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Denitrification in riparian buffer zones

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Executive summary

The three scientific objectives of the project were to: (i) determine suitable techniques for measuring denitrification in riparian zones; (ii) apply these to a number of riparian zones with different hydrological and sedimentological characteristics; and (iii) assess the functional role of riparian zone denitrification in ameliorating groundwater pollution through nitrate loss (with particular concern for the emission of N_2O).

The approach planned was to test and validate various techniques for measuring denitrification in riparian zones at a suitable floodplain site, and then to apply the chosen techniques to other riparian sites of different characteristic. A suitable riparian zone was identified at Cuddesdon Mill on the River Thame floodplain near Oxford. Measurements were made of water and nitrate moving from arable land through the zone and into the river. Techniques to measure denitrification were tested and applied and the factors controlling denitrification measured; the processes controlling nitrate flow and removal at this site were determined. Further measurements of nitrate movement and denitrification were then made in other riparian buffer zones (sites on the Cotswolds, in Shropshire, and in South Devon) and the combined results used to improve understanding of buffer zone processes, determine their true potential for removing nitrate and producing nitrous oxide, and develop better management strategies for buffer zones.

The results show primarily the importance of hydrology (groundwater flow patterns) in determining nitrate removal by denitrification in a riparian zone. While there was considerable potential for denitrification at the Cuddesdon site, this potential was not realised because much of the water moving off the farmland bypassed the riparian zone and entered the river directly via a spring or through gravel lenses beneath the floodplain soil. Management of this site would not reduce nitrate leaching unless the floodplain hydrology could be substantially modified, although creation of a buffer strip might well provide other water quality functions (e.g. sediment trapping), produce more varied habitats for wildlife and be aesthetically pleasing. The main conclusion is that nitrate buffer zones will only operate efficiently where the hydrology of the site is appropriate. In terms of 'greenhouse' gas emissions, losses of N_2O were found to be small, even when denitrification activity within the buffer zone was at its height.

Denitrification in riparian buffer zones

T.P. Burt, K.W.T. Goulding and L.S. Matchett

1. Aims and Objectives

The broad purpose of this study was to assess the functional role of denitrification within riparian zones as a filter for nitrate draining from agricultural land, and as a potential source of nitrous oxide to the atmosphere. The three scientific objectives of the project as laid out in the original proposal were:

(i) to determine suitable techniques for measuring denitrification in riparian zones;

(ii) to apply these to a number of riparian zones with different hydrological and sediment characteristics; and

(iii) to assess the functional role of riparian zone denitrification in ameliorating groundwater pollution through nitrate loss (with particular concern for the emission of N_2O).

These translated into more specific aims for the experimental work to be conducted:

(i) to define the interactions between the hydrological regime of a riparian site, groundwater quality and denitrification;

(ii) to gain further insight into the factors regulating denitrification within the soil environment and the nature of their contribution to its inherent variability;

(iii) to assess the relative role of denitrification as a source of N_2O emission from soil;

(iv) to make a contribution to the compilation of a trace gas flux inventory; and

(v) to facilitate a more informed assessment as to how land management policy and practice may impact the environment, enabling the formulation of more efficient catchment management schemes.

2. Research Methods

The approach planned was to test and validate various techniques for measuring denitrification in riparian zones at a suitable floodplain site, and then to apply the chosen technique(s) to other riparian sites of different characteristics. Denitrification and nitrate in the waters were measured along a sampling sequence across the floodplain, and nitrate loss related to the rate of denitrification, water table level, nitrate and carbon content. We selected a site for testing techniques at Cuddesdon Mill on the floodplain of the River

Thame, about 10 km SE of Oxford (Figure 1). The 100 m wide buffer strip consisted of unimproved pasture for summer grazing and a narrow section of scrub. Above this were several hundred metres of intensively farmed arable land. The floodplain soil was a silty clay. The site was instrumented with a grid network of dipwell piezometers which allowed weekly measurements of the water table and the sampling of ground water, with analysis being made for nitrate (NO_3-N), nitrite (NO_2-N) and ammonium (NH_4-N). A transect was established across the riparian strip, along which soil samples were collected from the top 10 cm and denitrification measured each month over a period of one year, from April 1994 to May 1995. Samples were taken at 6 points, chosen on the basis of topographical, soil and management characteristics of the buffer zone: riverbank [A], oxbow [B], mid-floodplain [C], footslope [D], topslope [E], scrub [F]. Denitrification was quantified in the field using intact core incubation, with and without acetylene-inhibition. Two estimates of potential denitrification were made in the laboratory using the denitrifying enzyme assay (DEA) technique; both involved slurrying the soil in a flask under anaerobic conditions (a N_2 + 10% acetylene atmosphere). In the physically-optimised assay only the indigenous substrates were available for denitrification; in the chemically-optimised assay excess nitrate and carbon were added. Having perfected the incubated core and slurrying techniques and conducted measurements at the Cuddesdon site throughout one annual cycle, further measurements of nitrate movement and denitrification were then made in other riparian buffer zones, near Hook Norton on the Cotswolds, near Bridgnorth in east Shropshire, and at Slapton Ley in South Devon.

3. Results and Discussion

3.1 Removal of nitrate from groundwater

Figure 2 shows nitrate concentrations over the study period for the river, a piezometer in the middle of the floodplain, and for a nearby spring which drains directly into the river from the limestone aquifer (thus bypassing the buffer zone completely). Nitrate levels in the river may be interpreted as a mixture of groundwater diluted by water draining through the riparian buffer zone. If the spring water represents the groundwater before it enters the buffer zone, then these results suggest some nitrate loss even before the groundwater reaches the monitored section. Note that the spring water is well above the legal limit for nitrate in drinking water (11.3 mg l^{-1} NO_3-N).

Only the floodplain water shows the seasonal regime which is commonly associated with nitrate; lack of seasonality in the groundwater suggests a well-mixed aquifer.

3.2 Hydrology of the floodplain-hillslope transect

The six distinct geomorphic units of the Cuddesdon riparian site have distinct hydrologies resulting from the differential influence of the River Thame and hillslope runoff. The topslope [E] and scrub [F] are beyond direct fluvial influence, and are only affected by hillslope processes; the remainder of the transect is affected by both the river and hillslope drainage to varying degrees. The water table data demonstrated a confluence of subsurface flow in the footslope [D]; in so far as groundwater flows through the floodplain sediments, this is an important site where nitrate-rich water returns towards the soil surface. The maximum extent of the floodwater was delimited by the backslope, but such inundation was not always achieved. Greater persistence of flood water and rapidly fluctuating water tables were evident within the middle of the floodplain [C]. Zones [C] and [D] hence form a dynamic fringe between the terrestrial and aquatic components of the riparian zone's hydrology. The merging of these two systems results in a confluence of sediment and nutrient fluxes. A fringe of detritus apparent on retreat of the flood water and the presence of occasional seeps are further evidence of this. Zone [A] is primarily under the influence of the river, the extent varying seasonally with river stage. The soil environment of the oxbow [B] is also dominantly under the control of the aquatic system, most notably during the winter months.

3.3 Groundwater nitrate transect across the riparian zone

Figure 3 shows that there is a decrease in nitrate concentration as groundwater enters the riparian zone. Using spring water as a baseline, some nitrate loss must have occurred upslope of the piezometer network. There is some evidence of nitrate-rich water upwelling at the base of the backslope (zone D, piezometer row 5), especially in the winter months. Closer to the river, nitrate concentrations remain consistently low. There is no evidence of 'true' groundwater within the floodplain alluvium; however, any groundwater which flows into these sediments loses its nitrate content quickly, with an average reduction of *ca.* 75% in nitrate content over a distance of 15 metres.

Probably only a modest fraction of the groundwater passes through the relatively impermeable alluvium; much is thought to flow beneath the alluvium via gravel lenses, thus effectively bypassing the floodplain buffer zone. A gravel lens was encountered at a depth of 2.5 - 3 m. when installing the piezometer network and these are known to be generally characteristic of the Fladbury soil series.

3.4 Potential denitrification activity along the riparian transect as measured using the slurrying technique

In both the physically-optimised and chemically-optimised assays there are no diffusional constraints in the structureless slurry and the atmosphere is anaerobic. The difference between the incubations is that the chemically-optimised assay maximises the chemical substrate availability for denitrifiers via additions of C (glucose) and N (nitrate). The plot (Figure 4) of physically-optimised denitrification activity is, not surprisingly, a substantially muted version of the chemically-optimised (and thus full) potential activity. Both assays depict the same spatial pattern, with more denitrification activity on the floodplain than on the hillslope, and a significant decrease in the oxbow. The gradient in nitrate content of the groundwater evident within the first 15 metres of the floodplain (Figure 3) is not a consequence of greater potential for denitrification within this 'edge' zone therefore. However, although the potential denitrification rates within the hillslope section (zones E & F) are less than those within the floodplain (A-D), comparison of the results from the physically-optimised and chemically-optimised assays suggests that it is the hillslope which is utilising its denitrification capacity to a greater degree. This may help explain the nitrate gradient referred to above.

3.5 Field measurements of denitrification using chambers and intact soil cores

Closed chambers were used in an attempt to measure actual rates of denitrification at the Cuddesdon site. The chamber study showed a diurnal regulation of N_2O-N emissions by soil temperature, and N_2O-N flux as comparable with those derived from field incubated intact soil cores. The chamber-core comparison also highlighted the relative insensitivity of the chambers to the spatial dynamics of N_2O-N production.

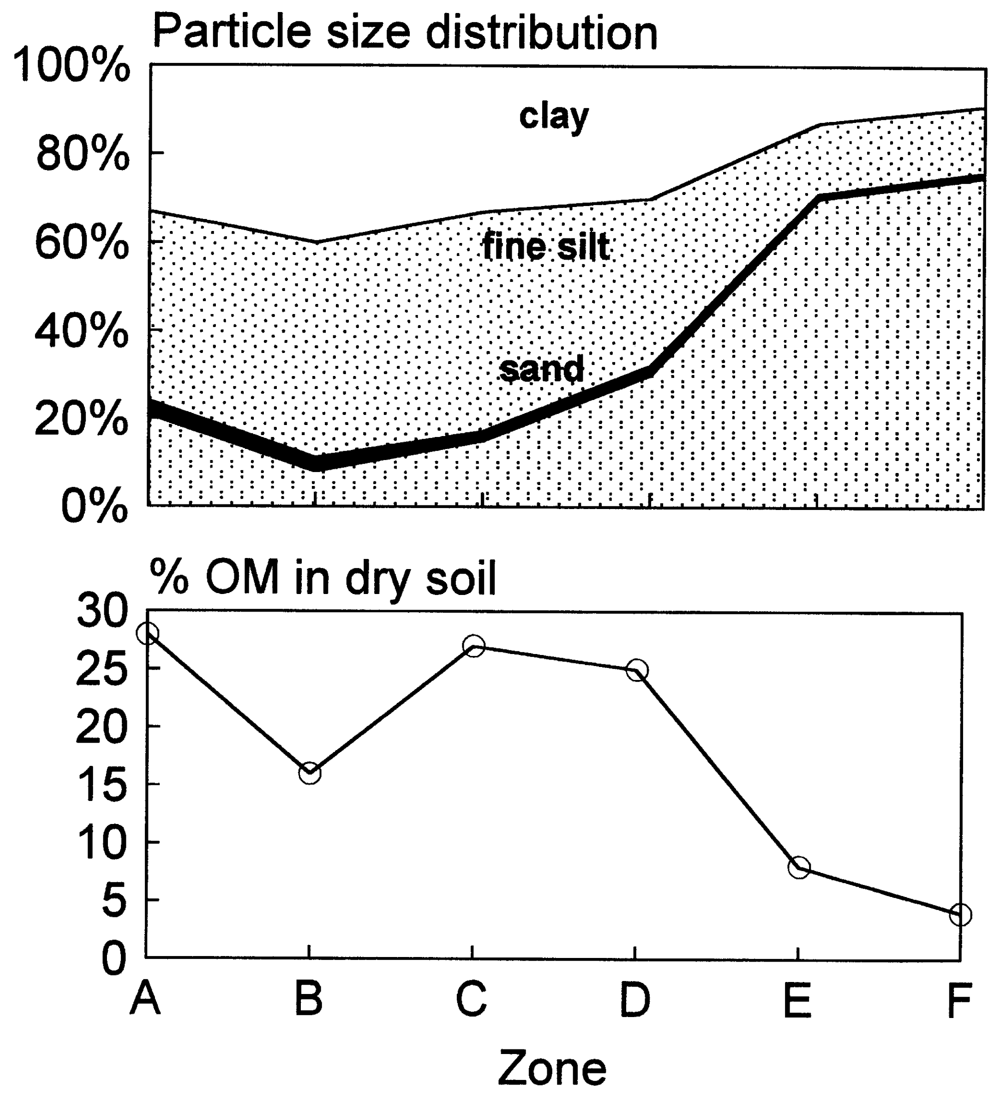

Figure 6. Soil heterogeneity across the buffer zone at Cuddesdon Mill: particle size distribution and organic matter content.

The N_2O-N emissions are regulated by site hydrology and land use. The hydrological regime of the site controls anaerobicity (the wetter months are associated with denitrification and the drier months with nitrification). Nitrogen cycling associated with the grazing of the site is also a fundamental determinant of the N_2O-N source. NO_2^- is a key intermediate in both denitrification and nitrification, with an inhibitory effect on the reduction of N_2O to N_2. Nitrite is generally oxidised too rapidly to allow high soil concentrations to build up. However, exceptional accumulations of soil nitrite may follow periods of urea application or urination from cattle, the urea of which can be rapidly hydrolysed to NH_4^+ within a few hours to a few days. As high concentrations of NH_4^+ are toxic to nitrobacter, the nitrification pathway may be halted at NO_2^-, inhibiting the N_2O to N_2 step of denitrification. Large fluxes of N_2O may thus result from urine patches of grazed pasture, so that emissions from grazed land may be 3 to 4 times those of ungrazed areas, but very variable. Cattle were released on to the study site in late spring, and removed early autumn. Their grazing was confined by a fence to below the scrub section, and they tended to remain on the floodplain section rather than the hillslope. The dynamics of cattle grazing were closely allied to those of N_2O emissions from nitrification; the latter were higher when grazing significantly dominated the N cycle during the spring and summer, particularly within the floodplain.

The greater availability of anaerobic microsites within the fine-textured soil of the oxbow relative to its surroundings promoted an earlier switch from nitrification to denitrification when mineralisation of carbon occurred in early autumn. However, a small denitrifier population, an inherently low soil nitrate content and its diversion of nitrate-rich water prevented denitrification activity within the oxbow reaching the same level as further back along the transect. The dominance of denitrification in the more open textured soils suggests that a juxtaposition of aerobic and anaerobic sites is more conducive to denitrification than complete saturation. It also implies that the water status of the soil need not be a primary factor in the regulation of denitrification; when anaerobiosis is non-limiting, other factors exert an influence.

from 0.1 to 9.1 kg N ha^{-1} $year^{-1}$ (mostly falling below 1); in tropical regions fluxes were 0.2 to 2.6 (mostly below 2), under irrigated and heavily fertilised horticultural crops 19.6 to 41.8, and from cropped peat soils from 7 to 165 kg N ha^{-1} $year^{-1}$. Over half of the 36 sets of fluxes were at or below 2.5 kg N ha^{-1} $year^{-1}$. In this context the 26 kg N ha^{-1} $year^{-1}$ from the Cuddesdon site seems relatively high, but it it represents the 'worst case scenario' with denitrification producing only N_2O-N. During times of most prolific activity (the wet autumn and winter months) N_2 will dominate and the true annual N_2O-N flux is likely to be *ca.* 25 % of this rate - about 6 kg N ha^{-1} $year^{-1}$. Thus relative to other sources of N_2O-N, the environmental benefits to the aquatic system of an actively denitrifying riparian environment outweigh the comparative costs to the atmosphere.

3.7 Physical and chemical controls of potential denitrification

The data from slurry assays suggested that the provision of both excess carbon and nitrate facilitated a general and specific activity increase relative to an unamended system, i.e. the activity of both the microbiomass as a whole (CO_2-C data) and of the denitrifers (N_2O-N data) increased. Adding the substrates in isolation confirmed the distinct spatial and temporal variability to the chemical regulation of denitrification implied by the 12-month comparison of field monitored physiochemistry and denitrification. These earlier comparisons showed the strongest controller of floodplain denitrification to be soil nitrate, and that whilst nitrate was also crucial in the hillslope it was not as limiting, and the strongest control of hillslope denitrification was the readily available carbon. The anaerobic slurry manipulations adding only nitrate or only carbon confirmed these findings: denitrification although ubiquitously enhanced by nitrate addition increased most within the floodplain soil, whilst adding carbon caused a denitrification increase only in the hillslope soil. Over the 12-month study period adding only nitrate always elicited an increase in denitrifier activity and, although there was no strong seasonality to this, the data imply a smaller limitation from nitrate during the autumn and winter months. In the floodplain adding only carbon appeared rather to reduce denitrification, suggesting an alternative fate for nitrate when an excess of electron donors are made available. The management implications of this carbon effect occurring in the field may be substantial, and justify a arable land, bordering the river. Six sites were studied in total, two in each of the three catchments. The 6 sites together provided a sequence of vegetation cover from recently ploughed bare soil, new grass, old grass to shrubs.

1. Bridgnorth, Shropshire

i) Shrubs 80-100 m wide strip of mature vegetation (reeds, grasses and a number of recently planted shrubs and trees).
ii) Grass 30 m wide strip seeded with a rye grass mix in October 1994.

2. Churchend, Cotswolds.

iii) Old Grass 10 m wide strip of permanent pasture.
iv) New Grass. 50 m wide grass strip planted October 1994.

3. Slapton, Devon

v) Old Grass 10 m wide strip of permanent pasture.
vi) Ploughed 10 m wide strip of ploughed soil adjacent to grass strip v)

The 3 sampling depths used to produce a profile at each of the sites were: 0 - 20 cm, 40 - 60 cm, 80 - 100 cm. Slurry assays followed the pattern establishes at the Cuddesdon site.

A comparison of the potential denitrification activity at these 6 sites of varying surface cover showed that the restricted availability of C and N within the soil of all sites prevented the enzymatic potential being attained. Recently ploughed soils or those with young vegetation cover had higher denitrification rates and realised more of their metabolic potential to denitrify than those with relatively older, more established vegetation. Denitrification activity was thus least constrained by substrate availability in the soils that had been recently disturbed (promoting mineralisation and leaching of C and N), and those with a more actively growing vegetation (exuding C and N from roots, perhaps). However, the enzymatic potential to denitrify remained relatively high in the soils with an older vegetation cover, and thus a more established root network and microbial biomass.

- Denitrification activity is concentrated in the surface soil and decreases exponentially with depth.
- Combining the soil 'reactor volume' concept with hydrological data provides a useful aid to estimating denitrification; this technique offers a potentially valuable decision support tool within catchment management schemes.
- The ability of riparian zones to denitrify appears to be greater under recently established rather than mature vegetation.
- Denitrification may be higher (at least temporarily) in freshly ploughed soil compared to vegetated sites by virtue of a higher supply of C and N distinct from that supplied by the vegetation.
- Immobilisation of nitrate or its reduction to ammonium may dominate N transformation under conditions of high soil carbon (high soil C:N ratio).
- Riparian denitrification offers an invaluable form of *in situ* bioremediation of high nitrate water.
- The potential for denitrification within riparian systems is generally underused, primarily because of site hydrology and the lack of a sustained water table throughout the year.
- Even in agricultural catchments, the potential to denitrify within riparian soils may remain confined by the availability of nitrate as opposed to carbon.

4.2 Policy

- The crucial first step in determining the effectiveness of a buffer zone is the development of a thorough understanding of how catchment hydrology and land use interact. If the hydrology of the site allows, or can be managed to allow, denitrification, then further management to optimise the process may be practicable.
- Headwater streams have a large fraction of riparian land compared to the rest of the catchment area. Moreover, such basins comprise a large fraction of the total catchment area. It follows that headwater basins may be the best locations for a co-ordinated scheme of nitrate buffer zone implementation.