CONTROLS ON TRANSFER OF NITROGEN DEPOSITION TO SOILS THROUGH TO UPLAND RIVERS

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ABSTRACT

Upland areas of drainage basins are often regarded as sources of water with negligible nitrate concentrations, which beneficially dilutes nitrate from farmland runoff down stream. However, some upland catchments in GB exhibit substantial levels of leaching of nitrate, ammonium, and DON, even in the summer months when biological N uptake might be expected to retain atmospheric N inputs. To help understand and quantify the factors regulating the leaching of N species from soils in such catchments, we have used intensive temporal and spatial sampling in an upland area heavily polluted by atmospheric N deposition and known to give rise to high levels of nitrate leaching, even in summer months. From monthly sampling at 13 sites, higher ammonium, nitrate and DON concentrations appeared to be associated with water draining more acidic soils, especially under high flow conditions. A spatially intensive sampling programme (>300 samples) at base flow in early summer also showed that elevated nitrate concentrations were associated with heather burning. Studies of N species transformation dynamics in peat clearly showed why burning may lead to elevated nitrate concentrations in adjacent streams.

Keywords: nitrogen deposition, ammonium, nitrate leaching, upland drainage basins, integrated management

INTRODUCTION

While minimisation of N eutrophication of surface waters may be a desirable facet of integrated catchment management, it is difficult to define diagnostic criteria for soils or catchments that are indicative of thresholds for onset of nitrate or ammonium leaching. Currently therefore we are unable to predict quantitatively and precisely the fate of N inputs to specific natural and semi-natural habitats. The development and parameterisation of predictive, dynamic models to address the issue of nitrate and ammonium leaching to upland streams is limited by inadequate understanding of what controls the dynamics of some key transformation processes. There are also gaps in our understanding of the interactions between the soil and hydrological process and their interactive influence on leaching of N species.

Previous research by the authors using bi-weekly data from 59 upland and lowland agricultural catchments in north-east Scotland showed distinctive and consistent seasonality patterns in nitrate and ammonium leaching to rivers and lakes in UK uplands, with concentration peaks in late autumn/winter, and little or no nitrate or ammonium in river water in summer (Edwards *et al*., 1985, Chapman *et al*., 2001, Clark *et al*., 2002). It has been shown in this region that peat in the riparian zone is particularly susceptible to nitrate leaching, though the level of leaching is reduced during the summer period of active growth (Black *et al*., 1993). We have developed a model to account for seasonal variation in river water nitrate concentrations using primarily catchment temperature parameters (Clark *et al*., 2002). While this yielded very significant correlations between observed and predicted nitrate concentrations throughout the year, in some catchments there were 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 possibly soil characteristics and their spatial distribution (in 3 dimensions), vegetation type and 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 have therefore examined the spatial distribution of nitrate mobilization in a catchment previously studied over extended periods by the UK Acid Waters Monitoring Network, the River Etherow catchment between Sheffield and Manchester. This paper investigates importance of some of these key parameters, to give clearer insight into the causes of spatial and temporal heterogeneity of nitrate and ammonium leaching in upland catchments.

SITE AND METHODS

The study was comprised of two components: a catchment-based investigation of how the interactions between catchment characteristics, soil-type and hydrological processes (as reflected in discharge conditions) influence N species concentrations in upland rivers, and a laboratory-based study of soil N transformation dynamics, to test the hypothesis that that measurement of N transformation rates in soils may provide a useful diagnostic criterion for N saturation.

The headwaters of the River Etherow catchment cover an altitude range of from 300 m OS 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. Nitrogen deposition to the catchment is estimated to be in excess of 25 kg ha^{-1} yr^{-1} (NEGTAP, 2001). Stream-water was sampled monthly over 18 months along the main stem of the Etherow, and its main tributaries just upstream confluence points. These are shown in Fig. 1.

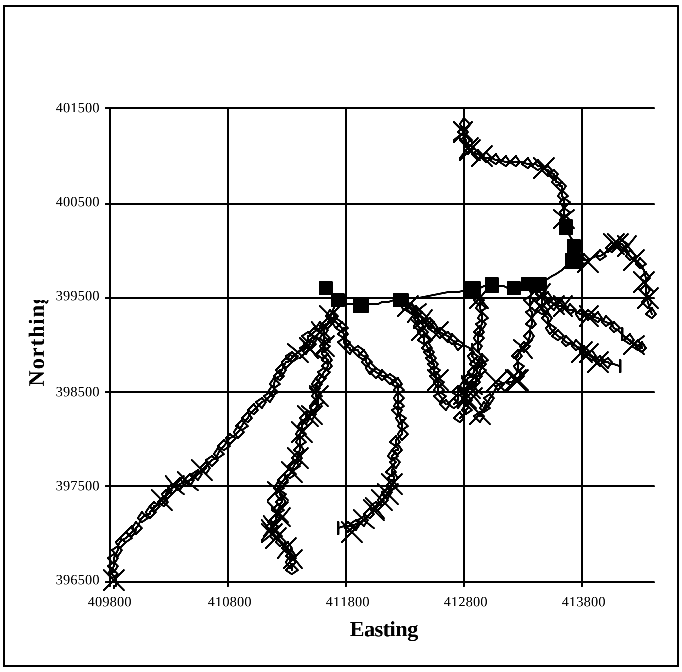

Figure 1. *Sampling points used in the Etherow catchment. (■), main stem monthly sampling points, (◇), main tributary sampling points, and (×), extra tributaries sampling points.*

During late May and early June of 2001, a high intensity sampling was also carried out at the Etherow catchment. Over 300 samples were taken at 100-m intervals along all the main tributaries (Fig. 1). All samples were analysed for pH, alkalinity, NH_4-N, NO_3-N and organic-N as well as the major cations and anions.

To investigate N transformation dynamics, peat samples from 5-15 cm depth were collected from areas of *Calluna* moorland at the Etherow catchment. Four sites were chosen in close proximity, where there had been no burning for a decade, very recent burning (no sign of regeneration), or burning had taken place two and five years prior to sampling. Four individual soil samples from each site were mixed thoroughly by hand, and roots removed. The four soil samples were reduced to two 200-g replicates for each of the four post-burn ages by thoroughly mixing 100-g samples of pairs of soils. Each sample was removed from the refrigerator for the minimal amount of time possible to prevent effects from warming of the sample. Moisture content was measured on duplicate 10-g sub-samples of each soil thus produced.

Sub-samples (5 $^{+}/_{-}$ 0.1 g) of each peat were weighed into a series of eighteen 100-ml bottles, and to each 1 ml of a 625 µg ml^{-1} NH_4^+-N solution (as $(NH_4)_2SO_4$) was added dropwise. After 0, 3, 7, 24, 72, and 120 h, 25 ml of 1 M KCl was added to triplicate bottles, and the bottles were shaken for 1 h. The contents were filtered into clean, labelled bottles, and refrigerated at 4 °C, prior to analysis. Replicates of the soil samples were used, together with controls containing 1 ml deionised water instead of NH_4^+-N solution.

An identical experiment was performed in parallel, but with 1 ml of 625 µg ml^{-1} NO_3^-- N as KNO_3 added to the 5-g soil sample instead of 1 ml of 625 µg ml^{-1} NH_4^+-N.

The NH_4^+-N and NO_3^--N contents of the samples were determined using a Bran and Luebbe Auto Analyser.

RESULTS

A preliminary assessment of the temporal and spatial distribution of catchment analytical data did not reveal any significant relationships between N species concentrations and topographic parameters. Nor was a soil map of the catchment useful, because of its limited resolution. However, when the spatial distribution of nitrate concentrations was compared with an air-photograph of the catchment, there did appear to be a link between elevated N species concentrations and areas of heather burning.

The results from the monthly sampling programme showed some very strong links between both ammonium and nitrate concentrations and pH of river waters for the Etherow river system at periods of high to moderate flow, suggesting that these species were most readily mobilized from more acid soils. For example, the R^2 values for power relationships for the six highest flows, in reducing order of flow, were 0.710, 0.765, 0.474, 0.447, 0.184 and 0.349 for nitrate and 0.839, 0.845, 0.769, 0.621, 0.597 and 0.707 for ammonium. The relationships are also illustrated graphically in Fig. 2. The corresponding months were February (02), October (01), November (01), March (02), August (02) and November (02). In the April to September months, significant relationships were in addition observed for ammonium in June, July and August, during periods of moderately high flow, but for nitrate the relationship was only significant in June (R^2, 0.636). Whenever trends were found, higher nitrate and ammonium concentrations were always associated with higher acidity. They were similarly negatively correlated with alkalinity values.

Cursory examination of Fig. 2 might appear to suggest that the relationships depend upon the concentrations of both ammonium and hydrogen ion being driven by the concentration of the mobile anion, nitrate. However it has to be pointed out the molar concentrations of sulphate and chloride exceeded those of nitrate by at least 2 - to 3- fold, so in this instance, soil type distribution and hydrological pathway almost certainly are responsible for the inter-relationships.

Dissolved organic nitrogen (DON) behaved similarly to ammonium and nitrate, though correlations tended to be weaker. The water analysis data from the high-intensity sampling programme in the summer of 2002 corroborated the relationships found in the monthly sampling between DON and ammonium concentrations and pH. The links between DON or ammonium and acidity could be very clearly seen when spatial trends in pH and DON concentration along the lengths of individual tributaries were compared (see, for example, Figs. 3 & 4).

Two-way ANOVA of the extractable N species data showed no significant change over time (5 days) in the concentrations of ammonium or nitrate extracted from the four peat soils. The apparent recoveries over time of added ammonium- and nitrate-N for each peat type (period after burning) are shown in Fig. 5. The burnt peat gave significantly (at $p \leq 0.001$) more ammonium than all other soils, and the peat at 2 yr post-burn gave significantly more ammonium than the peat at 5 yr post-burn. The recently burnt and 2 yr post-burn peats gave significantly more nitrate than the other two peats.

DISCUSSION

The fact that even after 5 days there was very small net change in the nitrate concentrations extracted from the peat soils from this heavily polluted site shows that the peat microflora have a very low requirement for N, and any biotic removal of N inputs from the atmosphere is likely to be a direct consequence of uptake by plants (Edwards *et al*., 1985) during periods of active growth. Uptake of N by litter microflora may also be important (e.g. Bringmark, 1980, Duckworth and Cresser, 1991). Nevertheless, more nitrate was obtained in the most recently burnt and two yr post burn peats. This, plus the negligible to limited plant N uptake for these soils, explains why there was a clearly visible link between the spatial distribution of higher nitrate concentrations and recent heather burning. Behaviour in this heavily N-polluted peat is in marked contrast to that in peats from a less polluted area of north-eastern Scotland, where biological immobilization of added ammonium was very pronounced over 5 d (Dawod, 1996). The high recovery of ammonium-N for the peat from the recently burnt area could partly reflect the fact that loss of vegetative cover would result in smaller reduction of exchangeable ammonium in this peat by plant N uptake over the growing season. Loss of vegetation canopy would also probably result in reduced N deposition to the site, however.

Based upon examination of the results obtained, 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 less polluted 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.

The analytical data from the high intensity sampling programme in the Etherow catchment clearly showed significant levels of nitrate leaching from both peaty and the more mineral soils virtually throughout the catchment. However some minor tributaries exhibited very low nitrate concentrations. These appeared to flow through continuously saturated *sphagnum/carex* flushes, however, and in these soils favourable conditions for denitrification predominate so low nitrate concentrations could be predicted. Two examples of this can be seen in Fig. 7, which shows how nitrate-N concentration varied along the length of one major tributary and in associated minor tributaries flowing into it. 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.

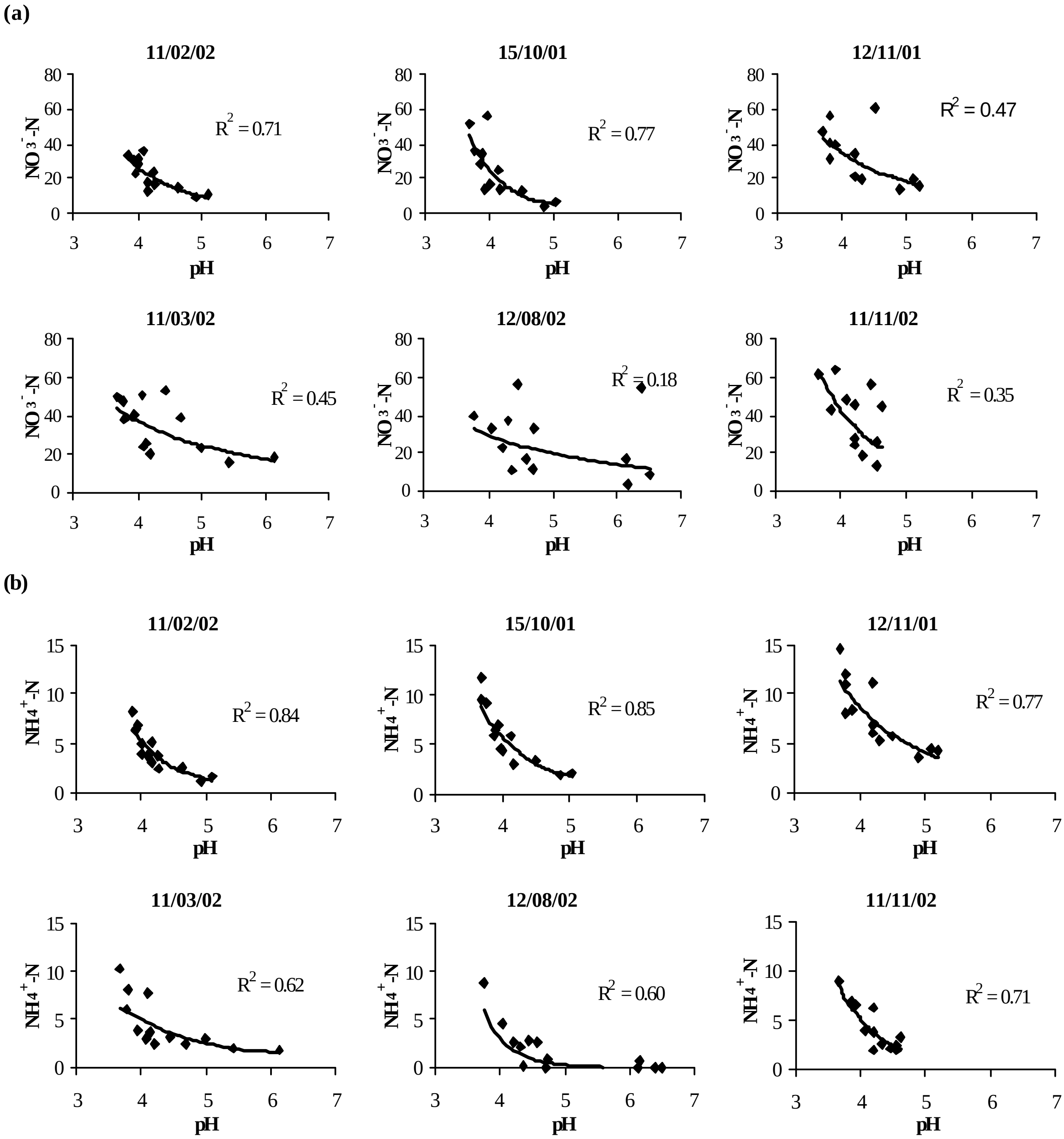

Figure 2. *Relationships between (a) nitrate-N and pH (µmol$_c$ l^{-1}) and (b) ammonium-N and pH (µmol$_c$ l^{-1}) in stream waters for the six highest flows sampled (top left = highest, bottom right = lowest) from the River Etherow catchment, Derbyshire, UK.*

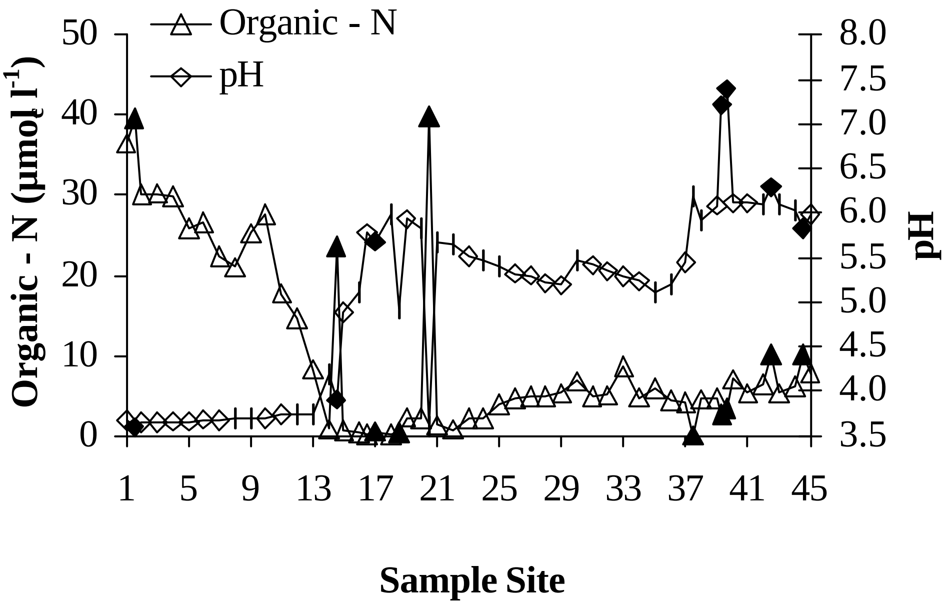

Figure 3. Change in DON concentration and pH of river water samples as a function of sample number along a major tributary in the intensive sampling programme. Solid symbols are for minor tributaries at confluence points.

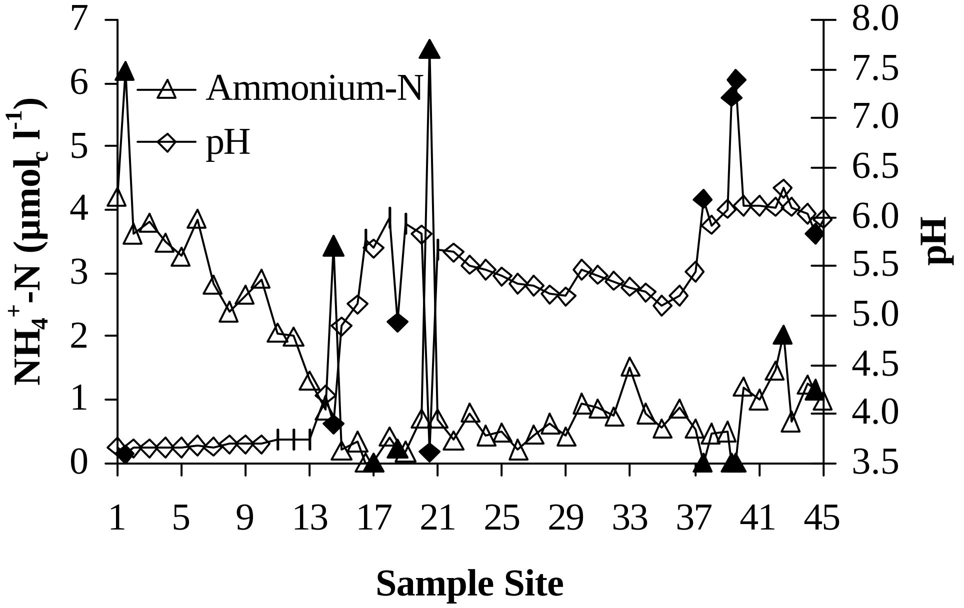

Figure 4. *Change in ammonium-N concentration and pH of river water samples as a function of sample number along a major tributary in the intensive sampling programme. Solid symbols are for minor tributaries at confluence points.*

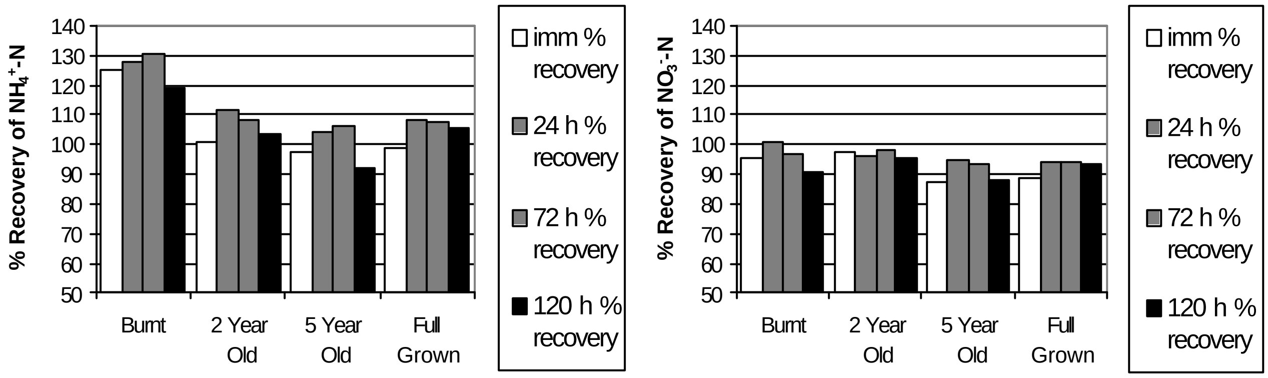

Figure 5. *Effects of post-burn period and time upon the recoveries of added ammonium-N and nitrate-N. Data are corrected for the initial water contents of the most peats.*

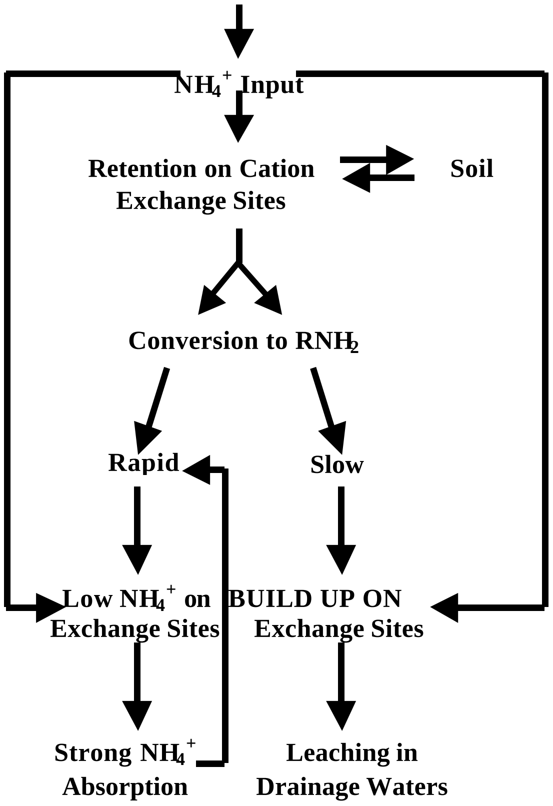

Figure 6. *Possible routes of atmospherically-deposited ammonium-N through acidic upland soils into surface waters.*

While high nitrate mobility appeared to be primarily associated with the more acidic, peaty soils, especially in immediate post-burn years, in some tributaries the impact of improved grazing, and possibly residual liming effects may be important. Thus in Fig. 7, pH and nitrate are positively correlated using data along the length of a single stream. This is to be expected, as liming of organic-rich, upland soils will accelerate mineralization and nitrification processes. However such effects counteract the trends discussed earlier. Moreover this interpretation of Fig. 7 is not unequivocal, because of the possible occurrence of ground water inputs at the Etherow catchment.

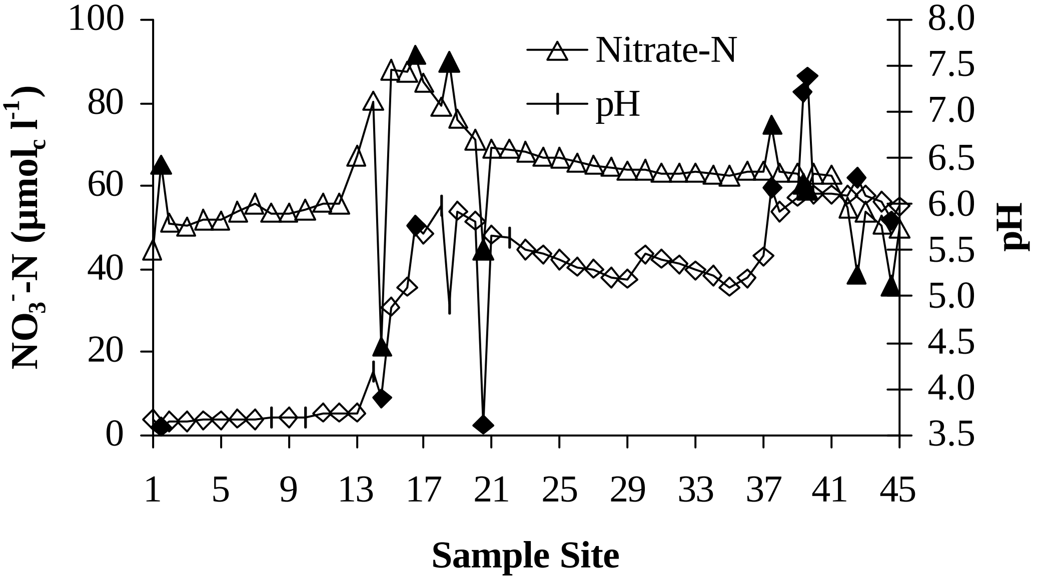

Figure 7. *Change in nitrate-N concentration and pH of river water samples as a function of sample number in the intensive summer sampling programme of 2002. Minor tributary results are denoted by solid symbols. Note that some of these tributaries drain very boggy areas, and give acid waters with very low nitrate concentrations.*

CONCLUSIONS

Peaty soils in the Etherow catchment are N saturated, and have severely limited capacity to retain N deposition inputs. As a consequence both ammonium and nitrate leaching into the river system may be observed even in the summer months, especially during periods of high flow. Comparison of the results of this study with those in that by Dawod (1996) suggests that monitoring dynamics of N-species transformation over ca. 5 days may be a useful approach to providing a diagnostic test for N saturation status of peat soils.

ACKNOWLEDGMENTS

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