

Work Package 2 Task 8:

Characterisation and quantification of key processes controlling the response of soil-plant systems to enhanced N deposition and the leaching of nitrate to surface waters

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CENTRE OF ECOLOGY AND HYDROLOGY
Bangor Project No C01837 – Task 4
NERC - DEFRA Terrestrial Umbrella (Workpackage 2 – Task 8)

**Controls on Soil Nitrogen Processes:
The ¹⁵N pool dilution approach**

by

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August 2002

1. Background

Inorganic nitrogen availability in soil is dependent on the balance between supply and demand of nitrogen within the system. These are determined by several processes:

Supply

deposition
gross microbial mineralisation
gross microbial nitrification

Demand

plant uptake
abiotic fixation
microbial immobilisation

There are many uncertainties surrounding the relative importance of these different processes in semi-natural soils. In this project we aim to reduce the uncertainty surrounding the microbial processes using isotope methods which enable the separation and quantification of the individual processes. Standard incubation methods only permit the end result or net effect of several microbial processes to be quantified (Figure 1).

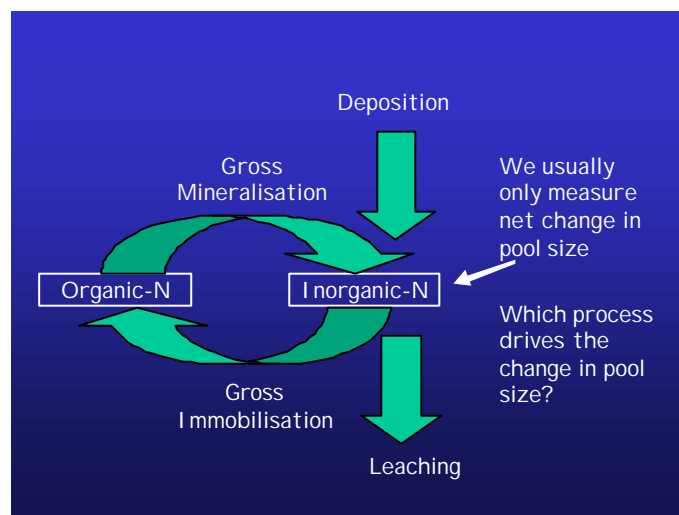


Figure 1 A schematic representation of the microbial processes involved in determining the availability of inorganic-N in soils.

A key question we hope to answer is whether the onset of nitrate leaching in upland moorland soils is due to an increase in the mineralisation rate from the soil organic nitrogen pool or whether it is due to a decline in the immobilisation capacity of the soil. If we are to model the availability of nitrogen in soil we need to gain a greater understanding of the relative change of these different processes under enhanced nitrogen deposition. The overall aim of the study is to identify the underlying processes which result in the onset of N leaching in control and N addition plots focussing on grassland and heathland soils as some data is already available for forest soils.

2. Method

We chose a manipulation site which was close to Bangor to test and develop the isotope method. The site is an upland acid grassland located at ADAS Pwllpeiran which is lightly grazed. Low levels of N have been applied for 5 years to 9m² experimental treatment plots in different doses and forms and under two grazing regimes. For this study we selected to work in the control and ammonium sulphate 20 kgN/ha/yr treatment plots in the lightly grazed area. No significant change in soil nitrogen transformation rates has been observed using conventional techniques.

There are 3 replicate plots per treatment. Six soil cores (5cm in diameter and 9cm in height) were sampled from each plot. Two were spiked with 99% ¹⁵N labelled ammonium sulphate and two with 99% ¹⁵N labelled sodium nitrate. These cores were placed in bags and incubated *in situ*. The two remaining cores were returned to the lab in cold bags. The injections were repeated in the laboratory within 24 hours but immediately the soils were extracted with 1M KCl to determine the initial dilution and loss of ¹⁵N into the extractable N pools. After 1.5 days, two cores incubated in the field were recovered and extracted as for the initial cores. This was repeated after 3 days. The rate of dilution and rate of increase of N content reflects the rate of production and consumption of ammonium and nitrate.

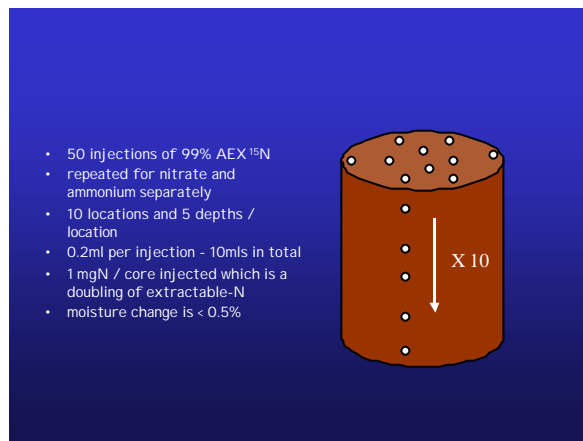


Figure 2 An illustration showing the method of injection of the ¹⁵N substrate.

3. Results

This method was originally developed in the laboratory for intensively managed agricultural soils. The results presented here indicate that the method can also be employed in the field and on semi-natural soils. However, some modifications will be used in future applications due to the extremely slow rates of soil nitrogen transformations we have encountered. These changes include sampling more replicates and extending the incubation time.

Data have been used to calculate rates of gross mineralisation, gross nitrogen immobilisation and net nitrogen mineralisation in the soil from control and nitrogen addition plots (Figure 3). The results indicate nitrogen mineralisation rates are extremely slow and beyond detection limits in most soil cores (i.e. not significantly different to zero). This emphasises the need to increase incubation time in future studies. No significant differences were observed between treatments.

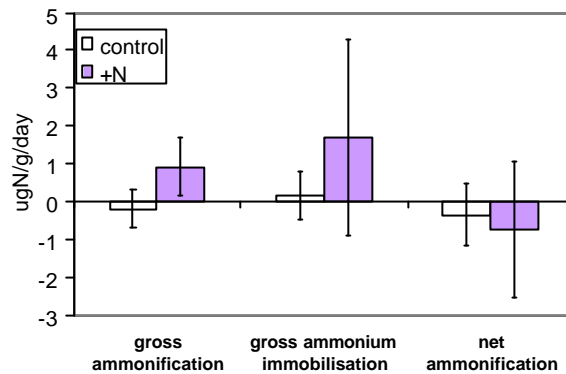


Figure 3 The effect of nitrogen additions on nitrogen mineralisation and immobilisation rates in the control and nitrogen addition plots.

With respect to transformations involving nitrate, positive rates were recorded in contrast to mineralisation (Figure 4). No significant treatment differences were recorded at the $P < 0.05$ level, however, a trend towards lower nitrate immobilisation in the nitrate treatment plot was observed.

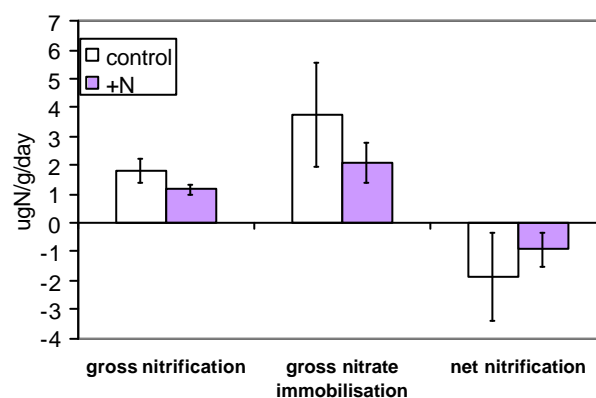


Figure 4 The effect of nitrogen additions on net and gross nitrification in the control and nitrogen addition plots.

4. Conclusions

The results suggest this is a promising method to increase our understanding of the internal functioning of the soil 'black box'. Some modifications will be made as the method is applied to other manipulation sites around the UK due to lessons learnt from this initial trial. Initial results although not significant, suggest that nitrate immobilisation may be suppressed under elevated nitrogen deposition. This may be specifically linked to an increase in ammonium availability affecting the microbial gene expression for nitrate assimilation (Bradley 2001). Further work is needed to test this hypothesis further.

5. References

Bradley R.L. (2001) An alternative explanation for the post-disturbance NO₃⁻ flush in some forest ecosystems. *Ecology Letters* 4:412-416.

CATCHMENT-BASED STUDIES FOR ELUCIDATION OF FACTORS REGULATING NITRATE LEACHING TO UPLAND STREAMS

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Introduction

This report covers work completed at the University of York Environment Department over the 12-month period to the end of June, 2002, as a contribution to Task 8 of the CEH tender document to DEFRA, namely: *Characterisation and quantification of key processes controlling the response of soil-plant systems to enhanced N deposition and the leaching of nitrate to surface waters*. The co-ordinating lead PI for this task is Dr. Bridget Emmett at CEH Bangor. This introduction covers briefly the integrated programme as discussed under objective 8 to set our study in context, though the results concentrate upon what has been achieved at York.

Task 8 stems from the observation that enhanced deposition of N is linked to changes in species composition of vegetation and ecosystem function, and to enhanced nitrate leaching to surface waters. The impacts vary between habitats, sites and over time. The impacts of N deposition to terrestrial and freshwater systems are determined by the availability and fate of the deposited N once it enters the plant-soil system. Thus the dynamics of N species transformations need to be understood quantitatively if N species leaching is to be reliably predicted on a quantitative basis.

We currently are not able confidently to predict the fate of N inputs, their impacts on given habitats and the likely onset of nitrate leaching for particular systems. The development and parameterisation of predictive, dynamic models to address these issues is currently frustrated by limited detailed understanding of some processes and lack of adequate quantification of transfers via these pathways. There are also gaps in our understanding of the interactions between the soil and hydrological process and their interactive influence on nitrate leaching. The current studies will investigate some of these key processes to underpin model development and to provide quantification of the transfers via the related pathways. They are designed particularly to give clearer insight into the causes of spatial and temporal heterogeneity of nitrate leaching in upland catchments. The aims of the York Environment Department research are therefore:

- To assist in quantification of N transfers via key pathways in acid upland, soil systems.
- To evaluate the importance of the interactions between soil and hydrological processes in determining nitrate leaching to surface waters at the catchment level.

Approach:

The York study will comprise of two components: a lab-based study of soil N transformation dynamics and mobility and, primarily, a catchment level investigation of

how the interactions between catchment characteristics, soil and hydrological processes influence N species concentrations in upland rivers, with particular emphasis upon nitrate.

Previous research by the York group, and data generated by the Freshwaters Monitoring programme and by others, have indicated distinctive seasonality patterns in nitrate leaching to rivers and lakes in UK uplands, with concentration peaks in late autumn/winter, and little or no nitrate in river water in summer. Currently under a NERC GANE programme award at York, models have been developed to account for seasonal variation in river water nitrate concentrations using primarily catchment temperature parameters (*Biogeochem.*, in press). While these yield very significant correlations between observed and predicted nitrate concentrations throughout the year, in some catchments there are significant systematic errors in predicted values, with nitrate leakage in some catchments being substantially greater than predicted.

Inter-catchment differences clearly therefore depend upon catchment parameters other than temperature, including for example soil types and their spatial distribution (in 3 dimensions), vegetation type and its spatial distribution, deposition history, aspect, slope and other topographic characteristics, and grazing usage and current and historical soil/catchment management patterns (including heather burning). We are therefore examining in detail the spatial distribution of nitrate mobilization in two catchments studied over extended periods by the Acid Waters Monitoring Network, The Nether Beck, including Scoat Tarn, in the Lake District and the River Etherow catchment off the A628 between Sheffield and Manchester.

Site Descriptions

The Nether Beck catchment covers an altitude range of from 70 m OS at the outflow to Wast Water, to 841 m at Long Crag Steeple on the corrie ridge above Scoat Tarn. The catchment comprises of the mountain corrie at the head of the valley leading into a classical U-shaped valley leading west initially, and then south to Wast Water. The underlying geology comprises predominantly of Ordovician tuff and plagioclase-phyric andesite lavas of the Borrowdale volcanic group. The steeper slopes of the corrie and of the valley sides are dominated by boulder fields and by scree. The shallower slopes are covered by rough grass and sphagnum underlain by peaty rankers and till, but surface boulders are still common. The majority of the soils are thin, though there are sporadic patches of deeper soils and peats. The area is characterised by rapid runoff, the mean annual runoff being >2300 mm of the 2700 mean rainfall.

The headwaters of the River Etherow catchment cover an altitude range of from 300 m OS at the v-notch weir to 633 m in the SW corner. The catchment comprises *calluna* and *vaccinium* moorland interspersed with patches of grassland (*agrostis* and *molinia*) and some areas of deciduous woodland. *Juncus* is abundant on wetter areas. The lower slopes contain both improved and rough grazing and are mainly utilized for sheep grazing. The upper areas are mainly grouse moor. The underlying parent material is millstone grit interspersed with bands of marine deposited mudstone. Mean annual rainfall is 1480 mm with the mean annual runoff being reported to be >529 mm.

Sampling Approach and Analysis

The sampling program so far consists of monthly stream-water sampling at intervals along the main stem of the Etherow and Nether Beck, together with sampling from the main tributaries just upstream of the confluence. These are shown by the blue line on the map below in Fig. 1. The monthly sampling programme includes 13 sample sites in the Etherow catchment and 16 in the Nether Beck catchment.

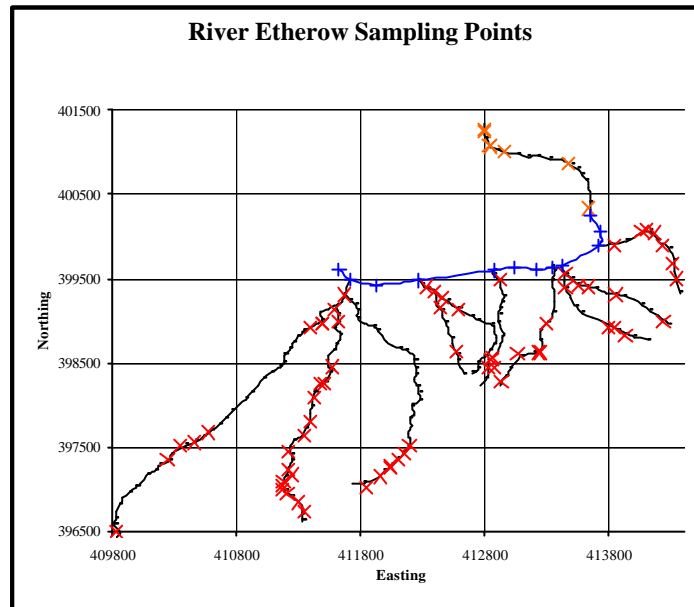


Fig. 1. Sampling points used in the Etherow catchment. + = main stem monthly sampling points, - = main tributary sampling points, and x = extra tributaries sampling points.

During late May and early June of this year, high intensity sampling was carried out at the Etherow by Smart, Clark, Cresser, with help from Crowe, Moberley and Stockley, PhD students in the Environment Department, with a view to identifying the catchment characteristics associated with leaching of each particular N-species at differing concentrations. Over 300 samples were taken at 100-m intervals along all the main tributaries (black dashes in Figure below) with minor tributaries sampled as they were crossed (red crosses).

All samples have been analysed for pH, Alkalinity, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Org-N as well as the major cations and anions. Analysis of the high intensity sampling will be completed by the end of July 2002.

Results

Preliminary results from the monthly sampling programme suggest, from the link between both ammonium and nitrate concentrations and pH of river water for the

Etherow (Fig. 2), that ammonium and nitrate leaching to stream waters in autumn under high flow conditions are particularly associated with adjacent acid, peaty soils. This is also true for DON. This gives rise to significant -ve correlations between both ammonium or DON and pH or alkalinity in the stream waters. This suggests that the rate of utilization of ammonium inputs (both internal and external) is low in these very acid soils. With one notable exception, the Scoat data fit the same plot (note the scale differences).

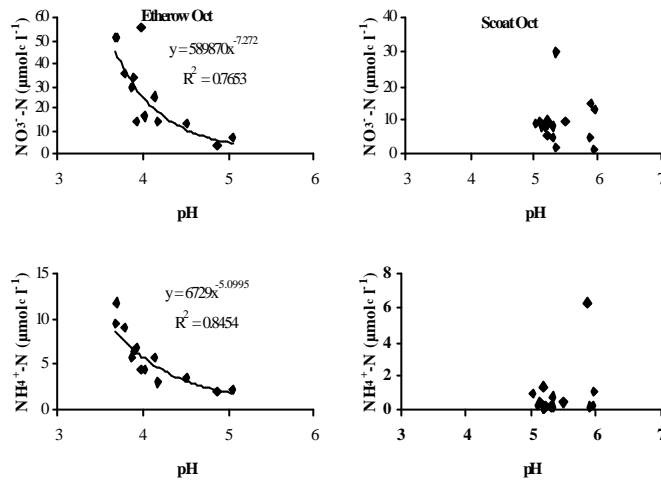


Fig. 2. Relationships in October 2001 between nitrate (upper graphs) and ammonium (lower graphs) and river water pH for the Etherow (left) and for Scoat Tarn (right) catchments.

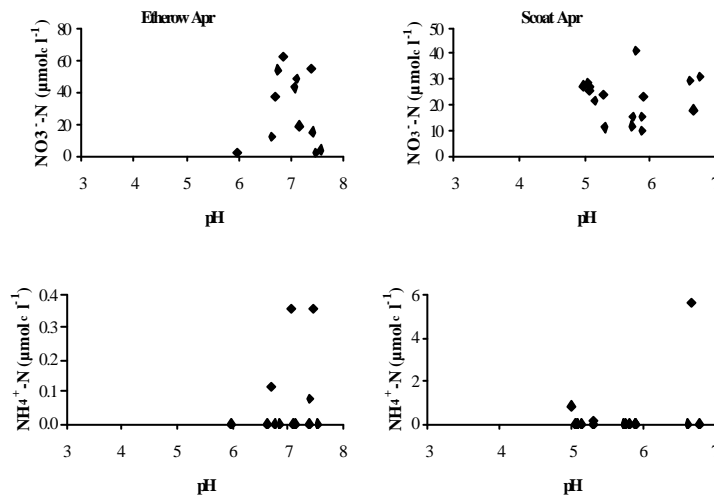


Fig. 3. Relationships in April 2002 between nitrate (upper graphs) and ammonium (lower graphs) and river water pH for the Etherow (left) and for Scoat Tarn (right) catchments.

The thinner, less acidic soils of the Nether Beck catchment, together with higher rainfall volumes, produce lower stream water ammonium and DON concentrations.

The monthly data indicate that higher levels of nitrate leaching were associated with the more acidic conditions under high flow conditions in Autumn, but not at near-base flow conditions in April (Fig. 3). This implies that residence time may have a major impact on the fate of nitrate inputs, possibly highlighting the need to be able to quantify nitrate-N transformation dynamics. Lower flows during the winter months also lead to lower stream water ammonium and SON concentrations, indicating less flow through organic surface horizons and possibly that longer residence times may lead to greater absorption of ammonium on exchange sites lower down in the more mineral horizons.

Tributary 1

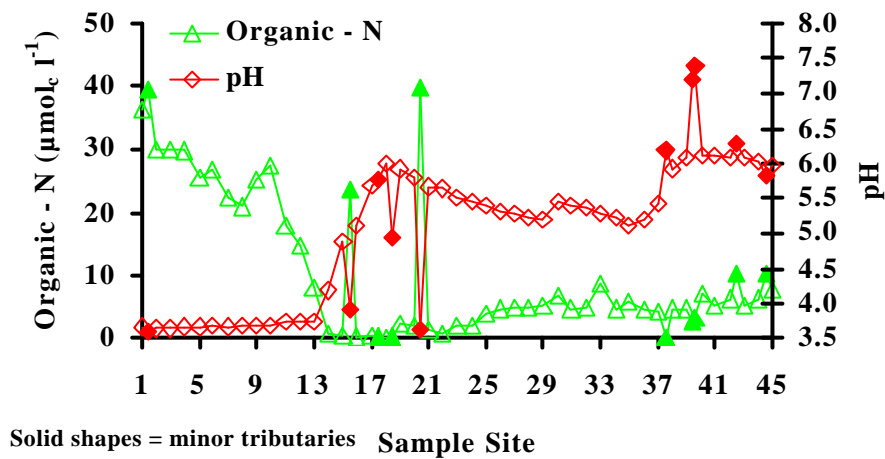


Fig. 4. Change in DON concentration and pH of river water samples as a function of sample number in the intensive summer sampling programme of 2002.

The water analysis data from the high intensity sampling programme in the summer of 2002 corroborates the results from the monthly sampling for DON (Fig. 4) and for ammonium concentration (Fig. 5). The higher stream water concentrations of ammonium and DON once again originate from the more acidic, peaty soils. Minor tributaries originating from acid flushes or peat (plotted as solid triangles or diamonds in Figures 4 and 5) also emphasize this point for both ammonium and DON.

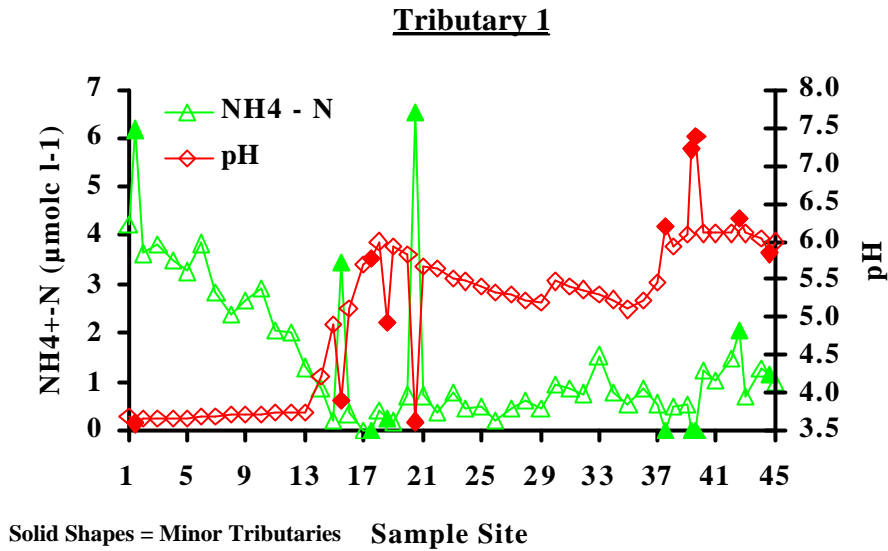
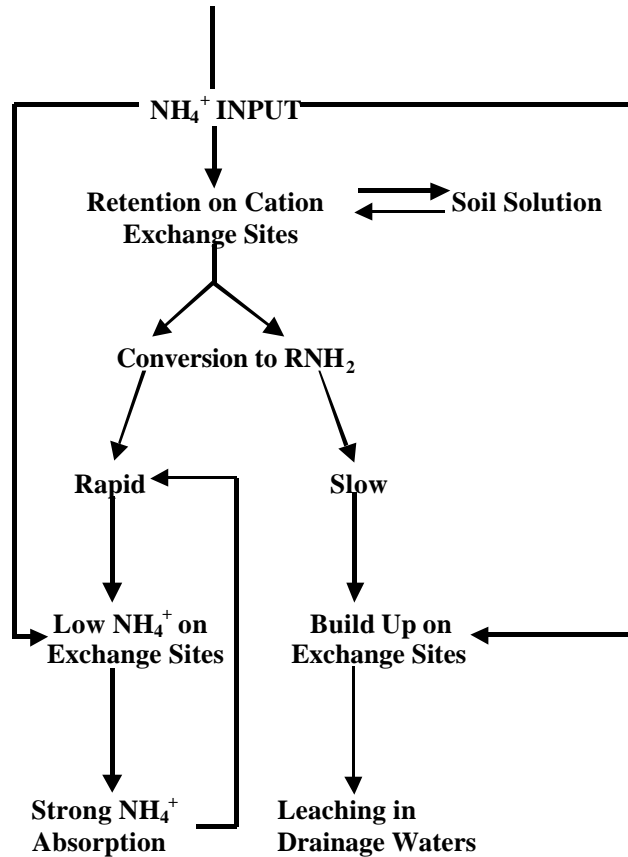


Fig. 5. Change in ammonium-N concentration and pH of river water samples as a function of sample number in the intensive summer sampling programme of 2002.

Even based upon this preliminary examination of the data obtained to date, it is possible to construct a flow diagram representing the mechanism for regulation of leaching of ammonium inputs through acid peats or peaty soils. Atmospherically deposited ammonium input equilibrates with the soil, being held on either the cation exchange sites or in solution. This soil solution ammonium is then converted biologically to organic N species. In unpolluted, less acidic soils, and even peats, this conversion may be rapid, leading to more ammonium leaving exchange sites and being transformed in turn to organic N. Such stripping of ammonium facilitates the absorption of subsequent ammonium inputs from the atmosphere. Thus the system is being regulated by biological transformation rate, so that simple physico-chemical equilibrium is not attained. However, under highly polluted, more acidic conditions, such as those found at the Etherow, conversion of ammonium through biological activity is relatively much slower. This leads to a build up of ammonium on exchange sites and therefore greater equilibrium concentration in soil solution and hence greater leaching to drainage waters. Under these conditions, physico-chemical equilibrium becomes the important regulating process. This is summarized in Fig. 6 on the following page.

Fig. 6.

**Possible Routes of Atmospherically Deposited NH_4^+ - N
Through Acidic Upland Soils**



The analytical data from the high intensity sampling programme in the Etherow catchment clearly show high levels of nitrate leaching from both peaty and the more mineral soils virtually throughout the catchment. The continuously saturated *sphagnum/carex* flushes, however, show very low concentrations, but in these soils favourable conditions for denitrification predominate so low nitrate concentrations could be predicted. Low nitrate concentrations are also found in drainage waters from areas of improved grazing. This is probably due to greater utilization of nitrate by the grasses, although other factors may also be playing a part.

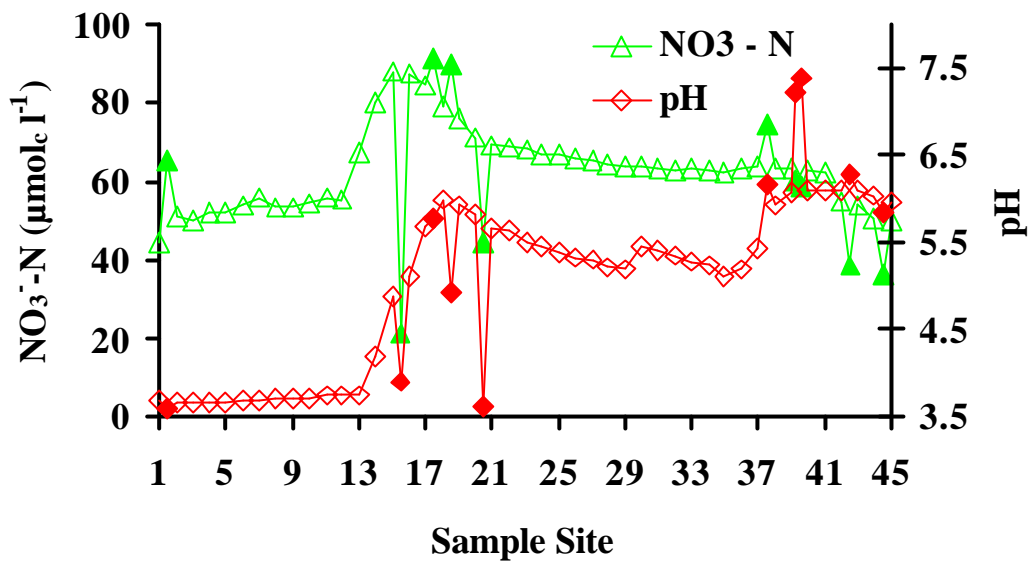


Fig. 7. Change in nitrate-N concentration and pH of river water samples as a function of sample number in the intensive summer sampling programme of 2002. Minor tributary results are denoted by slid symbols.

Future Programme

The project so far has been predominately field based, and this is set to continue. The monthly sampling programme will continue till May 2003 and a further high intensity sampling programme is to be completed at Nether Beck. However, intact core experiments are also to be completed to investigate nitrification rate changes with soil depth in relation to soil type and temperature. This procedure will involve injection of dilute ammonium solution via horizontal rhizon samplers, followed by nitrate extraction via the same samplers after a suitable time delay. This procedure will be applied to soils selected on the basis of N species concentrations in adjacent surface waters.

Soil microcosms are also to be used to assess factors influencing the transformation dynamics of ammonium and nitrate inputs, since these determine whether or not ammonium and nitrate leaching from soils will occur.

Catchment characteristics and accompanying numerical data are also currently being installed on a GIS system. Data sets include: IH-DTM, HOST Class and Rivers Network, BGS solid and drift geology and stream sediment chemical data. We are also collating soil data from colleagues at Silsoe and rainfall volumes from local EPA sites. The GIS will then provide data such as slope angle, aspect and altitude for any point, and will enable easy correlation of catchment characteristics with stream water and soil chemical variables.

We therefore feel that we are on target to deliver on our objectives from this project, as most of our initial surveys are complete and sampling is well under way. The majority of data for incorporation onto the GIS has also been collected.