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The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland

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Abstract. Data from 13 catchments with no arable land in Northern Scotland were used to develop empirical linear regression models of average monthly NO_3^- concentrations and average summer and winter concentrations for NH_4^+, dissolved organic N (DON) and dissolved organic carbon (DOC) as a function of catchment characteristics. All catchments displayed a pronounced seasonal NO_3^- cycle. Variation in monthly mean NO_3^- concentration within and between catchments could be predicted from mean monthly air temperature using separate regression equations for temperatures < and $\geqslant$ 5 °C. Soil type, climate and land use influenced NH_4^+ concentrations. In summer, concentrations of NH_4^+ were largest in catchments with extensive areas of brown forest soils, which are less acidic and more base-rich than other upland soils. However, concentrations declined with increasing conifer cover and summer rainfall. In winter, however, % conifer cover had a positive effect, while higher temperature and higher humus iron podzol cover had negative influences. DON concentration decreased with increasing catchment elevation in both summer and winter. Surprisingly, concentrations of DON only displayed a positive relationship with percentage peat cover in the summer. The most important factor controlling DOC concentration was soil type, with a positive relationship being observed between DOC and peat and humus iron podzol coverage. Elevation was also important, but only in the winter when concentrations were negatively correlated with maximum catchment elevation. Overall, multivariate regression equations explained the spatial and seasonal variability in N species concentrations over a range of catchments within Northern Scotland.

Introduction

Over the past decade interest has grown in the capacity of catchments to retain nitrogen inputs, whether of fertiliser origin (Domburg et al. 2000) or from atmospheric pollution (Aber et al. 1989; Stoddard 1994). This was initially stimulated by interest in the quality, and especially the NO_3^- concentration (Heathwaite et al. 1993), of surface and ground waters contributing to potable water supplies, and more recently by interest in the impacts of N on the trophic status of fresh as well as marine waters (e.g. Howarth et al. (1996)).

The link between NO_3^--N concentration in rivers and the proportion of arable land use in their catchments is now well established (*e.g*. Edwards et al. (2000), Lee et al. (2000) and Scholefield et al. (1996)). Models such as INCA depend upon land use data for prediction of NH_4^+ and NO_3^- concentrations in the water of major river systems (Whitehead et al. 1998a, 1998b). Recently Wade et al. (2001) showed that INCA could simulate, to a first approximation, the variation in annual stream-water NO_3^- concentration along the length of the River Dee in northeast Scotland. However, few studies have attempted to model NO_3^- concentrations in rivers draining upland catchments containing no arable land. This partly reflects the fact that in a drainage basin with no arable land use, NO_3^- concentrations are small and may not represent the major form of N present (Reynolds and Edwards 1995).

In most studies of soluble N in aquatic ecosystems, emphasis has been placed on the behaviour and transport of dissolved inorganic N forms, almost to the exclusion of organic forms (Chapman and Edwards 1999). These N-containing organic compounds are collectively referred to as dissolved organic nitrogen (DON). In upland streams, DON can account for a high proportion (15 to 95%) of the total dissolved N (TDN) present (*e.g*. Adamson et al. (1988) and Chapman et al. (1998), Russell et al. (1998), Edwards et al. (2000), Campbell et al. (2000). The relative importance of inorganic and organic N species to total dissolved nitrogen (TDN) in rivers of upland Britain displays marked regional variation (Chapman et al. 1998). While ammonium N contributed less than 7% of TDN in all regions, DON contributed from 14 to 69% of TDN. In addition, NO_3^- and DON display contrasting seasonal patterns; NO_3^- concentrations were larger in the winter, while DON concentrations were larger in the summer (Chapman et al. 2001).

As increased leaching of NO_3^- can lead to the acidification or changes in the trophic status of upland waters (Edwards et al. 2000), it is important to understand the controls on concentrations of N species in stream water in semi-natural temperate ecosystems. High inputs of atmospheric N can exceed the retention capacity of soils and biota, resulting in saturation of the terrestrial N cycle and the leaching of significant amounts of NO_3^- (Aber et al. 1989). Changes in stream water NO_3^- concentration, particularly in its seasonal pattern, have been proposed as an indicator of terrestrial N saturation (Stoddard 1994). Afforestation and agricultural modification of upland soils, irrespective of whether N fertiliser has been applied or not, have also been shown to enhance NO_3^- leaching into upland streams and rivers (Roberts et al. 1989; Reynolds et al. 1994; Reynolds and Edwards 1995). Improved drainage and liming are both likely to increase N mineralisation and the concentration of NO_3^- leaching from upland soils.

In upland rivers of Britain, it has long been known that NO_3^- concentrations and fluxes both display a pronounced seasonal pattern, being lower over summer and early autumn than in winter or spring (Edwards et al. 1985). The effect reportedly is due to uptake from intercepted precipitation by vegetation (Edwards et al. 1985) as well as by litter horizons (e.g. Bringmark (1980)), the N uptake being reduced at lower temperatures (Duckworth and Cresser 1991). Thus it may be hypothesised that nitrate inputs in winter precipitation falling on upland catchments will, at least in part, pass unchanged into a river whereas those in summer precipitation will be retained within the catchment due to higher biological demand. Considerable inter-year variations in peak NO_3^- concentration have also been observed that have been ascribed to a number of contrasting climatic factors. These include summer drought (Reynolds et al. 1992), summer temperature (Murdoch et al. 1998), winter freeze-thaw (Mitchell et al. 1996) and the North Atlantic Oscillation Index and mean winter temperature (Monteith et al. 2000).

Recently Worrall and Burt (1999) have discussed the relative merits of detailed mechanistic approaches to NO_3^- modelling compared with simpler empirical models. They point out that the latter may be derived for a scale appropriate to a specified management problem, require fewer inputs, and are less complex in computational terms. They developed a model that very effectively predicted seasonal variations in N concentrations in lowland catchments. One objective of the present study was to see whether a simple empirical model based upon readily available catchment data could be developed for predicting seasonal variations in NO_3^--N concentrations in rivers draining semi-natural catchments over the whole of northern Scotland. As few studies have attempted to predict other N species, it was also decided that an attempt should be made to produce simple empirical models that could predict the between-catchment variation in NH_4^+-N and DON concentrations in northern Scotland. A similar approach would be used for DOC, to see if DOC and DON were subject to similar controls.

Overall, the main aim of this paper was to examine the extent and causes of variation in N species across northern Scotland, and to develop and test regression models that could predict concentrations of N species using national data sets or published data. It was hoped that such models could then be applied to other upland catchments without the need for recalibration. The models were constructed using river solute composition data collected in previous studies (Cresser et al. 2000; Edwards et al. 2000; Chapman et al. 2001) and by the Scottish Environment Protection Agency (SEPA), soils data from the Macaulay Land Use Research Institute (MLURI), and meteorological data from the British Atmospheric Data Centre (BADC 2000).

Methods

Study sites

The study included data from 13 catchments located in the Cairngorm and Highland regions of Northern Scotland, UK (Figure 1). The catchments range in size from 2.8 to 331 km^2 and are dominated by semi-natural vegetation (Table 1). No catchments contain any arable land and all have $< 3\%$ land that is classified as improved grazing.

Table 1. Grid references and selected catchment characteristic data for the 13 catchments used.

Site No.	Name	Grid ref.	Area (km^2)	Altitude range (m)	Land cover(in order of abundance)
1	Halladale	NC891561	205	23–580	Blanket bog, coniferous woodland, moorland, rough grazing, montane
2	Strathy	NC836652	112	9–346	Blanket bog, coniferous woodland, moorland, montane, rough grazing
3	Cassely	NC472022	188	3–998	Moorland, blanket bog, coniferous woodland, rough grazing, montane
4	Oykel	NC403001	331	16–998	Rough grazing, blanket bog, coniferous woodland, montane
5	Carron	NG942429	138	6–1053	Moorland, montane, blanket bog, coniferous woodland, rough grazing
6	Nevis	NN116742	77	4–1344	Montane, moorland, rough grazing, coniferous woodland
7	Tromie	NN789995	130	240–951	Moorland, blanket bog, montane, rough grazing, coniferous woodland
8	Linn of Dee	NO061896	158	360–1310	Moorland, blanket bog, montane, coniferous woodland, rough grazing
9	Quoich	NO118911	60	350–1197	Moorland, montane, blanket bog, coniferous woodland; broadleaf woodland, improved grazing
10	Girnock	NO325957	30	240–862	Moorland, blanket bog, coniferous woodland, rough grazing; improved grazing, broadleaf woodland
11	Meall Dubh	NO346935	2.8	240–563	Coniferous woodland, moorland, rough grazing
12	Allachy	NO466938	28	200–887	Moorland, coniferous woodland, blanket bog; broadleaf woodland
13	Muick	NO350929	102	240–1155	Moorland, blanket bog, coniferous woodland, montane, rough grazing; improved grazing, broad-leaf woodland

Six of the catchments (sites 8–13 in Figure 1) are upland sub-catchments in the relatively unpolluted River Dee catchment, which has an area of approximately 2100 km^2. It is typical of several UK catchments in that it contains both upland and lowland sub-catchments (Langan et al. 1997). The western part of the catchment, where the six study catchments are located, shows a transition from montane and heath type vegetation on the highest summits to heather (*Calluna vulgaris*) moorland on the upper and middle slopes. This area is considered upland (> 300 m) and extends over $\approx 60\%$ of the total catchment area. Some lower slopes are used for the establishment of managed deciduous and coniferous forest. The other seven study catchments (Figure 1, sites 1–7) were distributed throughout Northern Scotland; sites 1–6 were located within the Scottish Highlands and site 7 in the Cairngorms. See Chapman et al. (2001) for further details.

Nitrogen and carbon concentration data

For catchments 8–13, water samples were collected every 14 days, from June 1996 to May 1997. The sampling strategy and analytical methods used for major cations and anions, pH, DOC as well as N species have been discussed fully elsewhere (Smart et al. 1998; Edwards et al. 2000). Monthly samples of river water were collected from catchment 7 between April 1997 and March 1998, and from catchments 1–6 between June 1997 and May 1998. Nitrate-N and NH_4^+-N were determined colorimetrically using an autoanalyser and TDN was determined as NO_3^- after oxidation. The DON concentration was calculated by difference between total dissolved nitrogen and inorganic nitrogen (NO_3^- + NH_4^+). DOC was measured using a Labtoc carbon analyser (Smart et al. 1998).

Catchment characteristic data

Catchment boundaries were derived from 1:50 000 Ordnance Survey maps using a GIS ARC-INFO package (Wade 1999). Using the catchment boundaries, the percentage of different land cover within each catchment was obtained from the Land Cover of Scotland database (MLURI 1993). Data on the catchments' soils were taken from the 1:250 000 Soil Survey (MISR 1984) and the 1:63 360 survey (MISR 1963). Further information on the soils, land use, and climatic characteristics of catchments 8–13 may be found elsewhere (Langan et al. 1997; Smart et al. 1998). To look for possible effects of soil parent material upon N species variation between catchments, the geological groupings described by Smart et al. (2001) were used. As in previous investigations, distributions of catchment characteristics over whole catchments and just in riparian zones (50 m either side of the stream channel) were employed (Cresser et al. 2000; Smart et al. 2001).

Data analysis for seasonal trends

Time series plots were drawn for the 13 individual catchments for NH_4^+-N, NO_3^--N, DON and DOC. These were visually examined for seasonal trends, as it was an-

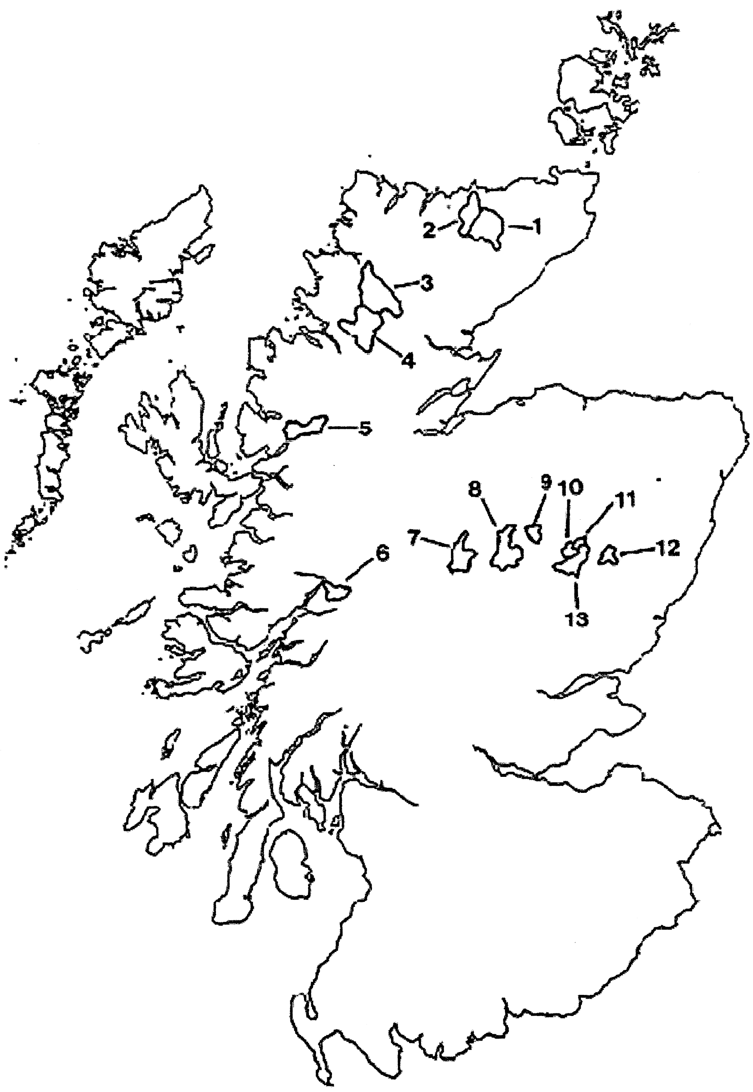

Figure 1. Map of Scotland showing the relative positions of the 13 study catchments.

ticipated that NO_3^- and possibly other N species would display seasonality, but that some N species might not. Occurrences of a consistent seasonal pattern for NO_3^--N suggested that it would be worth attempting to model monthly variations in NO_3^--N concentration from temperature and possibly other catchment characteristics. Temporal trends for NH_4^+-N, DON and DOC were much less pronounced. It was decided therefore only to attempt to produce predictive equations for mean concentrations for these three determinands over two sets of six-month periods, from October to March and from April to September. These periods were chosen because biological transformation processes that control N-cycling may differ in relative importance in summer and winter, and in recognition of the fact that soils will remain wetter longer in autumn and winter than in spring and summer. April was chosen as the start of summer as it represented a point when the soils (in general) began to warm. October marked the onset of cooling associated with winter.

Data analysis for spatial trends

Preliminary evaluation of influences of spatial variables on N species concentrations was performed using data for the Dee sub-catchments. The observed concentration of NH_4^+-N might be expected to depend upon N species inputs and biological transformation dynamics, mobile anion concentrations, and the relative abundances of competing cations on soil cation exchange sites. Therefore it might be expected that soil type could have a significant effect upon inter-catchment differences in river water NH_4^+-N concentrations. In temperate systems, mobile anion concentrations may show strong seasonal effects that are relevant in the present context.

For the Dee sub-catchments (8–13), more than 40 spatial variables, including topographic characteristics and geological parent material groups, were quantified. So too were variables that change over long time-scales, such as land use cover classes and soil type (Land use cover and soil distribution were expressed in km^2 and as % of total area, for both the riparian zone and for the whole catchment area). These variables were then used in a correlation matrix to determine possible relationships between catchment characteristics and N species. Concentrations of N species were then plotted against variables that demonstrated high r^2 values and the plots were visually examined to determine if apparently significant correlations were meaningful.

Variates which may change over relatively short time-scales, including river water pH, alkalinity, conductivity, concentrations of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, H^+ and SO_4^{2-}, and air and water temperature, were then, together with promising variates from the correlation matrix, subjected to stepwise multiple regression using Minitab 13 software, and their regression equations were determined using the same package. All quoted r^2 values are adjusted for degrees of freedom.

Results

Seasonal variation in Nitrate-N concentration

Figure 2 shows how monthly mean NO_3^--N concentration, for the 13 catchments varied seasonally. Nitrate-N concentration was low in the late spring to early autumn, and exhibited a maximum in late autumn and winter. Higher values for NO_3^--N have been observed over the autumn or winter period in earlier studies (*e.g.* Edwards et al. (1985) and Reynolds et al. (1992), Jenkins et al. (1996), Chapman et al. (2001)). Based upon the clear seasonal trends seen for NO_3^--N in Figure 2, which combines data collected in two separate years, stepwise regression analysis was used to factor out which of the available catchment characteristic data could best be employed to explain the variation in monthly mean NO_3^--N concentrations (Nitrate-N_{mm}) in mg l^{-1}. Only monthly mean air temperature (T °C, using monthly mean air temperature values from the nearest meteorological station) emerged as a significant factor, yielding the following linear relationship for the data from 13 catchments:

$$Nitrate - N_{mm} = 0.1235 - 0.006506T \qquad (r^2 = 0.82) \qquad (1)$$

Using the data for the Dee sub-catchments to look for effects of other variables, no other parameters helped to explain differences in NO_3^--N concentration values between catchments. Parameters tested included water temperature at time of sampling, rainfall, the % of any specified soil type in either the total catchment or riparian zone areas, the % of any specified underlying geology, or the % covers of coniferous or broadleaf forest or heathland vegetation.

Figure 3 shows the relationship graphically between monthly mean NO_3^--N concentration and monthly mean air temperature for the 13 catchments, for each of the 12 months, together with 95% confidence intervals and 95% prediction intervals. Figure 4 shows the relationships between predicted and observed monthly mean NO_3^--N concentrations when the above equation is applied to the six individual sub-catchments of the River Dee catchment. In the authors' experience such plots are sometimes useful pointers to mechanisms that might explain outliers associated with one or more catchments. The remaining seven catchments were not included as their data was less contiguous. Generally the correlation between the two variables is stronger when the observed NO_3^--N concentration range is higher (e.g. catchments 11–13), but the slopes were lower than expected for the catchments with higher NO_3^--N concentrations.

Examination of plots (not shown) of predicted and observed NO_3^--N versus temperature relationships for the individual River Dee sub catchments showed a clear trend in the reliability of the simple air temperature-based predictive equation. Below 5 °C, predicted values were generally too low, whereas above 5 °C they tended to be slightly too high. This is reflected in the low slopes and high predicted NO_3^--N intercepts at high NO_3^--N concentrations seen in Figure 4. A mechanistic cause of the apparent split at 5 °C is plausible, as it is below this temperature which biological activity is considered to be dramatically reduced. The authors speculate that there may have been a temperature-mediated change in activities of N-cycling bacteria at around 5 °C, or that plant-uptake of N may have been significantly reduced below 5 °C. Following the above visual observations, the mean monthly NO_3^--N data set was split into two sets, one for $T < 5$ °C and the other for $T \geqslant 5$ °C. Mean NO_3^--N concentration was then regressed separately against T for each data set to produce the following predictive equations for NO_3^--N concentrations (mg l^{-1}):

$$\text{If} \quad \text{Temperature} < 5°C: NO_3^- - N = 0.00843*\text{Mean} \quad \text{temp} + 0.11839 (r^2 = 0.62)$$

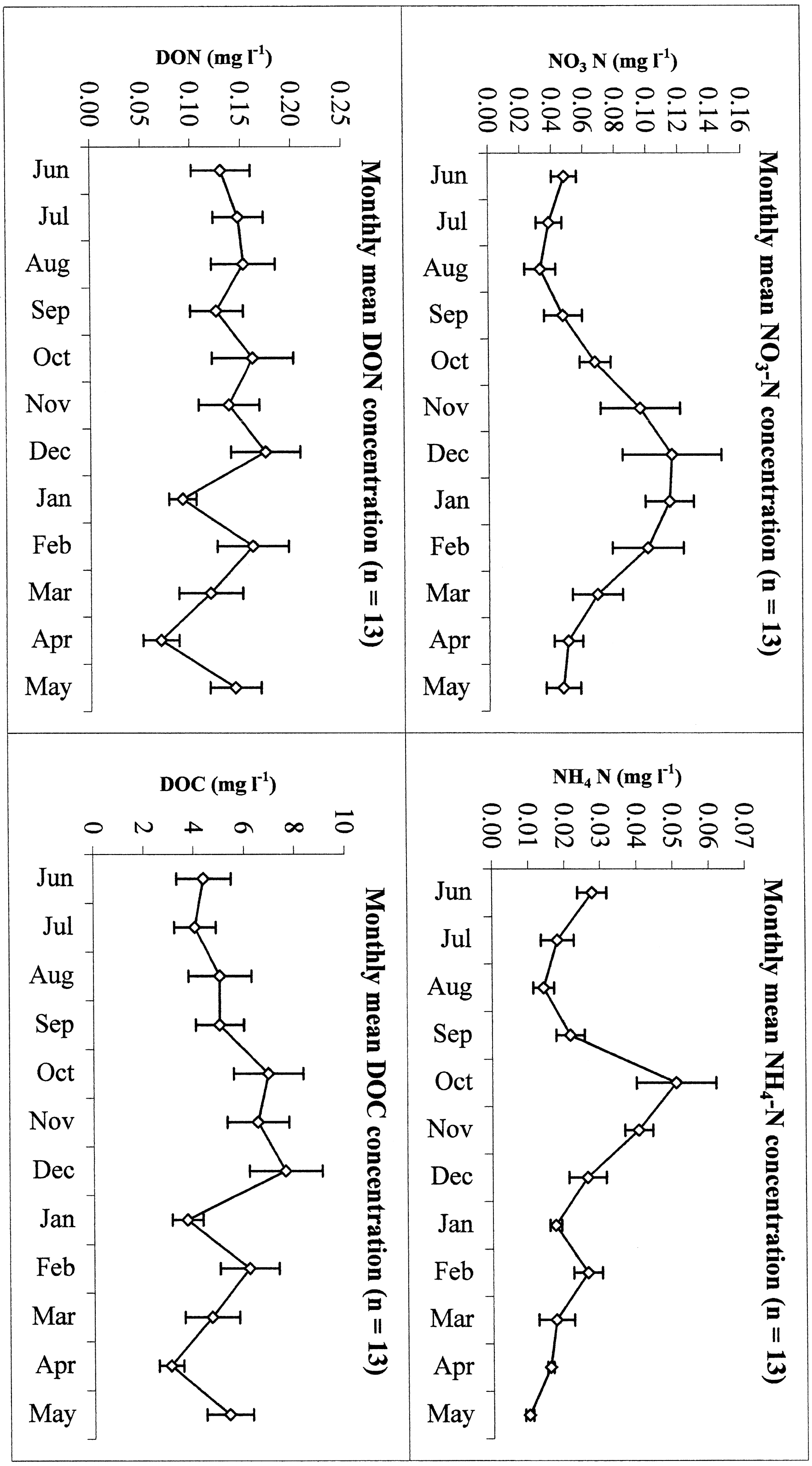

Figure 2. Monthly variation in the sampling frequency-weighted monthly mean NO_3^--N, NH_4^+-N, DON and DOC concentrations for the 13 catchments used to construct the predictive models.

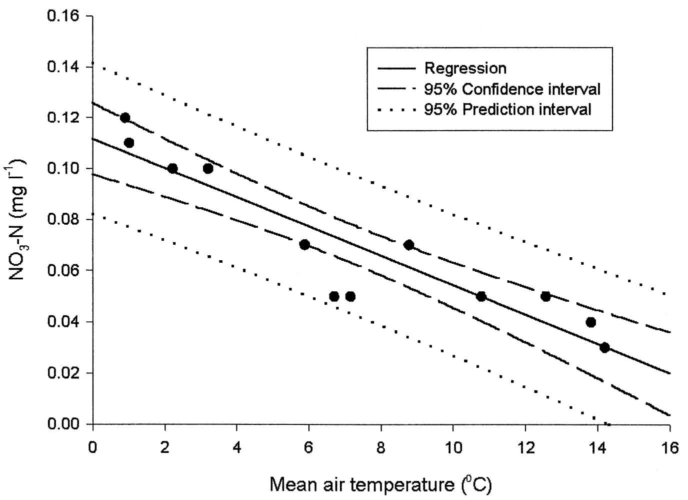

Figure 3. Monthly mean air temperature (°C) *versus* mean monthly NO_3^--N concentration (mg l^{-1}) for the 13 catchments.

$$\text{If}\quad \text{Temperature} \geqslant 5°C{:}NO_3 - N = -0.00432{*}\text{Mean}\quad \text{temp} + 0.09527(r^2 = 0.57)$$

The graphs of predicted vs. observed values of NO_3^--N concentration shown in Figure 4 were re-plotted for the six River Dee sub-catchments using the split temperature regression equations. The results (Figure 5) show that the slopes of the graphs are generally now closer to unity, and for 5 of the 6 catchments the correlations are improved.

To further validate these relationships, the split temperature regression equations derived using the Dee data were then applied to monthly mean air temperature data for the other Scottish catchments. This was done only for the 5 catchments for which 10 or more NO_3^--N concentration values (single values in 10 or more different months) were available. The predicted and observed values and means for five catchments are plotted as a function of time in Figure 6. Mean values across all 5 catchments are also plotted. Considering the simplicity of the modelling approach, the large regional scale involved, the low but variable concentrations involved and the use of single samples for each month for each catchment, the agreement is reasonable. The mean absolute deviations (%) of observed values from predicted values may be seen in Table 2.

Seasonal variation in Ammonium-N concentration

Seasonal trends in mean monthly NH_4^+-N concentrations for individual catchments were less obvious and less consistent than those for NO_3^--N (Figure 2). However,

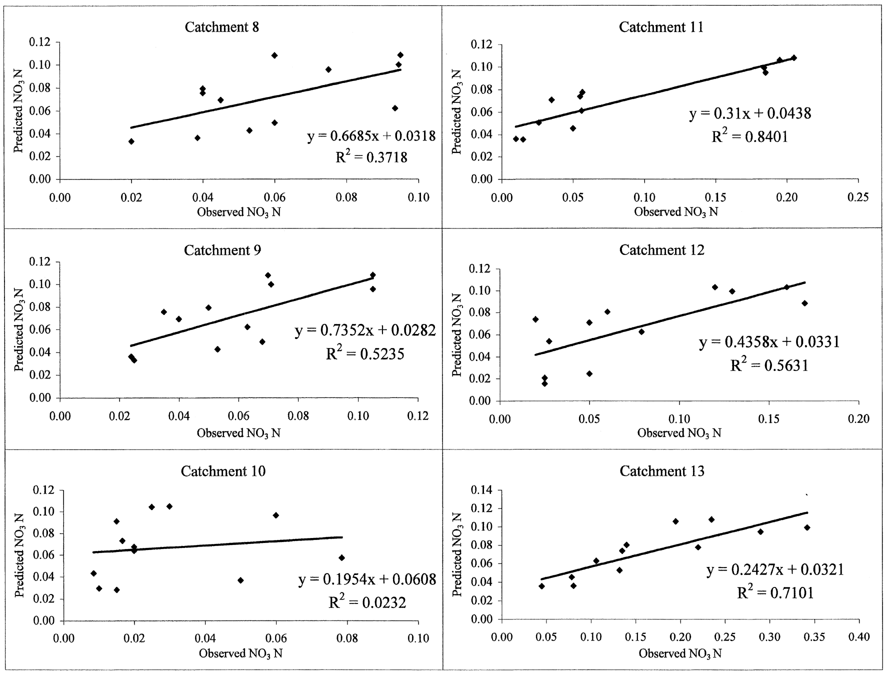

Figure 4. Comparison of predicted (from air temperature, °C) and observed NO_3^--N concentrations (mg l^{-1}) in the six sub-catchments of the River Dee catchment.

mean concentration data for each month across the 13 catchments do suggest that there is a seasonal trend in NH_4^+-N, with concentrations declining from a maximum in October to a minimum in May. Generally the concentration of NH_4^+-N was appreciably lower than that of NO_3^--N, and variation between catchments was almost as pronounced as variation from month to month.

Stepwise regression analysis was used to select variables for use in a simple multiple regression equation. For summer, the summer mean monthly rainfall ($Rain_{Sm}$, in mm – calculated as one sixth of the sum of daily precipitation over the 6 months), % coniferous forest cover and % brown forest soils cover emerged as key variables (Table 3). For winter, the % cover of humus iron podzols, mean daily temperature and % coniferous forest cover were most important. With the relatively small data set, a set of three variables was regarded as the maximum number that could be meaningfully used in predictive regression equations.

Variations in DON and DOC concentrations

Monthly mean concentrations of DON varied substantially between catchments and throughout the year in all of the catchments, but showed no consistent seasonal trend, whereas DOC concentrations tend to be slightly higher in late autumn and winter, than the summer (Figure 2).

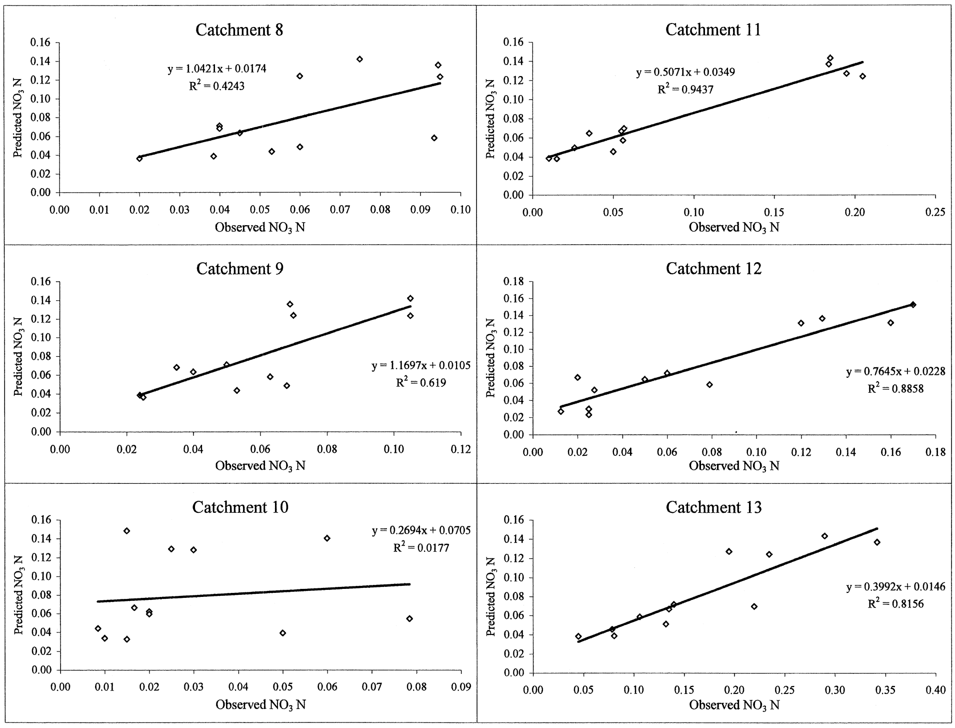

Figure 5. Comparison of predicted (from air temperature, °C, using the split temperature equations) and observed NO_3^--N concentrations (mg l^{-1}) in the six sub-catchments of the River Dee catchment.

ANOVA for six sub-catchments of the Dee showed that DON concentrations were significantly higher in catchment 11, which is heavily forested (88% coniferous cover), than in the other catchments ($p \leqslant 0.01$). DOC also exhibited significantly different ($p \leqslant 0.001$) mean concentrations between catchments, and catchment 11 again had the highest observed concentrations. The DON and DOC monthly mean concentrations were positively correlated ($r^2 = 0.54$). However, when the monthly mean data for all 13 catchments were considered, there was no significant relationship between DON and DOC.

Stepwise regression was used to select variables for an empirical regression equation for DON. For summer, % peat soil cover, catchment maximum elevation and summer mean rainfall emerged as the important variables. For winter, maximum elevation, % heather cover and % cover of sub-alpine soils were most useful (Table 3).

For DOC, % peat, % coniferous forest and % humus iron podzols in the catchment, were significant in summer. In winter, % humus iron podzol was most significant, followed by maximum altitude and peat cover.

Plots of observed values *versus* predicted values, obtained using the equations for which regression constants are listed in Table 3, generally display good fits for summer and winter mean values (Figure 7).

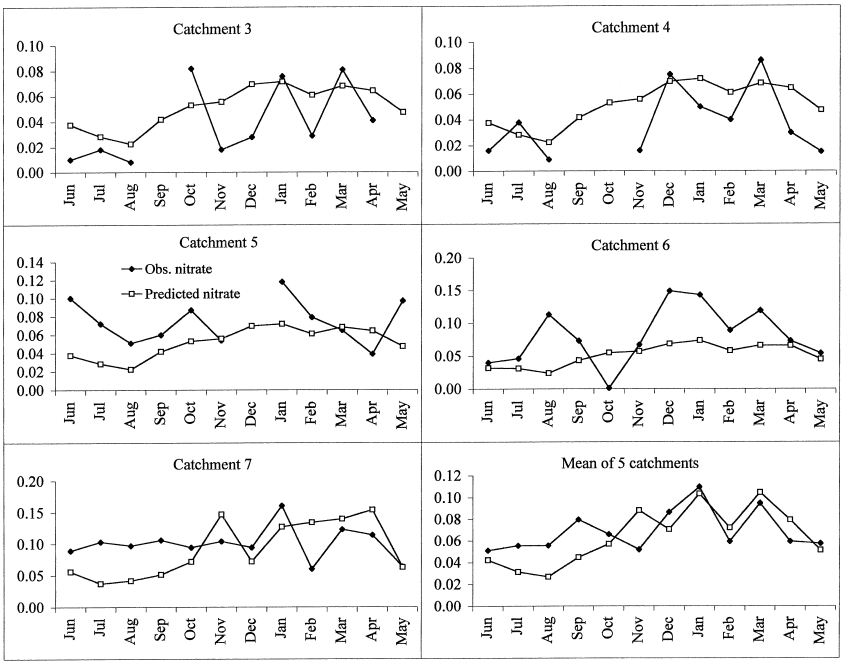

Figure 6. Comparison of predicted (from air temperature, °C, using the split temperature equations derived for the Dee sub-catchments) and observed NO_3^--N concentrations (mg l^{-1}) for the five other Scottish catchments shown, and for the mean values for these five catchments.

Table 2. Mean absolute deviations (M.A.D.) expressed as percentages of observed from predicted values.

Catchment	Carron	Casselly	Nevis	Oykel	Tromie	Mean
M.A.D. sign.	26.14 −ve	98.45+ve	36.02−ve	90.68+ve	5.46−ve	5.79−ve

Discussion

The seasonal trend in NO_3^--N concentrations observed in this study for individual sub-catchments has been reported in many other studies of semi-natural, temperate catchments (*e.g.* Reynolds and Edwards (1995) and Mitchell et al. (1996)) and may be explained by temperature-mediated availability of NO_3^- in the soil for leaching. During the warmer months, although mineralisation of soil organic N is more rapid, NO_3^- is immobilised by microbial and plant uptake. During the colder months biological uptake and transformation of NO_3^- is greatly reduced (Duckworth and Cresser 1991); thus the soil has a reduced ability to retain NO_3^- during the winter compared with its ability in the summer (Black et al. 1993). It is therefore not surprising that mean monthly air temperature is a useful predictor for mean monthly nitrate concentration. Arheimer et al. (1996) also observed that NO_3^- concentrations

Table 3. Variables fitted to multiple regression equations for NH_4-N, DON and DOC for summer and winter periods. *** = significant at p = 0.001; ** = significant at p = 0.01; * = significant at p = 0.05. BFS = brown forest soil; $Rain_{Sm}$ = summer mean monthly rainfall, mm; Conif = % coniferous cover; HIP = humus iron podzol % cover; T_{Wm} = mean winter temperature, °C; Alt_m = maximum altitude, m; Heather = % heather cover; SAS = sub-alpine soil % cover.

	NH_4 N summer	NH_4 N winter	DON summer	DON winter	DOC summer	DOC winter
R^2 (adj.)	0.73	0.81	0.93	0.87	0.93	0.93
Constant	0.0251	0.0529	0.300	0.419	0.359	9.77
BFS	0.000646***					
$Rain_{Sm}$	−0.000417**		−0.00438***			
Conif.	−0.000236***	0.000414*			0.0991**	
HIP		−0.000183			0.200***	0.256***
T_{Wm}		−0.00577***				
Alt_m			−0.000154**	−0.000161		−0.00746**
Heather				−0.00222***		
SAS				0.00251***		
Peat			0.00120***		0.124***	0.11*

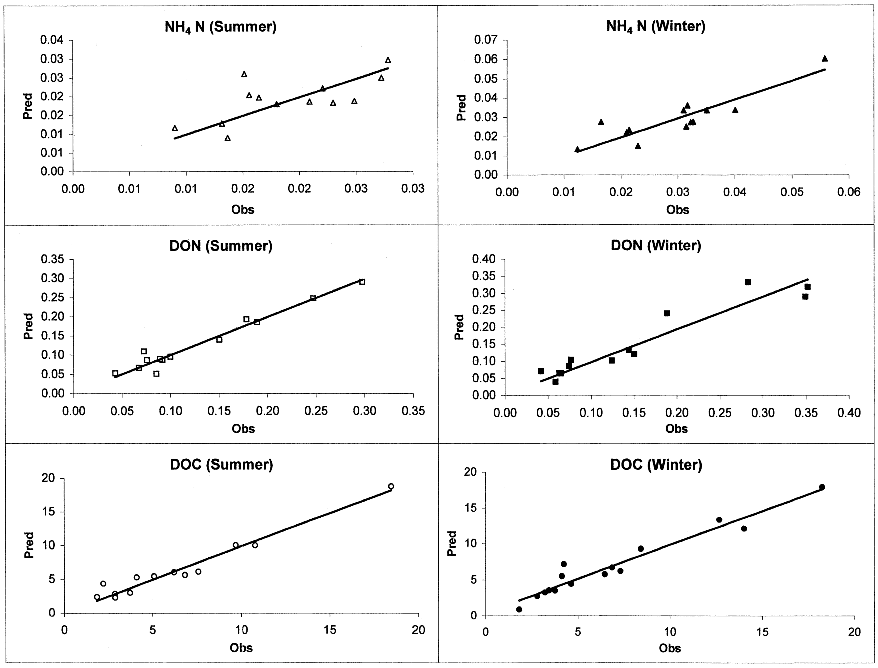

Figure 7. Comparison for summer (April–September) and winter (October–March) of predicted and observed concentrations of NH_4^+-N, DON and DOC in the 13 catchments used to develop the models.

in streams draining forested catchments in Finland and Sweden could be related to mean annual temperature. The fact that water temperature at the time of sampling did not have useful predictive potential suggests that in-stream mechanisms such as denitrification, which are also temperature dependant, are not controlling nitrate concentration. However, it may be that higher summer temperature increases denitrification in stream in summer, thus contributing to the lower summer nitrate concentrations in river water.

The low slopes for some catchments for the predicted NO_3^--N *versus* observed NO_3^--N plots using the single (Figure 4) and even the split (Figure 5) regression equations are not surprising. The air temperature data were taken from the meteorological station closest to each site because no data was available from the sites themselves. Temperature in northern Britain declines by 2 to 3 °C per 700 -m increase in elevation and per 10° of latitude (Whittaker and Tribe 1996). Soil temperature will also be substantially dependent on aspect (Watson et al. 1994). Catchments 12 and 13 contain predominantly north-facing slopes. It is probable, therefore, that the modelling approach would be much improved by using soil temperature in the equations.

Monteith et al. (2000) observed a strong relationship between the number of days with grass temperature $\leqslant -4$ °C and annual peak NO_3^- concentration for the River Gwy in mid-Wales over an 18-year period. They therefore suggested a link between cold winters and high NO_3^- maxima, as observed by Mitchell et al. (1996) for forested catchments in the north-eastern United States.

Previous studies on two moorland catchments of northeast Scotland suggested that there is an inverse correlation between seasonal precipitation amount (mm per 3 months) and seasonal mean NO_3^- concentration (Edwards et al. 1985). In the present study, discharge was used as a surrogate for amount of precipitation, but seasonal variation in discharge did not appear to control the seasonal variation in NO_3^--N concentration. This is not an ideal surrogate, because of seasonality of evapotranspiration, but reliable catchment precipitation data was not available, and moreover snow-lie would impair the usefulness of precipitation data in winter.

Over the 'summer' period, mean NH_4^+-N concentration was higher in catchments with higher proportion of brown forest soils. This could reflect greater mineralisation rate in these soils, which are the most base-rich of Scottish upland soils. Higher rate of base cation release by biogeochemical weathering also could favour displacement of NH_4^+ into drainage water. Increasing precipitation amount in summer also had a negative influence. This could be a dilution effect, or it could be a consequence of differences in soil moisture conditions and possibly aeration. In the 'winter' period, the presence of extensive areas of humus iron podzols and higher temperature were associated with lower mean NH_4^+-N concentration. In areas with moderate levels of atmospheric pollution by reduced N, the occurrence of NH_4^+ leaching depends upon the rate of deposition of NH_4^+, the rate of production of NH_4^+ by ammonification, and the rates of conversion to NO_3^- or organic N in biomass or soil organic matter. The latter processes remove NH_4^+, increasing the probability of any subsequent NH_4^+ input being retained on cation exchange sites in the soil. Warmer winter temperatures would increase ammonification rate, but also rate of conversion to organic N. The presence of coniferous woodland enhanced NH_4^+-N concentration in winter, possibly *via* a canopy filtering effect, either directly on reduced N species or on associated mobile anion species. It is not obvious why the extent of humus iron podzols should apparently be relatively more important than that of any other soil type.

Although Qualls (2000) has recently emphasised the close correlation between DON and DOC, the observation that DON and DOC concentrations for individual catchments were positively correlated only for a few of the catchments is not particularly surprising. Turnover rates of C and N in soil change substantially with depth in the soil profile, and C:N ratio of the soil organic matter also changes with depth. Under diverse flow conditions in a river, water draining from different soil horizons may predominate, so substantial variation in C:N ratio is to be expected in many catchments. Further modification will arise as a consequence of in-stream processing of DOC (Edwards et al. 2000; Chapman et al. 2001) and from organic matter inputs not derived from soil organic matter. It is therefore to be expected that the variables in predictive equations for DOC and DON will differ.

In spite of this, catchment elevation was a key parameter for mean DON concentration in both winter and summer and for DOC in winter, both variables declining with elevation. Chapman et al. (2001) also observed a decline in DON concentrations with catchment elevation. There could be many reasons for this. The maximum elevation may integrate effects of lower temperature, lower vegetation growth, lower microbial degradation rate and greater precipitation, resulting in greater probability of thin or skeletal sub-alpine soils on upper catchment slopes. Thicker organic horizons are more probable on intermediate upland catchments.

Conclusions

Nitrate-N was the most seasonally variable N species examined. The seasonal variation in its concentration could be predicted from seasonal temperature variation, especially if separate regression equations were used for temperatures $<$ or $\geqslant$ 5 °C. Concentrations of NH_4^+-N, DON and DOC displayed less obvious seasonality. However, regression equations could predict mean concentrations for ‘summer’ and ‘winter’ 6-month periods. It was possible to predict approximately 82% of observed mean monthly NO_3^--N variation and a significant proportion of mean seasonal NH_4^+-N, DON and DOC. The winter models were generally more robust than the summer models. The results suggest that readily available data for catchment characteristics may eventually allow useful models to be developed for prediction of N species leaching losses from upland catchments, which could be valuable for modelling N mass balance on broad regional scales.

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