NRE and nitrate loading.

4. Discussion

4.1. Dilution and nitrate removal

Seasonal variations in groundwater table levels in the intermediate (I) and near stream (S) strips were marginal in both riparian zones studied (Fig. 3). Constant discharge of deeper groundwater precluded rapid water table responses to weather conditions in these strips. This is a common situation in glacially mantled areas (Roulet, 1990; Hill, 1993; Hill and Waddington, 1993; Cirmo and McDonnell, 1997). Deeper groundwater also played an important role in diluting the shallow nitrate loaded runoff causing a significant decrease in nitrate concentration and a significant increase in chloride concentration along flow paths towards the stream. The higher chloride concentration found in the deep groundwater originated from the tertiary clay in the subsoil, which was formed under marine conditions (Van den Berg and Den Otter, 1993).

Inflow nitrate concentrations were significantly higher in the forested zone compared to grassland zone. A larger infiltration area and a higher percentage of intensively managed arable fields in the catchment are assumed causes for this higher loading. Increased atmospheric deposition of ammonium due to turbulence at the interface between the agricultural field and the riparian forest might also contribute to the higher N loading (Draaijers et al., 1988).

Corrected nitrate concentrations along the flow paths at both sites indicate that, besides the dilution effect, a considerable nitrate reduction took place. Average nitrogen removal efficiencies of 2–3% m^{-1} were found in both the grassland and the forested riparian zone (see Fig. 9B, but note the high spatial variation).

The overall nitrate removal effect of the riparian zones based on input and output and corrected for dilution, resulted in a nitrate removal of 63% for the grassland riparian zone and 38% for the forested riparian buffer zone. The nitrate removal percentage of the grassland zone is within the range found of 60–100% for wet riparian buffer zones Cooper, 1990 (64–94%); Haycock and Burt, 1993 (82%); Haycock and Pinay, 1993 (60–90%); Mander et al., 1995 (100%); Clément et al., 2002 (76– 99%). The lower removal percentage at the forested zone can be attributed to nitrogen saturation due to the relative high nitrate loading. Scenario calculations with the agricultural nitrogen model (ANIMO, Berghuijs-Van Dijk et al.,

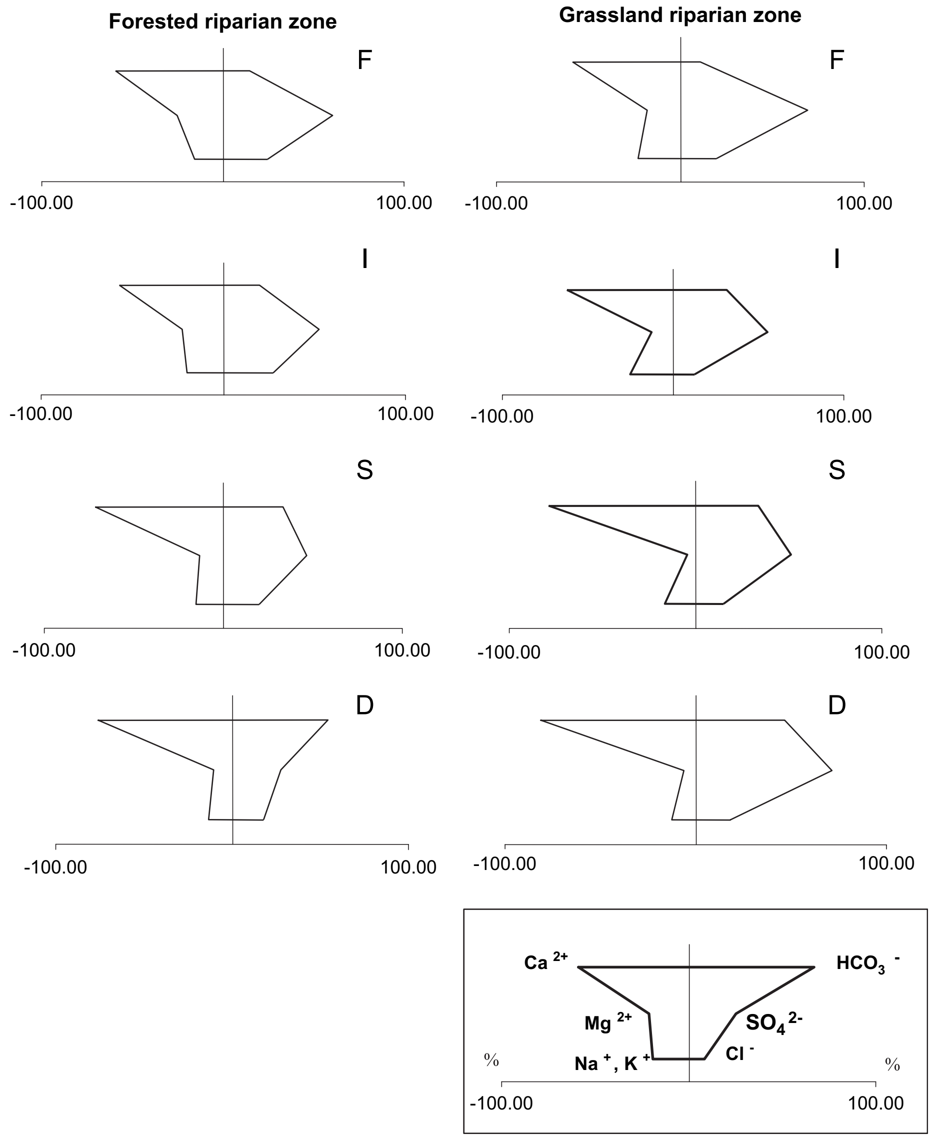

Fig. 8. Average macro ionic composition of water samples along the flow paths expressed in STIFF diagrams. Concentrations are expressed as % of the sum of cations (left) or anions (right) (meq l^{-1}). Abbreviations indicate the location within the riparian zone, i.e. field (F), intermediate (I) and near stream (S). D represents the water quality of the deep groundwater.

1985) calibrated with input data from a nearby forested riparian zone resulted in a comparable low removal percentage of 28% at a total buffer width of 10 m (Kruijne, 1996).

4.2. Processes responsible for nitrate removal

The lack of seasonal difference in nitrate removal between the winter and summer period, indicates the importance of nitrate removal processes other than plant uptake. Generally, heterotrophic denitrification is the dominant nitrate removal process during winter if the shallow subsurface groundwater flows through near-stream substrates rich in organic matter (Haycock and Pinay, 1993). Especially when groundwater levels are close to the soil surface, redox conditions are optimal for heterotrophic denitrification. Nitrate can, however, also be reduced through the oxidation of pyrite (FeS_2), if carbon availability is limited. Böhlke and Denver (1995) found a significant nitrate reduction in groundwater flowing through glauconite-rich sediments. The higher sulphate concentration observed in the deep groundwater (Table 1) may be partly attributed to autotrophic denitrification by *Thiobacillus denitrificans* (Blicher-Mathiesen, 1998; Lamers et al., 1998). Other possibilities for the higher sulphate concentrations are high concentrations of sulphate in manure and in tertiary (marine) clay layers. Nitrate removal under reduced conditions is also possible by dissimilatory nitrate reduction to ammonium. This process is not very likely to occur at

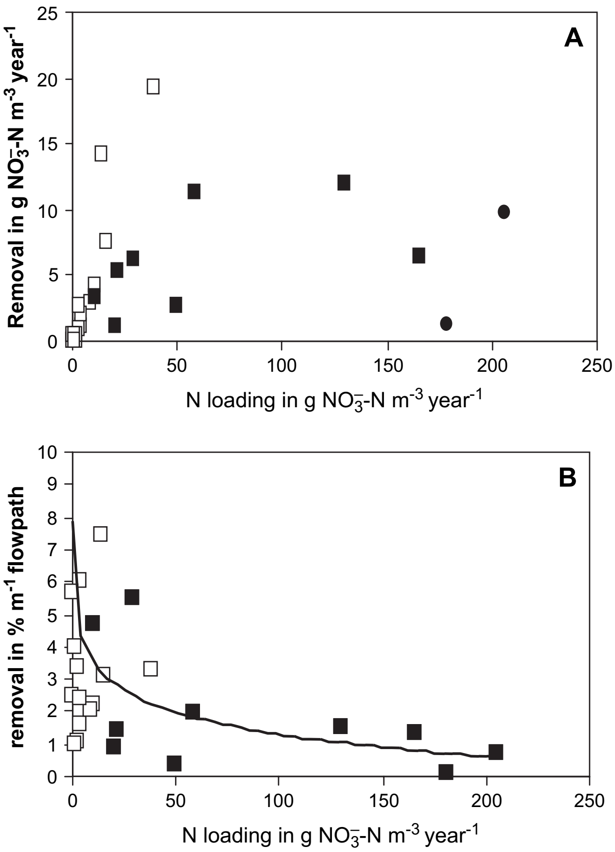

Fig. 9. Relationship between absolute nitrate removal (A) and nitrate removal efficiency (B) versus annual N loading. Open symbols indicate the grassland riparian zone, filled symbols indicate the forested riparian zone. Filled circles indicate the flow path 2 in the forested site with extremely low nitrate removal (see Fig. 6).

our study sites because the decrease in nitrate was certainly not reciprocated by an increase in ammonium.

Our results, in particular the sulphate concentrations and the negative relation between pH and nitrate, indicate that heterotrophic denitrification is the major mechanism of nitrate removal from the shallow groundwater. Detailed process studies on N transformation, denitrification and vegetation N uptake confirm this conclusion (Hefting et al., 2004, 2005).

4.3. Spatial differences in nitrate removal

The higher absolute nitrate removal rates in the upper part of the grassland zone were caused by a higher nitrate loading due to a combination of higher nitrate concentrations and higher flow rates. This spatial pattern with nitrate removal concentrated in the upper parts of the riparian zone is well known (Peterjohn and Correll, 1984; Pinay and Decamps, 1988; Cooper, 1990; Haycock and Pinay, 1993). However, this pattern is not caused by differences in denitrifying potential but rather by a lack of nitrate available for denitrification in the groundwater further down in the riparian zone.

Although nitrate loadings in the forested zone were significantly higher compared to these in the grassland zone, nitrate removal was not significantly higher. Moreover, some highly loaded flow paths at the forested zone had absolute nitrate removal rates close to zero. The spatial pattern of the absolute nitrate removal rates in the forested zone showed a deviating pattern with higher nitrate removal rates close to the stream in most flow paths. Observations in absolute nitrate removal can largely be explained by a pH effect on denitrification rates. The groundwater in the flow paths with low absolute removal rates had a pH around 4, whereas groundwater in other flow path with clear removal had pH values ranging from 5 to 6. Furthermore, dilution with deeper groundwater significantly increased the pH to 7.3 in the near stream area, resulting in higher absolute nitrate removal rates close to the stream.

The high absolute nitrate removal values found in the upper part of the grassland zone may also be related to a pH effect, as pH values of the subsurface inflow in the grassland zone were significantly higher compared to the forested zone with values ranging from 5.5 to 7.5. (Independent sample t-test, $F = 11.977$, $n = 27$, $p = 0.002$).

Heterotrophic denitrification, is found to be low to non-existent at pH values around 4.0 (Bremner and Shaw, 1958) and pH values below 3.5 totally inhibit the denitrification activity (Aulakh et al., 1992). However, significant denitrification activity at these low pH values, was found by Willems et al. (1997). In this low pH range interpretation of results can be complicated by the occurrence of chemo-denitrification (Van Cleemput et al., 1976, Van Cleemput and Baert, 1984).

4.4. Relation between pH and nitrate concentration

The significant negative relation found between pH and nitrate concentration can be explained by the acidifying effect of nitrification (Van Breemen et al., 1982; Corell, 1997) possibly combined with a de-acidifying effect of heterotrophic denitrification (Appelo and Postma, 1993; Corell, 1997; Blicher-Mathiesen and Hoffmann, 1998). The dominant form of fertilization on the agricultural fields is organic manure. The ammonia from this manure is transformed into nitrate by nitrification producing two protons for every nitrate molecule formed. Furthermore ammonium can originate from atmospheric ammonium deposition that is known to be higher at forested interfaces due to turbulence effects (Draaijers et al., 1988). When heterotrophic denitrification occurs one proton is consumed for every reduced nitrate molecule, resulting in a decrease in nitrate combined with an increase in pH.

4.5. Effect of vegetation type on nitrate removal

The type of vegetation may affect the nitrate removal capacity of riparian areas. Forests have been reported to be more effective than herbaceous vegetation (Osborne and Kovacic, 1993; Haycock et al., 1993). Opposite results, i.e. higher nitrate removal efficiencies in grassland were found by Groffman et al. (1991), Schnabel et al. (1996) and Kuusemets et al. (2001). Recent Europe-wide studies, including our research sites (Hefting et al., 2005, Sabater et al., 2003), have indicated that there is no significant difference in nitrate removal efficiency between vegetation types (Lyons et al., 2000). This study shows a significantly higher nitrate removal in the forested riparian zone compared to the grassland riparian zone, probably caused by the higher N loading in the forested zone, because nitrate removal efficiency was not significantly different between the two zones. No general conclusions on the effect of the type of vegetation could be drawn from this research, however based on the European comparison we believe that differences in nitrate removal between the two riparian zones are not caused by difference in vegetation type.

4.6. Nitrogen saturation effect

Riparian ecosystems in agricultural watersheds in the Netherlands are subject to increasingly high nitrate inputs, which has led to increased nitrogen cycling rates and probably to a reduced nitrate retention (Aerts et al.,1995; Verhoeven et al., 1996; Bobbink et al., 1998). In this study, a significant negative relation was found between nitrate removal efficiency (Fig. 9A) and nitrate loading for the forested zone ($R^2 = 0.409$, $p = 0.010$). This is consistent with Nichols (1983) who observed a rapid decline of N removal efficiency with increasing N loading rates over a broad range of natural wetlands. The low nitrate removal efficiency at high nitrate loading rates in the forested zone suggests a nitrate saturation effect; chronically high nitrate loading finally exceeds the buffering capacity of the riparian buffer zone (Aber et al., 1992; Sabater et al., 2003). Although nitrate removal still occurs, the efficiency is significantly decreased at higher nitrate loadings. Besides a significantly reduced nitrate removal, other symptoms of nitrogen saturation such as high soil nitrogen mineralization rates (Pinay and Burt, 2000; Hefting et al., 2004) and significantly higher N_2O emissions and nitrate concentration in pore water (Hefting et al., 2003) were observed in the forested riparian zone.

However, in this saturation trajectory even a decrease in absolute removal capacity was observed. This decrease suggests even an inhibitory effect of nitrate on the denitrification process. Such inhibiting effect is, however, not known for nitrate. It has well been established in the literature that absolute nitrogen retention in lakes, rivers and wetlands increases with nitrogen loading (Saunders and Kalff, 2001), and until now, no upper limit of the riparian buffering capacity has been reported. Hanson et al. (1994) observed clear symptoms of nitrogen saturation in a forested zone subjected to long-term enrichment but high rates of nitrate removal were still possible under enriched conditions. It seems that denitrification can continue at the same rate as the nitrate loading unless the carbon availability becomes limited (Saunders and Kalff, 2001). Yet, studies on denitrification potential in the highly N loaded wetland soils have generally indicated that the vast supply of organic carbon in the wetland soils does not limit the denitrification process (Nichols, 1983; Hanson et al., 1994). Although a large part of the carbon in wetlands is refractory, amendment studies in the laboratory did not show any signs of C-limitation on denitrification enzyme activity in the N saturated forested riparian zone (Hefting, 2003). Results, however, still showed an increase of denitrifier activity in the nitrate amended soil samples. Data from our field study, however, suggest an inhibitory or limiting effect above an input flux of approximately 50 g NO_3^--N m^{-2} y^{-1}. The fact that groundwater high in nitrate generally had a low pH (see above) might explain the observed decrease in absolute nitrate removal. Detailed studies on denitrification along selected groundwater pathways with high nitrate loading and low nitrate removal efficiencies underlined the pH effect on denitrification (Hefting, 2003).

5. Conclusion

Groundwater from the semi-confined aquifer played an important role in diluting the shallow nitrate-loaded agricultural runoff causing a decrease in nitrate concentration within the riparian zones. If this physical process is not taken into account in these study sites it leads to a significant over-estimation of the nitrate removal capacity up to 60% depending on the flow path. A detailed understanding of the flow system in riparian zones is therefore necessary to assess nitrate removal. However, besides this dilution effect, biological removal processes also significantly reduced the nitrate concentration in the shallow groundwater in both riparian zones studied. While nitrate-loading rates were high, on average a considerable percentage (38–63%) of the nitrate could be removed, although clear symptoms of "saturation" were visible in the forested zone. Concentrations at this zone were not reduced sufficiently to prevent eutrophication of the surface waters. The low pH of the nitrate-rich groundwater in the forested zone probably limited the denitrification activity, thus explaining the saturation effect in this case. Liming of the agricultural fields and riparian zones might increase the nitrate removal efficiency of these riparian zones, but source-directed measures to reduce leaching of nitrate in agricultural are still to be preferred to protect aquatic ecosystems from eutrophication.

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