Pergamon

PII: S0043-1354(96)00315-6

Wat. Res. Vol. 31, No. 4, pp. 841–849, 1997

0043-1354/97 $17.00 + 0.00

NITRATE REMOVAL IN RIPARIAN WETLAND SOILS: EFFECTS OF FLOW RATE, TEMPERATURE, NITRATE CONCENTRATION AND SOIL DEPTH

HANS P. L. WILLEMS[1], MATTHEW D. ROTELLI[2], DUANE F. BERRY[1]*, ERIC P. SMITH[2], RAYMOND B. RENEAU Jr[1] and SAIED MOSTAGHIMI[3]

Departments of Crop and Soil Environmental Sciences[1], Statistics[2], and Biological Systems Engineering[3], Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, U.S.A.

(First received January 1996; accepted in revised form September 1996)

Abstract—Riparian zones, located adjacent to intensely managed agricultural fields, are thought to play an important role in removal of nutrient contaminants including NO_3^- from groundwater. We studied the effect of flow rate, NO_3^- concentration and temperature on NO_3^- removal in soil columns under saturated-flow conditions. Bibb (coarse-loamy, siliceous, acid thermic Typic Fluvaquent) sandy loam soil was collected from a riparian forest located in Nomini Creek Watershed, Virginia. Soils included in the study were a permanently inundated surface horizon, a seasonally saturated surface horizon, a shallow subsurface horizon and a deep subsurface horizon. Soil columns were infiltrated with NO_3^- amended groundwater at concentrations from 14 to 36 mg NO_3^--N L^{-1}. Column operating temperatures varied between 8 and 20°C and flow rates between 0.01 and 0.09 mL min^{-1}. Following a 48 h equilibrium period, effluent NO_3^- and N_2O concentrations were determined. Denitrification was the primary mechanism of NO_3^- removal, with higher denitrification capacities found in the surface horizons. Effluent NO_3^- concentrations could be described by a linear combination of temperature, flow rate and influent NO_3^- concentrations. Low temperatures and increased flow rates reduced the denitrification capacity in all soils. Our results showed that the NO_3^- removal capacity present in the Bibb soil should theoretically be sufficient to remove most, if not all, NO_3^- from the groundwater at the Nomini Creek study site. However, on-site measurements of NO_3^- concentration in receiving streams indicated that this capacity is not fully realized in the field, suggesting the importance of other factors such as local hydrology and groundwater flow patterns. © 1997 Elsevier Science Ltd. All rights reserved

Key words—soil columns, nitrate removal, flow rate, temperature, soil depth

INTRODUCTION

The intensive use of nitrogen (N) fertilizers and increased production of N-fixing crops has led to increased levels of nitrates (NO_3^-) in ground and surface waters of the Atlantic Coastal Plain (Gambrell *et al.*, 1975; Kaushik *et al.*, 1981; Mostaghimi *et al.*, 1993). High levels of NO_3^- in drinking water supplies can be toxic to infants and cause eutrophication of surface waters. Riparian zones that are located between intensively managed agricultural fields and natural drainage ways may serve as important sites for NO_3^- removal as NO_3^- flows with groundwater through these buffer zones (Jacobs and Gilliam, 1985; Lowrance, 1992; Jordan *et al.*, 1993; Schipper *et al.*, 1993; Haycock and Pinay, 1993; Nelson *et al.*, 1995). Denitrification and plant uptake are believed to be the most important processes of NO_3^- removal in riparian wetlands. High organic carbon contents in surface horizons and saturated soil conditions favor denitrification. Denitrification is desirable because this process removes NO_3^- from the agroecosystem as N_2 or N_2O, while plant uptake results in a N-enrichment of the riparian ecosystem. N-enriched riparian ecosystems may lose their effectiveness for NO_3^- removal over time (Aber *et al.*, 1989; Groffman *et al.*, 1992). The effects of soil parameters, hydrology and temperature on NO_3^- removal processes are not fully understood, but it appears that the hydrology of riparian zones is one of the most important factors governing NO_3^- removal (Gilliam, 1994). Even though many questions remain, there is a general consensus that riparian buffer zones bordering agricultural fields are of major importance in maintaining ground and surface water quality in the Atlantic Coastal Plain. Therefore, information regarding the potential of riparian wetlands to act as decontamination buffer zones should be included in the development of best management practices (BMP), designed to reduce nonpoint source pollution problems.

We evaluated the effects of flow rate, soil and physical factors on NO_3^- removal from wetland soils, representative of the Coastal Plain region of Virginia,

*Author to whom all correspondence should be addressed [Fax: -1 540 231 3075].

in the laboratory using continuous feed soil columns. Models were developed relating groundwater flow rates, NO_3^- concentration and temperature to NO_3^- removal capacities of surface and subsurface horizons of a Bibb sandy loam.

MATERIALS AND METHODS

Soil and site description

The Nomini Creek watershed which is located 80 km northeast of Richmond, Virginia, was selected as the study site because it is typical of the Coastal Plain of Virginia with a land-use activity distribution of approximately 43% agricultural (crop production), 54% woodland and 3% homestead. Also, there are no point source pollution discharges in the watershed to impact water quality. Riparian wetland soils were collected down-gradient from an agricultural field, where corn, small grain and soybeans are grown in rotation. The stream draining this area is approximately 12 m lower in elevation than the field edge at a distance of 60–150 m. The seepage face formed at the outflow boundary of the aquifer generally contains large amounts of organic matter and low dissolved O_2 contents (1–2 mg L^{-1} as determined by an YSI model 57 oxygen meter), conditions suitable for maintaining denitrifying populations. The riparian wetland soils within the watershed were mapped as Bibb (coarse-loamy, siliceous, acid, thermic Typic Fluvaquent) and as a ponded Bibb and also Levy (fine, mixed, acid, thermic, Typic Hydroquent) soils (Nicholson, 1981). These poorly drained and very poorly drained soils, located along drainage ways and adjacent to or near tidal marshes, are frequently flooded. The soils used in this investigation were associated with freshwater marshes belonging to the Bibb sandy loam series. Information on texture, pH and organic matter of the four soil horizons collected are listed in Table 1. The existence of riparian zones in this region is due primarily to topographic restraints on cultivation practices.

Soil samples used for model development were collected in September 1993 at 12 (only six for the deep subsurface horizon) locations equidistant along a 250 m section of the riparian stream. At each location, samples were collected from: (1) a seasonally saturated surface horizon (1–15 cm), (2) a permanently saturated (ponded) surface horizon (1–15 cm), (3) a shallow subsurface horizon (25–45 cm), located 15–30 cm higher in elevation than the ponded surface horizon and (4) a deep subsurface horizon (50–75 cm), located 5 m upgradient from the stream. The ponded surface horizon was located adjacent to the seepage face. Both subsurface horizons are saturated most of the time. Groundwater flows through the surface horizon only during periods of seasonally high water tables. For each horizon and at each of the 12 (or six) locations, soil samples were collected (~200 g wet wt per location) and combined in 4 L polypropylene wide-mouth bottles (one bottle/horizon), thoroughly mixed and transported to the laboratory on ice in coolers. Soil from the ponded surface horizon was wet sieved through a 2 mm sieve to remove large pieces of undecomposed organic matter. These four soils were used in the laboratory to study the effects of groundwater flow rates, NO_3^- concentration and temperature on rates of NO_3^- removal and denitrification activities.

A second set of soils were collected and used in a model validation study. Soils for the model validation study were collected in October 1994 from the original site (site 1) and one other site which was located 0.75 km north of the first site (site 2). Site 2 was located near a riparian stream that bisects two agricultural fields planted in a corn, soybean, small grain rotation. Only the seasonally saturated surface horizon and shallow subsurface horizon were sampled for model validation. For the validation study, soil (from site 1) was collected from six locations equidistant along a 250 m section of the riparian stream. Site 2 soil was collected from four locations along a 50 m section of the riparian stream. Approximately 200 g wet weight of each soil was collected per location and combined (per soil) in 4 L polypropylene wide-mouth bottles, thoroughly mixed and transported to the laboratory on ice in coolers. Column studies for model validation were started within one week of soil collection.

Column preparation and operation

Soils were set-packed into Plexiglas columns (6 cm length, 2.2 cm diameter). The soil was sealed with glass-wool plugs and rubber stoppers. The rubber stoppers were pierced by a 5 cm long and 3.18 mm o.d. SS tube fitted with Teflon tubing. Two (four channel) peristaltic pumps (MCP 2500, Haake Buchler Instruments, NJ) were used to deliver groundwater to the bottom of vertically positioned soil columns at the desired flow rate. Groundwater was collected from the site 1 at a groundwater monitoring well located 3 m upgradient from the stream. Prior to water collection, five well volumes were removed from the well. The groundwater was stored at ~4°C. Just prior to use, the groundwater was analyzed for NO_3^--N concentration and the groundwater NO_3^- concentration was adjusted to the desired value by adding KNO_3. The entire column set-up, including the groundwater reservoir and pumps, was placed in a large incubator for precise (±1°C) temperature control. Each column was run in duplicate. Detailed column operating procedures as well as analytical methods for nitrate and N_2O measurements in the column effluent can be found in Pavel *et al.* (1996) and are not repeated here.

After each run, the soils were removed from the columns and their wet weight and dry weight determined after 24 h drying at 80°C. Porosity of the column packed soils was calculated from the difference between wet and dry weight. Organic C content of the soils was determined by the method of Walkley and Black (1934).

Model development

The effects of influent NO_3^--N concentration, temperature, flow rate and soil horizon on NO_3^- removal in soil columns was investigated using a split plot experimental design. The whole plot temperature was a combination of three factors: influent NO_3^- concentration, temperature and flow rate. Soil horizon was the split plot treatment. To reduce the number of experiments to be conducted, combinations of whole plot factors were determined using a central composite design. For this central composite design, the whole plot combinations were randomly assigned to an experimental run. A total of 20 experimental runs were conducted over a period from February to August, 1994. The whole plot treatment combinations were taken from five different values of each factor. Influent NO_3^--N concentrations ranged between 14 and 36 mg

Table 1. Selected soil properties of the Bibb sandy loam soil used in model development

Soil depth	pH	Organic C (%)	Porosity (%)	Texture
Ponded surface	5.2	9	81	Silt loam, sandy loam, loamy sand
Seasonally saturated surface	4.1	11.5	83	Sandy loam, loamy sand
Shallow subsurface	4.2	1.4	53	Loamy sand, sand
Deep subsurface	4.2	0.07	42	Loamy sand, sand

Table 2. Parameter estimates for β_1, β_2 and β_3, p values and R^2 for multiple regression models

Soil horizon	Intercept	β_1	β_2	β_3	R^2
Ponded surface	17.84	3.69	5.96	−2.09	0.80
	0.0001[a]	0.0012	0.0001	0.0511	
Seasonally saturated surface	18.68	3.94	6.56	−2.60	0.87
	0.0001	0.0002	0.0001	0.0055	
Shallow subsurface	22.55	1.54	5.69	−1.08	0.95
	0.0001	0.0006	0.0001	0.006	
Deep subsurface	23.24	1.37	6.10	−1.49	0.90
	0.0001	0.0136	0.0001	0.0131	

[a]p value.

NO_3^--N L^{-1} with intervals of 5.5 mg L^{-1}. Flow rate levels were set at 0.01, 0.03, 0.05, 0.07 or 0.09 mL min^{-1}, and temperature at 8, 11, 14, 17 or 20°C. The selected values encompass the range of values measured in the field (Snyder, 1995). For each soil, multiple regression using normalized values for the whole plot factors was run to predict effluent NO_3^- concentrations. The whole plot factors were normalized on a scale from −2 to +2 according to the following equation:

normalized value = (value − median value)/interval

The interval was computed as one fourth of the total range of the factor levels. Normalizing the factors on the same scale allowed for evaluation of the effect and determination of the relative importance of each factor on NO_3^- effluent concentrations.

Model validation

Column studies for model cross-validation (seasonally saturated surface horizon and shallow subsurface horizon only) were run at an influent concentration of 25 mg NO_3^--N L^{-1} and a temperature of 15.5°C. Duplicate columns were run at a flow rate of 0.03 and 0.07 mL min^{-1}.

Model cross-validation was performed by comparing the measured NO_3^- effluent concentrations, obtained on the second set of soil samples, with their model predictions using the squared cross-validation correlation (R^2_{CV}), i.e. the squared correlation between the predicted values and the observed values for the cross-validation data set, and the difference between R^2 and R^2_{CF} for each model.

RESULTS AND DISCUSSION

Selected properties of the (site 1) soil horizons used are listed in Table 1. The seasonally saturated surface horizon and both subsurface horizons were all similar in pH (4.1–4.2), but the pH of the ponded surface horizon was less acidic. This is possibly the result of inundation with creek water of a higher pH (6.0) or differences in the types of microbial metabolism supported by these soil environments. When the ponded surface horizon was sampled there was an obvious volatile fatty acid odor present. Regardless of the depth sampled, the subsurface horizons were low in organic matter compared to the two surface horizons. The deep subsurface horizon clearly possessed the lowest amount of organic C. The organic C content of the shallow subsurface horizon is 20-fold higher than that of the deep subsurface horizon, while the surface horizons had a 200-fold higher organic C content than the deep subsurface horizon. The difference in organic C content between the two surface horizons was not significant.

The amount of NO_3^- removed from groundwater passing through the horizons was positively correlated (Spearman Rank correlation coefficient of 0.771) with the amount of N_2O measured in the effluent irrespective of temperature, flow rate and influent NO_3^- concentration. As indicated by the shape of the regression equation, on the average, 76% of the NO_3^--N was transformed to N_2O-N. Hence, the low pH of the studied horizons does not exclude denitrification activity. This was also mentioned by Tiedje (1988). Assuming that our N_2O measurements most likely underestimated the actual amount of N_2O produced because of the presence of some air pockets in the columns, we suggest that denitrification was primarily responsible for the decrease in nitrate concentration. These results are consistent with results of several other studies showing that denitrification acts as the primary mechanism for NO_3^- removal in riparian wetlands (Jacobs and Gilliam, 1985; Jordan *et al.*, 1993; Ambus and Lowrance, 1991; Smith and Duff, 1988; Schipper *et al.*, 1993).

For each of the four soils, between 80 and 95% of the variability in effluent NO_3^--N concentrations could be predicted by multiple regression equations based on normalized influent NO_3^- concentration, temperature and flow rate:

$$\text{Effluent } NO_3^- = \text{intercept} + \beta_1(\text{flow}) + \beta_2(\text{influent } NO_3^-\text{-N}) + \beta_3(\text{temperature})$$

The parameter estimates for β_1, β_2 and β_3, p values, and R^2 for the four models are given in Table 2. As would be expected, the cross-validation experiment indicated that the model for the surface horizon ($R^2 - R^2_{CV} < 0.05$) and shallow subsurface horizon ($R^2 - R^2_{CV} < 0.4$) performed well for soils collected from site 1. According to Kleinbaum *et al.* (1988), differences between R^2 and R^2_{CV} which are greater than 0.9 indicate unreliable models, whereas differences about 0.1 are expected for excellent models. Thus, the model for the surface horizon in particular performs very well. However, the models for the seasonally saturated surface horizon and shallow subsurface horizon did not perform as well as for soils from site 2 (R^2_{CV} of 0.69 and 0.64 respectively). On average, less NO_3^- was removed from groundwater as it passed through site 2 soils. This observation largely reflects differences in microbial activities in the surface and shallow subsurface horizons collected from the two different sites as indicated by the lower denitrification activity in the site 2 soils. We attribute the decreased microbial activities, in terms of NO_3^- removal capacities, to differences in nutrient availability which we believe is reflected in the C content of the horizons. The organic C content of the surface and shallow subsurface horizons collected from site 2 were 9.4 and 0.15%, respectively, which is lower than the recorded values for these same horizons (sampled at the same depth in the profile) at site 1. These results suggest that the amount of organic C present may be a useful covariate when comparing soils of the Bibb series, or possibly other related series, in this region.

Three-dimensional surface response models for the four soils were estimated using the multiple regression equations for a NO_3^--N influent concentration of 9.2 mg L^{-1} (Fig. 1A–D). This NO_3^- concentration was similar to that detected in the groundwater entering the Nomini Creek riparian zone (Snyder, 1995). The surface plot for the seasonally saturated surface horizon (Fig. 1A) was similar to the plot for the ponded surface horizon (Fig. 1B) and the shallow subsurface horizon (Fig. 1C) was very similar to the plot for deep subsurface horizon (Fig. 1D). For each temperature–flow combination, a nitrate removal rate was calculated by multiplying the difference between influent (9.2 mg L^{-1}) and effluent NO_3^--N concentration (as obtained from the multiple regression equation) with the flow rate. The calculated nitrate removal rates are represented by surface contour plots (Fig. 1A–D).

In general, effluent NO_3^- concentrations were greatest for the subsurface soils while surface horizons maintained lower effluent NO_3^- concentrations. Differences in NO_3^- removal capacities among the four horizons were most likely the result of differences in microbial activity which in turn are correlated with organic matter. Surface horizons contained 20–200 times more organic C than the

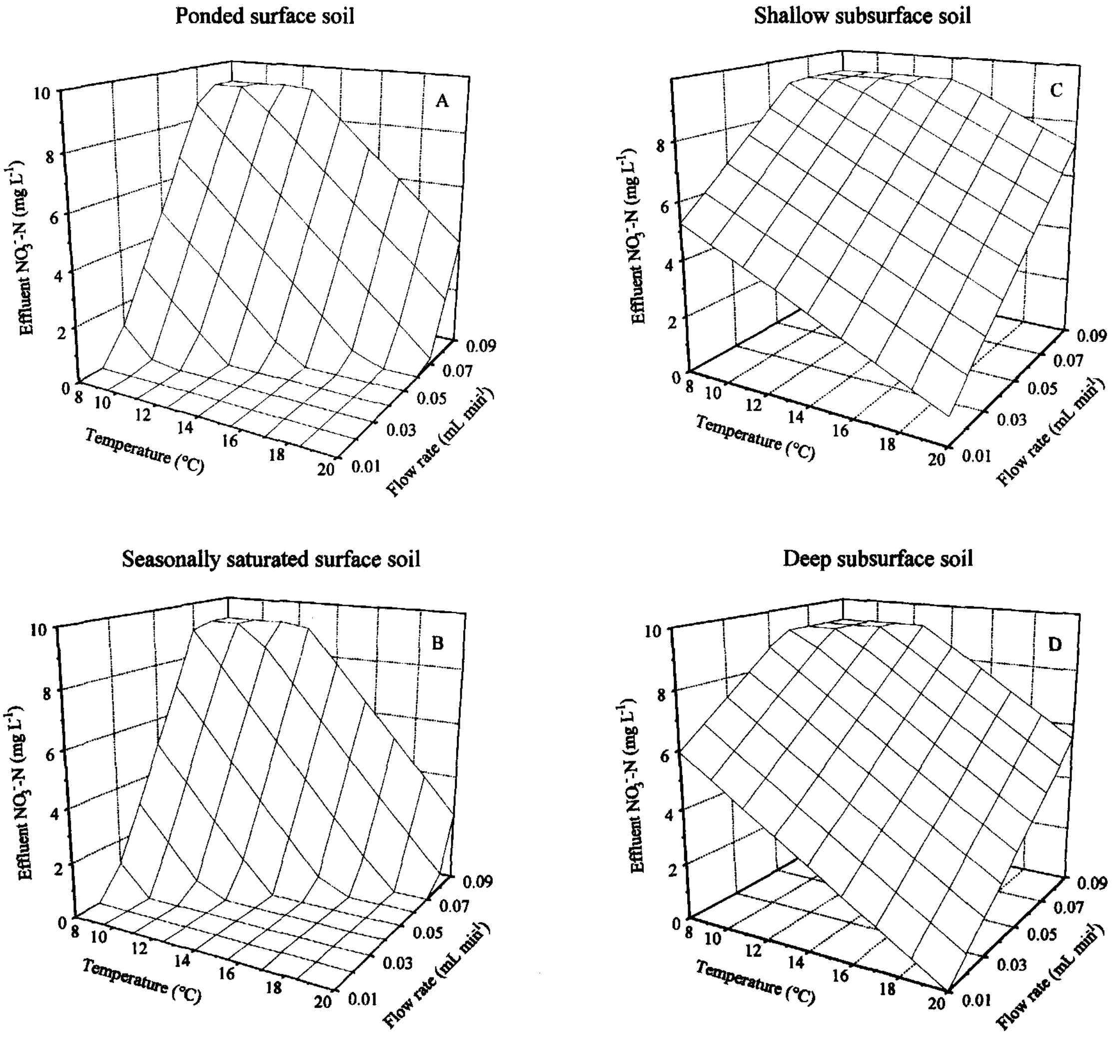


Fig. 1. Predicted effluent NO_3^--N concentration as a function of temperature and flow rate for an influent concentration of 9.2 mg NO_3^--N L^{-1} for columns packed with ponded surface soil (A), seasonally saturated surface soil (B), shallow subsurface (C) and deep subsurface (D) soils.

subsurface soils. Several studies (Lowrance, 1992; Ambus and Lowrance, 1991; Groffman *et al.*, 1992) have also shown that denitrification in riparian wetland soils is highest in surface horizons and depends on organic matter content. Although the subsurface soils were low in organic C content and microbial activity, they still showed significant amounts of denitrification. Hence, in the field, subsurface horizons may still be responsible for most of the NO_3^- removal in riparian wetland zones (assuming that most of the groundwater flows through the often extensive subsurface horizons as compared to the thin surface layer). This is in contrast with work of Groffman *et al.* (1992), Lowrance (1992) and Ambus and Lowrance (1991) who concluded that NO_3^- removal in subsurface soils was not the result of denitrification, but in agreement with work of Smith and Duff (1988) who detected significant denitrification in a sand and gravel aquifer. We did not observe important differences between the two surface horizons, or between the two subsurface horizons. It should be noted that, although all soil columns received the same volumetric flow rates, pore flow velocities were different for each horizon. Pore flow velocity, defined as the volumetric flow rate divided by the porosity, was approximately two times higher in the two subsurface soils (lowest porosities) compared to the surface soils (highest porosities). Nitrate diffusion to sites of denitrification probably becomes limiting at high pore flow velocities. Thus, in addition to reduced microbial activity (as a result of low amounts of organic C), increased pore flow velocity may further reduce denitrification rates in the subsurface soils compared to the surface horizons. Interestingly, no difference between the subsurface and surface horizons with respect to effluent quality was observed at high flow rate–low temperature combinations. It appears that the high flow rate–low temperature combinations retard denitrification regardless of the soil type.

Higher temperatures enhance biological and chemical reactions including denitrification. Indeed, at all flow rates and in all soil horizons, increasing temperature decreased effluent NO_3^- concentrations. For the surface horizons, temperature had no visible effect on effluent concentration at the lowest flow rates, given an influent concentration of 9.2 mg L^{-1}. At the lower flow rates, the denitrification capacity in the surface horizons is sufficient to remove all incoming NO_3^- (9.2 mg L^{-1}) even at the lower temperatures. Effluent NO_3^- concentration in both subsurface soils was influenced by temperature at all flow rates, except at the low temperature–high flow rate combinations where no NO_3^- removal was predicted and temperature effects could not be observed. The surface contour plots (Fig. 2A–D) indicate that the effect of temperature on denitrification rate is highest at the faster flow rates (contour lines closer together). The Q_{10} values were in the range of 1.8–3 at a flow rate of 0.01 mL min^{-1}, and increased to 10 at a flow rate of 0.09 mL min^{-1}. Such high Q_{10} values are normally not observed in biological systems. However, it is important to realize that at higher flow rates the reported Q_{10} values represent a combination of temperature effects (on biochemical reactions) and physical factors (i.e. diffusion). At low flow rates, Q_{10} values will reflect primarily temperature effects on biochemical reactions (expected to be around 2) and will be less impacted by diffusion limitations. Indeed, the Q_{10} values observed at the lower flow rates (1.8–3) were similar to the values reported by Schipper *et al.* (1993) and Reddy *et al.* (1980).

Effluent NO_3^- concentrations were greatly affected by changing flow rates. The large NO_3^- removing capacity in the surface horizons masked the effect of flow rate, especially at the higher temperatures. We observed that denitrification rates initially increased with increasing flow rates and then decreased with further increasing flow rate (Fig. 3A–D). The initial increase in denitrification per unit time was the result of an increased supply in NO_3^- per unit time (higher flow rates). In the subsurface soils the initial increase in denitrification rate was always less than the increase in NO_3^- supply, resulting in an increased effluent NO_3^- concentration. Only at higher temperatures in the surface horizons was the increase in denitrification rate sufficient to maintain zero effluent NO_3^- concentrations with increasing flow rates. With a further increase in flow rate, the denitrification rates started to drop. The flow rate at which denitrification rates started to drop was dependent upon the temperature and soil horizon. The drop started at higher flow rates in the surface horizons compared to the subsurface horizons. Denitrification rates also started to drop at higher flow rates with increasing temperatures. At the higher flow rates, denitrification may be limited by NO_3^- diffusion rates to the sites of denitrification resulting in higher effluent concentrations. This effect is attenuated when a large denitrification capacity is present (e.g. in surface horizons) or at higher temperatures (enhancement of microbial activity).

So far, we have interpreted the models based on an influent NO_3^--N concentration of 9.2 mg L^{-1}. Increasing the influent concentration resulted in an increase in the effluent concentration as indicated by the relatively large and positive value of β_2 (Table 2). Temperature, flow rate and soil type effects were similar as described above. We were not able to accurately determine the effect of influent NO_3^- concentration on the denitrification rate.

Relating the results of our laboratory experiments to NO_3^- removal in the field remains a difficult task. Groundwater temperatures at the study site ranged between 12°C (winter) and 16°C (summer) and the maximum volumetric flow rate was 0.05 mL min^{-1}. The groundwater flowing beneath the agricultural field contained between 7.5 and 9.2 mg NO_3^--N L^{-1}

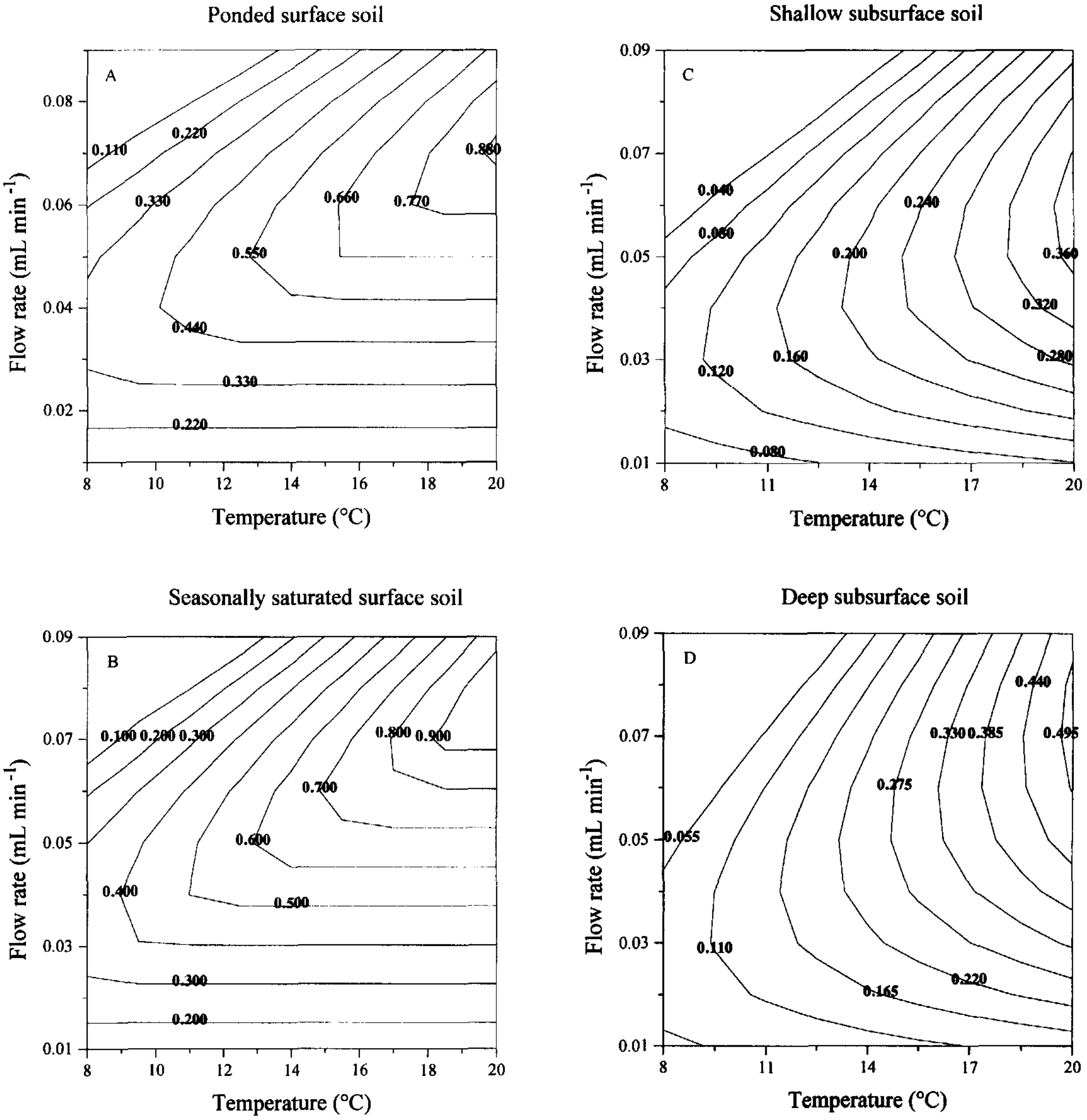
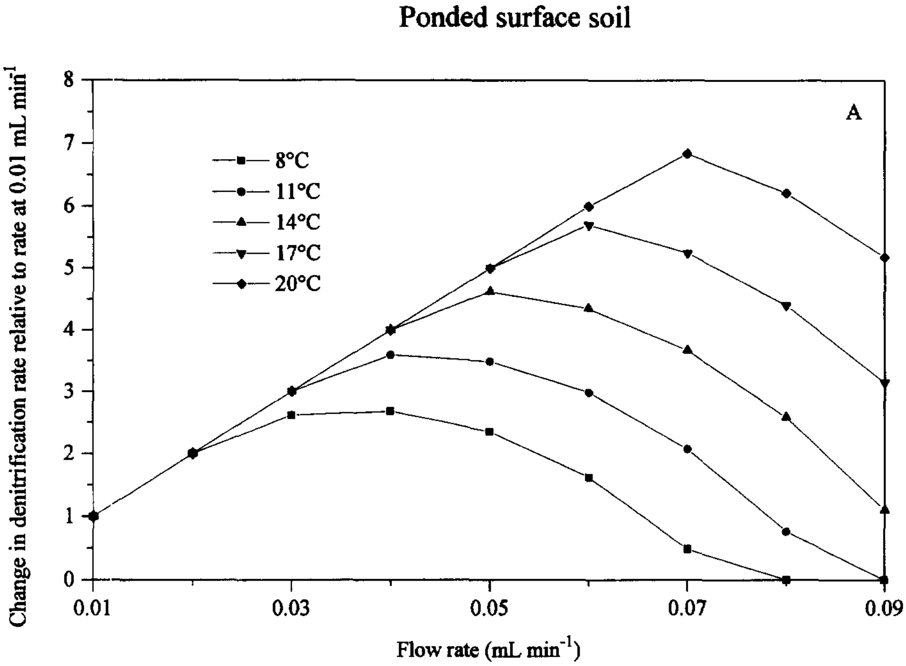


Fig. 2. Calculated denitrification rates (mg day^{-1} column^{-1}) as a function of temperature and flow rates or columns packed with ponded surface soil (A), seasonally saturated surface soil (B), shallow subsurface (C) and deep subsurface (D) soils.

(Snyder, 1995). The minimum column length necessary to obtain zero effluent NO_3^--N concentrations for an influent concentration of 9.2 mg NO_3^--N L^{-1} was calculated based on the multiple regression equations (0.05 mL min^{-1} and 12°C), the fact that the soil columns were 6 cm in length and under the assumption that NO_3^- concentrations decreased linear over the length of the soil column. We calculated 22 and 24 cm for the deep subsurface and shallow subsurface horizons, respectively, and 8 cm for the two surface horizons. The small minimum lengths indicate again that a large NO_3^- removing capacity is present in all horizons. However, groundwater measurements near the stream still contained NO_3^- concentrations ranging from 0.9 to 7.7 mg NO_3^--N L^{-1} (mean 4.4) (Snyder, 1995). Thus, although our experiments showed that a large denitrifying capacity was present in the four horizons, this capacity was apparently not realized in the field. We suggest that the local hydrology and a combination of other factors such as temperature, root depth, depth to water table and variable groundwater flow rates may be responsible for the relatively high NO_3^- concentrations in the groundwater near the stream. Some portions of the groundwater may flow through channels and macropores and thus bypass the sites where denitrification takes place. The importance of local hydrology was also stressed by Schipper *et al.* (1993) and Gilliam (1994). Nelson *et al.* (1995) concluded that high resolution soil and groundwater maps may be needed to accurately assess NO_3^- removal capacity of riparian forests.

SUMMARY AND CONCLUSIONS

Our experiments showed that the riparian wetland soils of the Nomini Creek retain a high capacity for the removal of NO_3^- from groundwater through denitrification. We found that denitrification was higher in the surface soils than in the subsurface soils. Our results suggest that this was primarily caused by differences in organic C content (which influenced microbial activity) and flow characteristics. Though subsurface horizons are less effective in removing NO_3^- from groundwater than surface horizons, they still may be responsible for the bulk of NO_3^- removal in the field because a major percentage of the groundwater most likely flows through subsurface horizons. Nitrate removal was reduced with increasing flow rates and increased with increasing temperatures. Higher flow rates most likely limit diffusion of NO_3^- to sites of denitrification, resulting



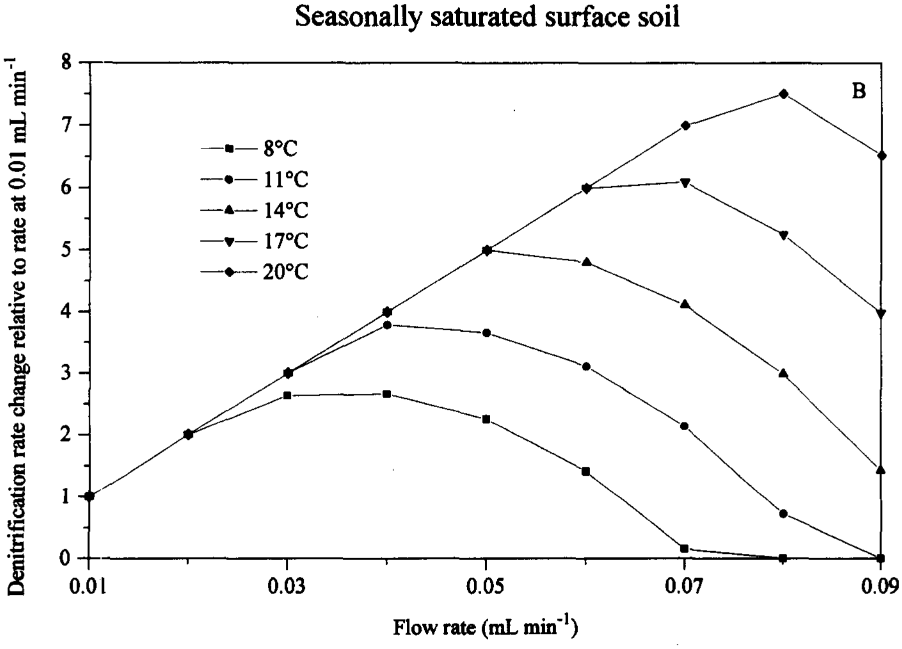


Fig. 3(A) and (B)—*(caption overleaf)*

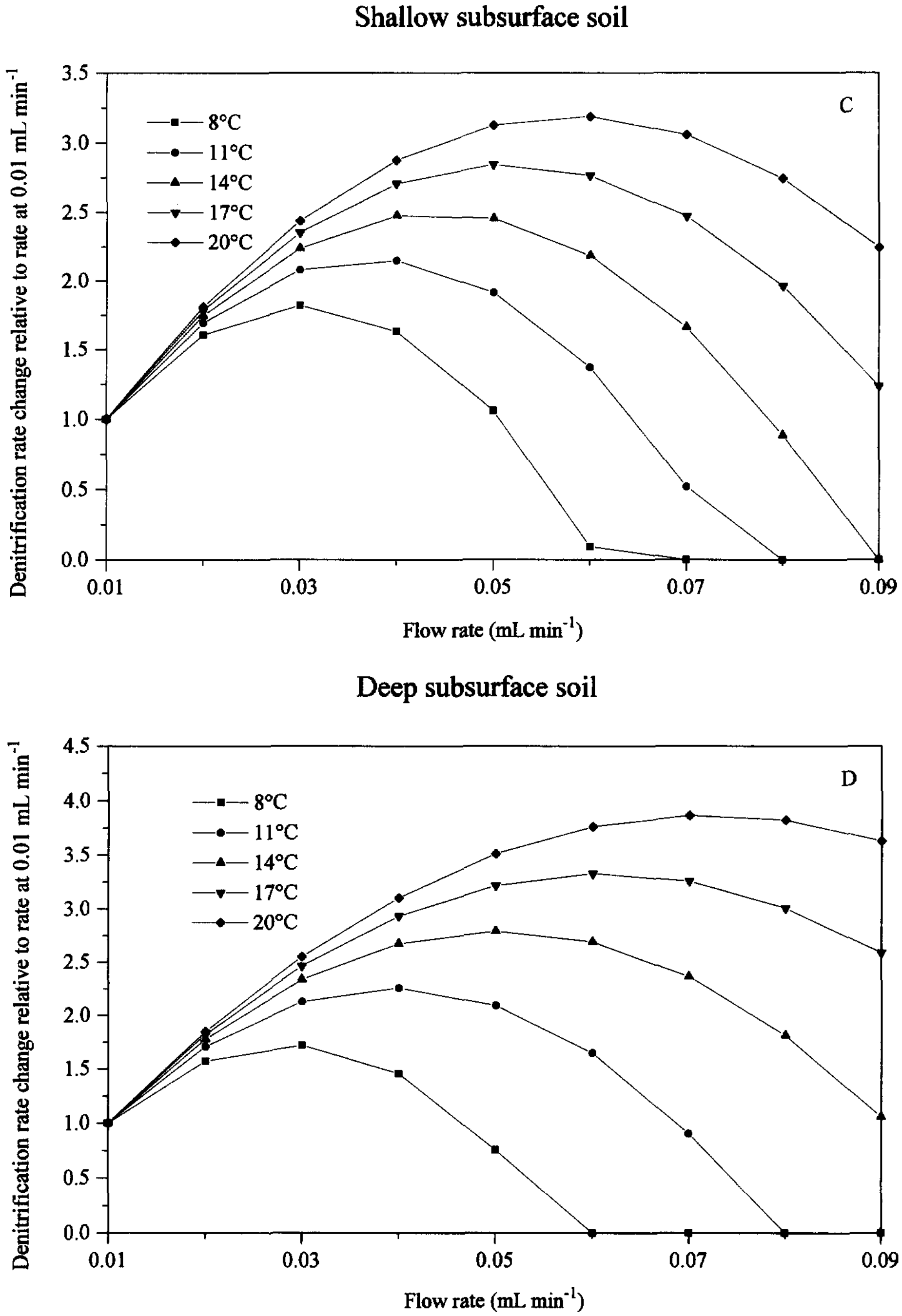


Fig. 3. Relative change in denitrification rate with increasing flow rates at different temperatures (relative change, y = denitrification rate at x mL min^{-1}/rate at 0.01 mL min^{-1}) for columns containing ponded surface soil (A), seasonally saturated surface soil (B), shallow subsurface (C) and deep subsurface (D) soils.

in reduced NO_3^- removal. Field measurements (Snyder, 1995) indicated that the large denitrifying capacity observed in laboratory experiments was not fully expressed in the field. We contend that local hydrology may be responsible for incomplete nitrate removal in riparian buffer zones. Further insight into the local hydrology is required for the development of appropriate BMPs.

Acknowledgement—This research was supported by a grant from the Virginia Water Resources Research Center, Blacksburg, Virginia, USA.

REFERENCES

Aber J. D., Nadelhoffer K. J., Steudler P and Melillo J. M. (1989) Nitrogen saturation in northern forest ecosystems. *Bioscience* **39**, 378–386.

Ambus P. and Lowrance R. (1991) Comparison of denitrification in two riparian soils. *Soil Sci. Soc. Am. J.* **55**, 994–997.

APHA (1992) *Standard Methods for Examination of Water and Wastewater*, 18th edition. American Public Health Association, Washington, DC.

Gambrell R. P., Gilliam J. W. and Weed S. B. (1975) Nitrogen losses from the North Carolina coastal plain. *J. Environ. Qual.* **4**, 317–323.

Gilliam J. W. (1994) Riparian wetlands and water quality. *J. Environ. Qual.* **23**, 896–900.

Groffman P. M., Gold A. J. and Simmons R. C. (1992) Nitrate dynamics in riparian forests: microbial studies. *J. Environ. Qual.* **21**, 666–671.

Haycock N. E. and Pinay G. (1993) Nitrate retention in grass and poplar vegetated buffer strips during winter. *J. Environ. Qual.* **22**, 273–278.

Jacobs T. C. and Gilliam J. W. (1985) Riparian losses of nitrate from agricultural drainage waters. *J. Environ. Qual.* **14**, 472–478.

Jordan T. E., Correll D. L. and Weller D. E. (1993) Nutrient interception by a riparian forest receiving inputs from adjacent cropland. *J. Environ. Qual.* **22**, 467–473.

Kaushik N. K., Robinson J. B., Stammers W. N. and Whiteley H. R. (1981) Aspects of nitrogen transport and transformations in headwater streams. In *Perspectives in Running Water Ecology* (Edited by Lock M. A. and Williams D. D.), pp. 113–119. Plenum Press, New York.

Kleinbaum D. G., Kupper L. L. and Muller K. E. (1988) *Applied Regression Analysis and Other Multivariate Methods*. PWS-Kent Publishing Co., Boston, MA.

Lowrance R. (1992) Groundwater nitrate and denitrification in a coastal plain riparian forest. *J. Environ. Qual.* **21**, 401–405.

Mostaghimi S., McClellan P. W. and Cooke R. A. (1993) Pesticide contamination of groundwater in Virginia: BMP impact assessment. *Wat. Sci. Technol.* **28**, 379–387.

Nelson W. M., Gold A. J. and Groffman P. M. (1995) Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *J. Environ. Qual.* **24**, 691–699.

Nicholson J. C. (1981) *Soil Survey of Westmoreland County, Virginia*. U.S. Department of Agriculture, Soil Conservation Service.

Pavel E. W., Reneau R. B., Berry D. F., Smith E. P. and Mostaghimi S. (1996) Denitrification potential of nontidal riparian wetland soils in the Virginia Coastal Plain. *Wat. Res.* **30**, 2798–2804.

Reddy K. R., Sacco P. D. and Graetz D. A. (1980) Nitrate reduction in an organic soil-water system. *J. Environ. Qual.* **9**, 283–288.

Schipper L. A., Cooper, A. B., Harfoot C. G. and Dyck W. J. (1993) Regulations of denitrification in an organic riparian soil. *Soil Biol. Biochem.* **25**, 925–933.

Smith R. L. and Duff J. H. (1988) Denitrification in a sand and gravel aquifer. *Appl. Environ. Microbiol.* **54**, 1071–1078.

Snyder N. J. (1995) Evaluation of a nontidal riparian wetland as a naturally occurring decontamination zone. M. S. Thesis. Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Tiedje J. M. (1982) Denitrification. In *Methods of Soil Analysis* (Edited by Page A. L., Miller R. H. and Keeney D. R.), Part 2, 2nd edition, pp. 1011–1026. Agron. Monogr. ASA and SSSA, Madison, WI.

Tiedje J. M. (1988) Ecology of denitrification and dissimilatory nitrate reduction to ammonium. *Biology of Anaerobic Microorganisms* (Edited by Zehnder A. J. B.), pp. 179–244. John Wiley & Sons, NY.

Walkley A. and Black T. A. (1934) An examination of the Vegtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* **37**, 29–38.

Yoshinari T., Hynes R. and Knowles R. (1977) Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. *Soil Biol. Biochem.* **9**, 177–83.