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Defra Freshwater Umbrella Programme - Final Report

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FRESHWATER UMBRELLA - THE EFFECTS OF NITROGEN DEPOSITION & CLIMATE CHANGE ON FRESHWATERS IN THE UK

FINAL REPORT
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***Reporting jointly with DEFRA Terrestrial Umbrella; see TU Report**

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****Task 4.2: Recovery and climate manipulation experiments at the Afon Gwy (*Reported in Terrestrial Umbrella Final Report)***

ABSTRACT

In upland areas of the UK located away from direct human disturbance through agriculture, industrial activities and urban pollution, atmospheric pollution poses one of the major threats to the chemical and biological quality of lakes and streams. One of the most important groups of pollutants is nitrogen (N) compounds, including oxidised forms of N called NO_x, generated mainly by fossil fuel combustion especially in motor vehicles, and reduced forms of N (ammonia gas or dissolved ammonium compounds) generated mainly from agricultural activities and livestock. These nitrogen compounds may dissolve in rain or soilwater to form acids, or may be taken up as nutrients by plants and soil microbes in upland catchments, and then subsequently released in acid form associated with nitrate leaching at a later date. It is well established that nitrate leaching contributes to acidification of upland waters, with damage to aquatic ecosystems including plants, invertebrates and fish. However it has recently been suggested that nitrate leaching may also be associated with nutrient enrichment of upland waters that contain biological communities adapted to very low nutrient levels.

Issues of acidification, nutrient enrichment and biological controls on nitrate leaching are therefore intrinsically linked and need to be understood in order to determine current and future impacts of N deposition on water quality and ecological status of upland waters. The Freshwater Umbrella programme was specifically designed to tackle these scientifically challenging problems, with key objectives and methods to:

1. assess the importance of inorganic forms of N (i.e. nitrate and ammonium) as nutrients in upland lakes through a combination of literature review, lake sediment studies and experimental work;
2. improve understanding of nitrate leaching pathways and controls using complementary isotopic tracer and dual isotope approaches. The first approach allows N compounds to be marked and then tracked through the environment, while the second uses naturally occurring isotopic differences between atmospherically deposited nitrate that is leached unchanged from catchments and nitrate produced from ammonium by the microbial process of nitrification in soils;
3. develop models for predicting which nutrient (N or phosphorus) is the major control of biological productivity in upland waters from catchment characteristics and other nationally available datasets, including studies of catchment soils and mosses as possible controlling factors;
4. assess the impacts of climate change on effects of atmospheric pollutants in upland catchments through literature review and experimental work; and
5. review and develop models linking deposition loads to ecological effects (with a quantified biologically relevant threshold or "critical load") for acidity in UK freshwaters and review the case for application of nutrient N critical loads.

Results from this contract have provided substantial evidence for adverse effects of N deposition on sensitive water bodies of the UK. Previous work under DEFRA contracts has already demonstrated the major importance of sulphur deposition in causing acidification but with the implementation of emission reduction measures in the UK and Europe the role of sulphur is declining. All sites still impacted by acidification are at least partly affected by N and more than half would exceed critical loads on the basis of N deposition alone, even following implementation of the EU National Emissions Ceiling Directive in 2010. Reductions in emissions targets for total N would be required to prevent critical load exceedance in the majority of sensitive freshwaters.

The role of N deposition in causing changes to lake nutrient cycles and productivity has been demonstrated through a review of the recent literature and through direct measurement of phytoplankton (microscopic, free-floating aquatic algae) responses to nutrient additions in laboratory studies. Growth and productivity are limited almost as frequently by N availability

as by P in upland lakes but joint- or co-limitation of growth by both N and P together is the most common status. Independent evidence for historical changes in lake nutrient inputs and productivity has been found through studies of N stable isotopes in lake sediments. This approach may allow the role of anthropogenic N sources in lakes to be evaluated. The potential impacts of N deposition in increasing lake productivity are highly relevant to N emissions policy with respect to several international directives:

1. nutrient-poor lakes in the UK uplands designated under the EU Habitats Directive may be particularly sensitive to the effects of N deposition, with possible changes to phytoplankton species and productivity and changes to macrophyte flora;
2. these changes may be considered a deviation from the good ecological status required under the EU Water Framework Directive; and
3. there is a strong case for calculating nutrient N critical loads to feed into the integrated assessment modelling work under the UN-ECE Convention on Long-Range Transboundary Air Pollution, including the Gothenburg Protocol.

Confirmation that N deposition may lead to both acidification and nutrient enrichment highlights the increasing need to understand the processes that determine whether N deposition causes enhanced nitrate leaching over the short- or longer term. Results from this project using novel techniques in the UK have for the first time allowed the major controls on nitrate leaching to be separated and quantified at specific sites. Hydrological tracer experiments have proven that rapid flowpaths exist that can transport deposition through soils into surface waters in minutes to hours, but a large proportion of nitrate is still retained in soils. The nitrate dual isotope approach has further demonstrated that only 20-30% of leached nitrate is rapidly transported from NO_x deposition; the remainder is generated within soils by microbial processes. Hence a fraction of leached nitrate will respond rapidly to changes in NO_x deposition. However, a larger proportion of leached nitrate is generated in soils from N pools that may consist of accumulated NO_x and reduced N deposition. Therefore a large proportion of nitrate leaching may respond very slowly to changes in N deposition. Understanding the balance of these nitrate sources is essential for predicting timescales of response to changes in N deposition and for calculating target loads to achieve given water quality targets within a specified timescale. This programme has shown that nitrate leaching models will also need to incorporate catchment scale attributes such as the carbon:nitrogen ratio of soil organic matter and moss biomass which explain part of the variation in leaching relative to N deposition.

Literature reviews suggest that climate change will have a major effect on both nitrate and dissolved organic carbon (DOC) leaching. Higher temperatures will lead to higher production of both although the net balance between production and retention is harder to predict and they may be leached under different conditions. Increased storminess and more frequent droughts will probably lead to lower leaching throughout the summer but an increased susceptibility to episodic leaching events year round as DOC and nitrate may accumulate in soils during dry weather to be flushed out during rainstorms. For nitrate these flushing events may be associated with short-term harmful increases in surface water acidity. Future deposition levels of trace metals and persistent organic pollutants are unknown and therefore possible effects of climate change are very hard to predict. Furthermore there are strong links between the leaching and toxicity of trace metals and chemical variables like acidity and DOC which are also predicted to change in response to climate and deposition. While these interactions make it very difficult to model or predict future changes in concentrations and impacts of these pollutants they do demonstrate the intrinsic links between climate change, air quality and water quality impacts and policies.

The nature of these studies means that only a limited number of sites have been assessed and there are too few to scale up more widely to the national level. Attempts to scale up catchment models of N limitation were largely unsuccessful, partly due to the over-simplistic view that N limitation best defines sites most likely to be impacted by N deposition. In fact it became apparent during this programme that one of the indicators of the most severe N impacts could be the inducement of P limitation because of a large excess nitrate availability. Hence the classification of changed or impacted nutrient status needs better definition.

Priorities for future work should therefore include the following:

1. further work to define "harmful effects" for nutrient N critical load models;
2. expansion of the nutrient growth limitation and sediment isotope work to characterise more upland catchments in terms of the nutrient N impacts they have experienced;
3. investigation of the key determinants of N isotopic signatures in lake sediments, i.e. simple magnitude of input fluxes versus processes within the lake that cause changes in the isotopes stored in sedimenting organic matter;
4. development of catchment attribute models to upscale nutrient N impact classes across upland water bodies in the UK, including collation of new datasets and clearer definition of impacted sites;
5. upscaling of the nitrate dual isotope approach to characterise catchments vulnerable to rapid impacts from hydrological nitrate leaching and those more at risk over the longer term from N saturation and microbial nitrate leaching; and
6. identification of site characteristics other than soil C:N ratio and moss biomass that regulate nitrate leaching and therefore dictate vulnerability to the adverse effects of N deposition.

EXECUTIVE SUMMARY

Background

In upland areas of the UK, most lakes and streams are generally located above centres of urban development and intensive agriculture and are therefore not vulnerable to the major direct sources of pollution such as urban runoff, sewage or fertilizer applications. Instead, the main threats to the quality of upland freshwaters are long-range air pollution and climate change.

In the 1980s the importance of sulphur (S) deposition originating mainly from fossil fuel combustion was recognised, being associated with acidification of soils and surface waters and severe biological impacts in terrestrial and aquatic ecosystems. The problem was mainly restricted to upland areas of slow-weathering bedrock such as granite which offered little buffering capacity to prevent acidification. Throughout the 1980s and 1990s, critical load models were developed to link the load of acid deposition with chemical changes in soils and waters leading to adverse biological effects in specified elements of ecosystems. In surface waters the steady-state water chemistry model was initially used to determine the critical load of S deposition which would depress acid neutralizing capacity (ANC) to a level which harmed brown trout populations.

By the 1990s, critical load models were being further developed to account for the effects of nitrogen (N) deposition. It was recognised that oxidised forms of N (NO_x) reacted with rainfall and soilwater to form nitric acid, which could be leached into surface waters with a resultant increase in nitrate concentrations and a decrease in ANC. Furthermore, even reduced forms of N (ammonia and ammonium) could be converted to nitrate in soils to further exacerbate acidification if the nitrate was subsequently leached into surface waters. Whereas critical load models for S were very simple due to the mobile nature of S in catchments (i.e. it could be assumed that all deposited S would be leached as sulphuric acid - demonstrated by increasing sulphate concentrations), critical loads for N presented a greater problem. Nitrogen is a key nutrient in terrestrial and aquatic ecosystems and therefore deposited forms of N enter biological nutrient cycles through plant and microbial uptake and immobilisation processes. Therefore N is much less mobile than S and it cannot be assumed that all deposited N will be leached into surface waters. In fact only a small proportion of deposited N is generally leached, with most being retained in plants and soil organic matter over the longer term. The key to understanding how N deposition impacts on aquatic ecosystems is therefore understanding the pathways and controls for nitrate leaching, i.e. which factors determine whether deposited N is retained in the terrestrial catchment or leached into surface waters.

In addition to the acidifying impacts of N, a further complicating factor is the behaviour of N as a nutrient. In terrestrial ecosystems, the retention of deposited N clearly implies that N must be accumulating in an N-limited ecosystem. The presence of elevated nitrate concentrations in surface waters also demonstrates that availability of nutrient N in inorganic forms for aquatic ecosystems has increased. Until relatively recently, the issue of nutrient N in upland waters was though to be unimportant because it had been widely assumed since the 1970s that upland aquatic ecosystems tended to be generally phosphorus limited, i.e. the additional nitrate had little effect on biological nutrient cycles or productivity. This assumption stemmed largely from whole-lake manipulation experiments in North America which showed that addition of phosphorus to lakes generally had a much greater impact than addition of N compounds. However, recent work under this programme and elsewhere has demonstrated that N limitation is much more widespread in upland lakes than previously assumed, suggesting that leached nitrate must also be utilised as a nutrient in these ecosystems.

Issues of acidification, nutrient enrichment and biological controls on nitrate leaching are therefore intrinsically linked and need to be understood in order to determine current and future impacts of N deposition on water quality and ecological status of upland waters. The Freshwater Umbrella programme was specifically designed to tackle these scientifically challenging problems. The key objectives may be summarised as:

1. continue to review and develop critical load models for acidity (S+N) in freshwaters (WP1);
2. assess the importance of inorganic N as a nutrient in upland lakes through a combination of literature review, palaeolimnological investigation and experimental work (WP2);
3. develop models for predicting nutrient limitation status of upland waters from catchment characteristics and other nationally available datasets (WP2);
4. review the case for application of nutrient N critical loads in the UK (WP2);
5. improve understanding of nitrate leaching pathways and controls using complementary isotopic tracer and dual isotope approaches (WP3);
6. assess the importance of organic soil C:N ratios and bryophyte biomass as controls on nitrate leaching (WP3); and
7. assess the impacts of climate change on effects of atmospheric pollutants in upland catchments through literature review and experimental work (WP4).

The results of the individual work packages addressing these issues are described below. They are also described in detail in the attached Annex 1 and on the project website www.freshwaters.org which was developed under the current programme. In the past 12 months, the website has had over 70000 hits (200+ per day on average), serving up almost 35000 pages. It is returned in the top 10 or 15 Google search results for terms such as "freshwaters", "acidity in freshwater" and "nitrate leaching".

Work Package 1: Critical loads for acidity

Ongoing work on the development and application of critical loads for acidity models continues to demonstrate the crucial importance of N deposition in preventing recovery from acidification. In the current freshwaters data submission to CCE which forms the UK contribution under the UN-ECE Convention on Long Range Transboundary Air Pollution (CLRTAP), 38% of the 1722 water bodies in the dataset exceeded critical loads for 1999-2001 mean deposition levels. Re-analysis of the dataset under this contract showed that at more than half of exceeded sites (56%), N deposition alone was sufficient to cause critical load exceedance, while it contributed to exceedance at all sites. N deposition continues to play a major role in ongoing critical load exceedance by 2010 following implementation of the EU National Emissions Ceiling Directive. Over 30% of all mapping sites still exceed acidity critical loads in 2010 and N deposition alone is sufficiently high to cause exceedance at an increasing proportion (58%) of them. While reductions in sulphur deposition continue to allow improvement in acidity status of lakes and streams in the UK uplands, prevention of critical load exceedance cannot be achieved for most sites without corresponding reductions in total N deposition.

Summary

Critical load models for acidity and new deposition datasets continue to illustrate the importance of N deposition in contributing to critical load exceedance, with N deposition alone being high enough to cause acidification at more than half of exceeded sites even after implementation of the EU NECD. Prevention of critical load exceedance cannot therefore be achieved by reductions in S deposition alone for many upland sites in the UK.

Work package 2: Nitrogen as a nutrient

Review of the recent literature (Task 2.1) has demonstrated that the prevailing idea of almost universal P-limitation in lakes is a misconception and N-limitation is almost as frequent as P-limitation in UK upland lakes, with co-limitation by N and P being the most common state. Recent studies in Europe and North America employing bioassays and palaeolimnological techniques have demonstrated not only that N-limitation is widespread in semi-natural catchments, but also that even lakes currently P-limited may have been modified from a natural N-limited state by anthropogenic N deposition. Even remote, oligotrophic lakes in alpine and Arctic regions are very sensitive to the effects of N deposition since they are adapted to extremely low natural N availability. Changes recorded in the sediment cores from these lakes have been attributed to N deposition levels of less than 5 kgN ha^{-1} yr^{-1} which are lower than occur anywhere in the UK. The most commonly recorded effect is a change in algal communities towards more mesotrophic, planktonic assemblages with greater overall primary production.

The issue of N limitation in lakes and the impact of N deposition is now so well recognised that it was the subject of the editorial in the May 2005 issue of the respected journal Limnology and Oceanography, accompanying a paper which demonstrated the enriching effects of N deposition on hundreds of Swedish lakes.

Studies on the subject in the UK have been confounded by two issues; 1) a scarcity of sensitive lakes in undisturbed catchments without agricultural or other direct inputs of N that have not been impacted by acidification over a similar timescale to the growth of anthropogenic N deposition, and 2) cyclical and monotonic trends in nutrient cycling and concentrations in surface waters attributed to climatic effects and global change. In more remote regions such as the Arctic, the relative importance of climatic warming and anthropogenic N deposition as drivers of chemical and ecological change throughout the industrial period of the last 150 years is still being debated in the literature, but there is a consensus that both factors have become critically important since at least the mid-twentieth century.

Under this work programme, three complementary approaches were adopted to determine the importance of nutrient N deposition to sensitive upland lakes:

1. Task 2.2 - empirical modelling using existing and new nutrient limitation and catchment-scale datasets;
2. Tasks 2.3.1 & 2.3.3. - palaeolimnological and contemporary studies of lake sediments as indicators of N deposition and biological response; and
3. Task 2.3.2 - bioassays of selected sites identified in modelling work under Task 2.2 to extend gradients of N-, P- and co-limitation in lakes and test the model.

The results from these studies were then used to review the case for application of nutrient N critical loads to UK surface waters.

The 13 new sites bioassayed for phytoplankton response to N and P additions revealed a similar pattern to previous work under the NERC GANE programme, with P-limitation found in 33% of the cases, N-limitation in 18% of cases and co-limitation being most frequent, found in 49% of cases. This new work expanded the existing data for the UK to 43 bioassayed lakes using the same methods. Sixteen sites showed N- or co-limitation, 16 sites showed P- or co-limitation, three sites varied from N- to P-limitation and eight sites were always co-limited. Therefore identical proportions of sites (37% each) were seasonally N- or P- limited with co-limitation at other times of year. Only three of the 43 sites showed P-limitation in each bioassay, including the highly N saturated Scoat Tarn in the Lake District. Hence the bioassay studies support the evidence from the literature that N limitation is widespread in UK upland lakes and that even P-limited sites may once have been N-limited but are now so modified by anthropogenic N deposition their nutrient status has changed.

Nitrogen isotopes in lake sediments provide an independent strand of evidence for the effects of N deposition. Declining values of bulk sediment $\delta^{15}N$ over the last 50-150 years have been attributed to increasing inputs of isotopically depleted anthropogenic N deposition in various studies from North America and the Arctic, but actual measurements of deposition at the same lake sites have not been published. The isotopic signal in lake sediments is relevant for two reasons. The first reason is that increasing inputs of N deposition reflected by these patterns must have led to changes in nutrient cycling within terrestrial and aquatic ecosystems of lake catchments which resulted in the incorporation of this isotopically light N in the organic matter that makes up a large proportion of lake sediments. Some of this organic matter is made up of aquatic organisms such as diatoms that will have utilised this additional source of N. While the pathways for incorporation of deposited N into lake sediments are still unproven, it is reasonable to assume that increased N availability has resulted in changes to lake ecosystems that may go beyond the simple increases in planktonic production which have been demonstrated by the bioassay work carried out under this programme. The second reason that patterns in lake sediment $\delta^{15}N$ are of interest is that they may provide a historical proxy record of N deposition which would be of great value for modelling and understanding changes in catchment nutrient pools and leaching. Better understanding of these changes will result in improvements in the dynamic models that are widely used for assessing the impacts of future policy options for N emission controls.

The results of sediment core analysis for $\delta^{15}N$ under this programme have shown widespread and marked biogeochemical changes in the all the studied sites, with increased deposition of anthropogenic N from the atmosphere the most likely cause of decreasing $\delta^{15}N$ in recent decades at ten of the 12 sites studied. Unlike published studies from North America, this work programme included actual measurements of the isotopic composition of NO_3^- in bulk precipitation so it was not necessary to speculate that deposited N may be depleted in ^{15}N in the UK. The mean $\delta^{15}N$ value of NO_3^- in bulk deposition from four sites was substantially lower than the value in pre-industrial lake sediments. At two co-locates sites, Lochnagar and Scoat Tarn, historically increasing inputs of ^{15}N depleted NO_x deposition could therefore be a possible driver of declining lake sediment $\delta^{15}N$, but the evidence is circumstantial and the $\delta^{15}N$ of reduced N deposition was not measured. The available data cannot therefore point conclusively to increased deposition of N as the sole cause of these changes in $\delta^{15}N$.

The analysis of lake surface sediment $\delta^{15}N$ and modelled deposition data for both NO_x and reduced N species (NH_y) has provided encouraging results, with weak but highly significant relationships between all N species and sediment $\delta^{15}N$. While there is much scatter in the relationships the study does support the hypothesis that sediment $\delta^{15}N$ may provide a proxy for total N deposition. Measurements of $\delta^{15}N$ in ammonium in bulk deposition would be highly useful for advancing this work.

Attempts to improve on existing predictive models of N limitation using the new data collected here met with limited success. A re-analysis of an original GANE dataset for predicting N or P limitation using catchment attributes entailed the inclusion of updated land cover (LCM2000) datasets and restructuring of the model to restrict the range of predicted outputs to the probability range 0-1 for N or P limitation, thereby improving the statistical rigour of the model. However, predictive performance deteriorated as a result and only the percentage cover of coniferous forest emerged as a significant predictor of nutrient limitation status. The new model was not improved by the addition of 13 new data points from this programme to the original 30 GANE sites to provide the 43 bioassayed sites described above. It was concluded that there are still too few characterised catchments for this type of empirical modelling and a wider dataset is required to improve models. However it is essential to pursue this modelling approach through data collection to allow the upscaling of N limitation work and ascertain the spatial extent of the nutrient N problem in the UK uplands. The use of better data, more sophisticated modelling techniques and an intermediate stage of predicting NO_3^- leaching could provide the best methods for creating an upscalable predictive model.

The work under this programme on the effects of deposited N as a nutrient in sensitive upland waters has strengthened the case for application of nutrient N critical loads to freshwaters in the UK. Despite uncertainties attached to the definition of "harmful effects" for deriving critical loads of nutrient N deposition in the UK, there are several reasons to conclude that nutrient N critical loads should be further developed in this country:

1) the softwater lake ecosystem for which nutrient N critical loads are recommended in the CCE Mapping Manual is not only widespread in the UK uplands, but it is a designated habitat under EU legislation (Habitats Directive) for SACs and Natura 2000 sites (SAC type 3130);
2) most softwater lakes in Wales and England and many in Scotland receive total N deposition loads above the CCE recommended upper threshold of 10 kgN ha^{-1} yr^{-1} and in some important conservation and amenity regions where these lakes are numerous, such as the Lake District and Snowdonia National Parks, N deposition loads are among the highest in the country;
3) there is a paucity of empirical data for the UK linking N deposition to adverse ecological effects beyond acidification, but;
4) work under the current Freshwater Umbrella programme has built on previous GANE studies to demonstrate that N limitation of phytoplankton production is common so N deposition must be leading to increased production in some lakes, with inevitable effects across aquatic food webs which may impact on biodiversity in these highly adapted and relatively species-poor systems;
5) palaeolimnological analysis of lake sediments cores under the current programme have found changes in sediment $\delta^{15}N$ consistent with N deposition enrichment at 10 out of 12 sites, including the important SAC Wast Water;
6) the definition of good ecological status required under the Water Framework Directive needs clarification in this regard, but N enrichment of ecosystems adapted to low N availability is likely to result in a deviation from this status; and
7) water bodies other than softwater upland lakes may be impacted by atmospheric N deposition and the relative importance of atmospheric sources of N may be grossly underestimated in UK approaches to implementation of the EU Water Framework Directive in streams, rivers and lowland lakes.

Summary

i) Literature review has found that nutrient impacts of N deposition are widely reported in remote mountain and Arctic lakes even at very low deposition levels, while the reported incidence of N limitation is widespread in North America, Sweden and the UK.

ii) Bioassay work has expanded existing datasets for the UK and demonstrated that in upland lakes, N limitation of phytoplankton growth is almost as common as P limitation. Furthermore, very high nitrate concentrations in some P limited lakes suggests that N deposition and related nitrate leaching may have caused a shift from natural N limitation to P limitation.

iii) Analysis of stable N isotopes in lake sediment cores has shown widespread incidence of declining $\delta^{15}N$ throughout the industrial period that is consistent with increasing inputs of isotopically light N deposition from anthropogenic sources. These patterns indicate that N deposition affects sediment organic matter $\delta^{15}N$ suggesting that deposited N is biologically utilised in lakes and that sediment $\delta^{15}N$ may provide a historical surrogate for total N deposition.

iv) The relationship between lake sediment $\delta^{15}N$ and N deposition has been confirmed by spatial analysis of surface sediments and N deposition load.

v) Modelling N limitation from catchment attributes remains problematic, probably because of the small number of modelling sites and the importance of N deposition history (high N deposition sites may still be N limited or may have become P limited).

However, development of catchment models remains a priority for upscaling N limitation work to the national level.
vi) There is a strong case for application of nutrient N critical loads for softwater lakes in the UK given the importance of these habitats under the EU Habitats Directive and Water Framework Directive, but the default value for empirical critical loads (5-10 kgN ha^{-1} yr^{-1}) would result in exceedance across most of the UK. Further work to better define harmful effects associated with critical load exceedance is required.

Work package 3: Nitrate leaching

The requirement for understanding catchment controls on NO_3^- leaching has been strikingly demonstrated by the first two Work Packages of this programme, which show that N deposition makes a major contribution to both acidification and nutrient enrichment of upland waters across most of the UK. Two complementary approaches were adopted here for improving catchment specific assessments of NO_3^- leaching pathways and controls. The first employed hydrological tracers to directly measure retention and losses of N additions to an acid grassland hillslope at the Afon Gwy, while the second employed the NO_3^- dual isotope approach to determine the balance between microbially produced NO_3^- in catchment soils and the proportion of atmospherically deposited NO_3^- that leaches unchanged into surface waters.

An understanding of the processes controlling N retention versus N leaching in soils is vital in order to correctly predict how N deposition will impact on aquatic and terrestrial ecosystems in the future, and what levels of emission control are required to protect them. The different possible mechanisms to explain current levels of NO_3^- in surface waters have very different future consequences: if it is 'hydrological' NO_3^-, this indicates that the terrestrial ecosystems are not yet N saturated, and may be able to continue assimilating large amounts of deposited N into the future. It also suggests that reductions in N deposition should translate directly into reductions in surface water NO_3^- concentrations. Effectively, this is a 'best case' scenario. If, on the other hand, the NO_3^- we currently observe in surface waters is 'saturation' N, then this indicates that terrestrial ecosystems are already N saturated, are likely to leach an increasing amount of NO_3^- in future, and that reductions in N deposition may have only limited benefits for surface waters. This is the 'worst case' scenario for NO_3^- leaching controls. Constraining future model predictions within these extreme cases will greatly reduce uncertainty in model predictions.

Under Task 3.1 a ^{15}N isotope experiment was undertaken on a podzolic hillslope at Plynlimon, a component of the upland landscape typically responsible for much of the NO_3^- leaching to surface waters. The experiment was designed to test whether NO_3^- leaching occurred because the soil and vegetation were already receiving N deposition in excess of biological demand (i.e. 'N saturated'), or because N inputs during rain events simply overwhelmed soil assimilation capacity or bypassed the soil completely via 'macropores' such as soil cracks (so called 'hydrological' NO_3^-). Additions of ^{15}N-labelled NO_3^- and a conservative bromide (Br) tracer were applied during simulated rain to 12 replicate plots, and Br and $^{15}NO_3^-$ measured in lateral throughflow out of the soil. Results showed very rapid transport of Br tracer, suggesting that water infiltrates rapidly through soil cracks, and hence that a mechanism exists for fast transit of hydrological NO_3^- through the soil to the stream.

However, despite this rapid water transfer, 80% of the $^{15}NO_3^-$ in this water was on average retained as it passed through the vegetation and soils. This suggests that soil microbes, perhaps located on the surfaces of soil cracks, are highly efficient at assimilating incoming N in infiltrating water. In support of the dual-isotope work (Task 3.2), this study suggests that some hydrological NO_3^- transport *does* occur, but that it can only account for a small part of observed stream NO_3^- most of which must therefore result from terrestrial N saturation. Within the hillslope, N retention was found to be highly heterogeneous, with locally N enriched areas that leached more of the added NO_3^-. Conceptually, this suggests that N saturation develops within the landscape through the formation and expansion of nutrient rich 'hotspots', for example where soils are thinner or where water flowpaths converge and concentrate nutrients. These hotspots are likely to be responsible for much of the observed NO_3^- leaching to surface waters, and may also be most susceptible to eutrophication responses in terrestrial vegetation.

The dual isotope study (Tasks 3.2-3.3) at four Acid Waters Monitoring Network sites (Afon Gwy, Scoat Tarn, River Etherow and Lochnagar) demonstrated the over-riding importance of rapid uptake and microbial processing of deposited inorganic N in the terrestrial part of catchments, with microbially produced NO_3^- contributing 68-100% of leached NO_3^- on a seasonal basis and 79-97% on an annual mean basis. These results are consistent with the tracer experiment work carried out at the Afon Gwy under Task 3.1. Differences between sites probably reflect differences in hydrology, with more direct leaching of atmospheric nitrate in catchments with sparser, shallower soils and steeper slopes. Seasonal differences in the proportion of microbially produced nitrate are due to much higher microbial activity and lower precipitation to flush atmospheric nitrate directly into surface waters in summer, compared with the winter months. The greatest proportion of hydrological NO_3^- occurs during the period of higher flows in late winter and spring.

Microbially produced NO_3^- may be considered to reflect saturation NO_3^- whereby total N deposition reduces C:N ratios and increases N availability for mineralization and nitrification. Hence N deposition is already overwhelming biological demand and leading to N saturation in terrestrial ecosystems. This means that for a large proportion of NO_3^- leaching, soil processes are mediating catchment responses to N deposition so that emissions reductions may not result in rapid reductions in the production of microbial NO_3^-. Anthropogenic N that has already accumulated in catchment soils may cause a time lag in responses to changing N deposition. Furthermore, the deposition source of biologically cycled N may be either NO_x or reduced N compounds.

However, a proportion of leached NO_3^- is hydrological, i.e. rapidly leached, unchanged, from wet deposition, reaching 21% of total leaching at Lochnagar. On a seasonal basis this proportion increases to almost a third at Lochnagar and a quarter in a Scoat Tarn inflow stream. This proportion of NO_3^- may be attributed directly to NO_x deposition, so that emissions reductions should lead to an immediate response in this component of leached NO_3^-. Given that both concentrations and fluxes of NO_3^- are greatest at the time when the direct atmospheric contribution is greatest in late winter and spring, NO_x emissions reductions would be particularly beneficial in reducing peak values of both during the period of greatest potential impact on aquatic ecosystems.

This work has demonstrated that for individual catchments it is possible using the dual isotope approach to apportion NO_3^- leaching to microbial sources that may respond very slowly to changes in N deposition and hydrological sources that will respond very rapidly to changes in input. This finding is of major importance for dynamic modelling of future catchment responses to changes in N deposition. Models using catchment C pools and soil C:N ratios are required for the greater part of NO_3^- leaching responses but the remainder should respond proportionately to changes in NO_x deposition. Expansion of this approach to other sites would facilitate upscaling and modelling at a national scale in the UK.

The potential importance of soil C:N ratios and bryophyte biomass (identified under previous DEFRA studies) as catchment-scale controls on NO_3^- leaching was assessed by a programme of random sampling at 16 unforested Acid Waters Monitoring Network sites. There is only a weak relationship between long-term mean NO_3^- concentration or proportion of N deposition leached and bryophyte biomass, but up to 33% of variation in the proportion of N deposition leached is explained if an outlying site is excluded. For soil C:N ratio there is little relationship with NO_3^- leaching unless a number of sites with severe peat erosion are excluded, when C:N ratio explains 56% of the variation in proportion of N deposition leached.

This work confirms that both C:N ratio and moss biomass are important factors in regulating NO_3^- leaching. The weakness of these relationships does however indicate that other factors are important, probably related to land cover, dominant vegetation type and slope etc. Hence further multivariate statistical analyses are required to determine the relative importance of these controls on the retention and leaching of deposited N. The identification of outliers (e.g. with soil erosion or lowland, low rainfall sites) also requires more rigorous statistical definition before the strength and significance of these relationships may be properly quantified.

Summary

i) The hydrological tracer experiment at the Afon Gwy demonstrates that very rapid transport of solutes through catchment soils may occur over a timescale of minutes to hours. However, a large proportion of nitrate is still retained even with such rapid drainage.

ii) The importance of N retention and subsequent regeneration of nitrate through mineralisation-nitrification is corroborated by the dual isotope experiments. These studies show that a maximum of 20-30% of leached nitrate is "hydrological" (untransformed nitrate from NO_x which is rapidly transported); the remainder is generated microbially and hence subject to longer-term biological controls linked to processes of N saturation. The microbial fraction of leached nitrate may have originated as NO_x or reduced N deposition. There is a seasonal variation in the proportion of hydrological nitrate with a maximum in the spring when concentrations and fluxes are greatest. Hence reductions in NO_x deposition should be reflected in rapid reductions in spring peaks in nitrate. However, most leached nitrate has been generated microbially from ecosystem N pools so a large proportion of leached nitrate may respond very slowly to changes in N deposition. Characterisation of catchment

attributes linked to hydrological nitrate will allow the identification of catchments which will respond most rapidly to changes in NO_x deposition.
iii) The random sampling of bryophyte biomass and soil C:N ratio at AWMN sites has shown that both are contributory factors to controls on nitrate leaching but a large proportion of variations between N deposition and leaching is due to other factors. Identification of these other determinants of nitrate leaching is a key priority for future catchment modelling work.

Work package 4: Influence of climate change on the impacts of atmospheric deposition in upland freshwaters

The main climatic changes predicted under the UKCIP02 scenario for the UK may be summarised as:

1) increasing temperatures, which will be most pronounced in southern England and smallest in Northern Ireland and north-west Scotland;
2) small decreases in annual mean precipitation which will be greatest in southern England but still only a few per cent overall;
3) major changes in the seasonal distribution of precipitation with worst-case predictions of more than 50% reductions during summer for southern England and 30-50% for the rest of the UK, and increases of at most 10-25% in winter;
4) increasing incidence of extreme precipitation events and drought but reduced snowfall as a result of the above changes.

The implications of these changes for upland waters in the UK are complex and sometimes unpredictable but were assessed under this programme through reviews of the existing literature.

Three major issues linking upland water quality and climate change were explored separately in a series of literature reviews;

1. controls on nitrate leaching and associated problems of acidification and eutrophication;
2. trends in dissolved organic carbon (DOC) affecting water colour, recovery from acidification and biogeochemical cycles linked to both nitrogen species and organic pollutants; and
3. fluxes and toxicity of heavy metals and persistent organic pollutants (POPs).

Nitrate leaching

On a seasonal basis there is usually an inverse correlation between temperature and NO_3^- leaching but the relationship between annual mean temperatures and fluxes of N species is less well understood, with few clear predictions in terms of NO_3^- leaching. There is a general consensus that higher temperatures lead to higher rates of mineralization and nitrification in soils but there is usually a corresponding increase in vegetation production and N immobilization and the balance between NO_3^- production and retention will be very specific to local vegetation, soils, N deposition and climatic conditions. Hence there is no clear prediction of the net overall effect of increasing annual temperatures on NO_3^- leaching in the UK or elsewhere.

The great majority of studies in upland systems have found that NO_3^- fluxes, and sometimes concentrations, tend to increase with discharge. Hence a reduction in annual mean runoff due to lower precipitation could on this basis result in lower annual leaching fluxes of NO_3^-. However, this relationship is not constant throughout the year because NO_3^- concentrations and fluxes tend to be greatest during the dormant season (autumn/winter) and smallest during the summer, and the relationship between discharge and NO_3^- yield is steepest in winter when there is less biological demand. Furthermore, predicted changes in precipitation are in opposite directions for winter and summer so the seasonal responses will be very different.

In all but the most N impacted catchments of the UK uplands, summertime NO_3^- concentrations tend to be very low or undetectable. With reduced rainfall and prolonged droughts it is likely that summer NO_3^- leaching will remain low but production and storage in soils may increase so that the scope for event-based NO_3^- pulses is much greater. If droughts are very severe then vegetation damage could result in large increases in NO_3^- leaching through the following dormant season and effects may last several years. The effects of summertime storms such as those causing the recent flooding across much of Great Britain are unknown but there may be scope for summertime leaching pulses of NO_3^- if vegetation uptake is reduced by drought damage.

Given that maximum NO_3^- leaching fluxes and concentrations already occur during winter and early spring and that discharge-yield relationships are steepest at this time of year, the predicted increases in winter precipitation and storms is likely to result in larger seasonal fluxes of NO_3^-. This effect may be compounded by summer drought and vegetation damage which will allow inorganic N to accumulate in soils for longer periods prior to flushing during rainfall events. In lakes and especially streams, episodic inputs of NO_3^- leading to acid pulses may increase in frequency and magnitude.

An unexpected consequence of reduced snowcover may be an increase in soil freezing events despite the higher temperatures, as demonstrated in snow removal experiments in North America. While extremely cold events will become less frequent, thereby reducing the serious damage to fine roots and larger flushes of inorganic N associated with severe freeze-thaw action, an increased frequency of mild freezing events may occur. The net effect on NO_3^- leaching associated with freeze-thaw action is therefore difficult to predict.

Concentrations of NO_3^- in UK upland waters start to increase in the autumn and reach peak values in early spring, usually February or March in streams and a month or two later in lakes due to their residence time. These peaks are associated with increasing microbial generation of NO_3^- in soils prior to the onset of vegetation growth, combined with thawing of frozen soils or snowmelt and flushing of accumulated inorganic N in soils. Climate warming is likely to alter the timing of this seasonal pattern but the impact on peak fluxes is uncertain. Predicted changes in springtime precipitation are very minor so any changes are more likely to be associated with the spring thaw and snowmelt. There may be a reduction in the spring pulse of NO_3^- that is associated with snowmelt in the higher altitude regions of the UK. It is possible that spring peak yields may decrease while overall dormant season yields increase, i.e. the winter concentration curve may be flatter but broader.

While the likelihood of any of these responses is unknown, given the uncertainty in the precise pattern of predicted climate change on a regional basis, the balance of probabilities is that problems associated with NO_3^- leaching in the uplands will deteriorate in the coming decades.

DOC production and leaching

The dissolved organic concentration of UK upland surface waters is dependent on many processes influenced by climate, and particularly by the effects of temperature and soil moisture on net primary production (NPP), decomposition rates, and by the effect of the intensity of precipitation which governs flow paths. It had been proposed that several of these factors have influenced the large increase in DOC concentrations observed in UK waters and elsewhere over the last 20 years.

Increasingly however, evidence points to a governing role of precipitation chemistry on DOC concentration, and in recent decades the dominant effect on this has been anthropogenic sulphur deposition. DOC solubility is inversely linked to both soil acidity and soil water ionic strength. In the UK and southern parts of Scandinavia there have been reductions in both factors over the last 15 years due to falling levels of anthropogenic sulphur deposition and a decline in storm induced seasalt deposition.

The combination of trends in surface water sulphate and chloride concentration have been shown sufficient to explain DOC trends in several regions in North America and northern Europe in a paper currently in press in Nature. Hence future DOC leaching is related to both trends in acid deposition and climate change.

On balance it would seem that as solubility increases, synergistic effects of increased NPP and decomposition rates under a scenario of increasing summer temperatures and longer growth seasons should increase mean annual DOC fluxes and concentrations further. Added to this, increased hydrological variability, and particularly wetter winter conditions and increased seasalt events will increase seasonal variability, with higher DOC maxima (*cf.* NO_3^- leaching).

These potential effects of future climate change have major consequences for aquatic ecosystems, through changes to the light and heat environment, the extent of transport and (where DOC is lost in lakes through photo-oxidation) delivery of toxic metals and organic compounds and effects on acidity. Furthermore, future changes to water quality will have major implications for future water treatment costs.

Ultimately though, scientific understanding is insufficient for scenarios to be predicted with any certainty. It is vital, therefore that monitoring of these upland systems is continued and that, increasingly, in situ and laboratory experiments are encouraged, ideally using sites and soils in monitored catchments, so that the interactions between anthropogenic deposition and climate change effects on DOC can be modelled with greater confidence.

Trace metals and persistent organic pollutants

Based on the Aarhus Heavy Metal and Persistent Organic Pollutant (POP) Protocols, the Water Framework Directive lists of hazardous and priority hazardous substances and other legislation and guidelines, the main trace metals of concern are mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu) and zinc (Zn) while the main POPs include PAHs, organochlorine pesticides, brominated compounds and organometallic compounds such as tributyltin (TBT). The POP priority hazardous substances include anthracene, pentabromodiphenylether, chloroalkanes, endosulfan, HCB, HCBD, HCH, nonylphenol, pentachlorobenzene, PAHs and TBT. Annual average and maximum allowable concentration Environmental Quality Standards (EQS) for inland surface waters have been proposed for these but data for UK upland waters are very limited.

Predictions for how climate changes will impact emissions from industrial processes are rare except for electricity generation. It is predicted that despite the projected increase in electricity demand to 2020, UK coal consumption will continue to fall which could result in a decline in metals and POPs emissions. However, the UK will need to replace c. 30% of the current generating capacity (coal, nuclear) by 2025 and how this is undertaken will have a major impact on UK emissions. For Hg and volatile POPs the broader (possibly hemispherical) geographical scale needs to be considered. It is predicted that metal emissions in Europe will continue to decline and although coal consumption in developing countries could increase rapidly, the introduction of control technologies does not necessarily imply a similar increase in emissions. As a result, projected industrial metal emissions could either increase or decrease.

The potential for the increase in invasive species, in vector-borne disease, crop pests and the possibility of reduced efficacy of herbicides as a result of climate change may lead to increased usage of pesticides in the UK and further afield. Long-range transport and increased atmospheric residence times will provide the means for POPs to be transferred to the UK uplands. Increased usage of upland areas for agriculture could also result in elevated inputs of trace metals, from fertilisers, to waterbodies in these areas.

Warmer air temperatures will allow greater volatilisation of POPs and Hg and longer atmospheric life-times. The potential for greater distribution will therefore increase as will the movement of these pollutants to areas that are colder by virtue of their latitude or altitude. However, it is the retention of these compounds in upland waters that is critical. Warmer water temperatures will reduce retention and possibly lead to re-emission to the atmosphere from pollutant 'stores'. Changing wind patterns could alter distribution patterns and pollutant source areas.

Climate change is predicted to alter the distribution and seasonality of precipitation (drier summers, wetter winters) and dramatically reduce snowfall, while there is also potential to increase cloudiness in upland areas. Wet deposition and scavenging by snow and fog are efficient atmospheric removal processes for metals and POPs and so these changes will alter pollutant inputs to upland waters. However, projections of precipitation and cloudiness remain uncertain.

There is a vast store of previously deposited pollutants in catchment soils and lake sediments. Climate change may be a key factor in the re-mobilisation of these contaminants to upland waters. Climate-enhanced catchment soil erosion and leaching from catchment soils may elevate pollutant inputs to upland waters from this store.

Warmer and wetter conditions could increase mercury methylation while longer ice-free periods could increase algal scavenging of contaminants from the water column and into the food-web.

Many physico-chemical and biological factors influence the toxicity of trace metals and POPs to aquatic biota including pH, water hardness, dissolved oxygen content, water temperature, suspended solids content, DOC concentrations, metabolic rate, diet, generation rate, etc. Climate change will influence all these factors though the direction (improvement or deterioration), scale of impact and interactions may vary from site to site.

In conclusion, there is considerable potential for climate change to impact on the emission, transport, deposition, re-mobilisation, re-emission and toxicity of trace metals and POPs in UK upland waters. While many predictions and scenarios, especially with regard to projected air temperatures, appear to give reasonable agreement (to direction if not to scale), there is still considerable uncertainty as regards future changes to precipitation, cloudiness, wind speeds and the magnitude and frequency of extreme events.

Uncertainties relating to how climate effects will impact upon trace metals and POPs in upland ecosystems are compounded by a lack of basic information on these substances (especially Hg and POPs) in UK upland waters. The baseline against which we may measure the future effects of trace metals and POPs in upland ecosystems is largely missing and unless this significant gap in knowledge is filled as a matter of some urgency, it will not be possible to assess future changes at these sensitive sites.

There is an urgent need to establish a monitoring programme to undertake empirical measurements at a wide range of upland waterbodies, in all areas of the UK over an extended period of time. Such knowledge will allow a better understanding of the key processes and drivers affecting the levels of toxic substances in upland aquatic food-webs. These data are also required to improve models for future prediction. Without such basic background knowledge, even the most robust models will lack 'ground-truth' and may offer only poor projections of future impacts.

Summary

National climate change scenarios for the UK (UKCIP02) indicate a general warming trend across the whole country, with a slight decrease in annual precipitation. However, drier summers and wetter winters are predicted with an increasing incidence of extreme precipitation events and droughts, but milder winters.

i) Nitrate leaching

There are no clear predictions of the impacts of increased temperatures on nitrate leaching, since both microbial nitrate production and plant uptake of N may increase simultaneously. Precipitation changes will have very different effects in summer and winter. Drier summers should result in less nitrate leaching but possibly greater accumulation of inorganic N in soils which may be washed out in storm events, leading to much more episodic leaching events. Increased summer drought could damage plants leading to higher nitrate leaching during subsequent seasons. Increased winter precipitation could lead to greater nitrate leaching during the period when fluxes and concentrations are already greatest. The effects of snowmelt on seasonal patterns will be reduced (i.e. smaller peak concentrations at snowmelt) but with reduced snow cover, soil freezing events may increase in frequency and magnitude which may again result in increased episodic nitrate leaching.

ii) DOC production and leaching

Surface water DOC concentrations are governed largely by factors affecting net primary production, decomposition rates and hydrological flow paths, but recent evidence suggests that the chemistry of precipitation is the governing factor in observed increasing trends. DOC solubility is inversely linked to both soil acidity and soil water ionic strength. In the UK and southern parts of Scandinavia there have been reductions in both factors over the last 15 years due to falling levels of anthropogenic sulphur deposition and a decline in storm induced seasalt deposition. The combination of trends in surface water sulphate and chloride concentration have been shown sufficient to explain DOC trends in several regions in North America and northern Europe in a paper currently in press in Nature. Hence future DOC leaching is related to both trends in acid deposition and climate change. With increasing summer temperatures, longer growing seasons and a continued rise in organic matter solubility it is likely that DOC fluxes and concentrations will increase. More frequent extreme weather events may increase seasonal variability and lead to higher maximum concentrations.

iii) Trace metals and persistent organic pollutants (POPs)

Trace metal emissions are expected to continue to decline in Europe though future emissions from developing countries are uncertain. If climate change increases invasive species, vector-borne diseases and crop pests it is possible that pesticide usage and hence emissions may increase. Warmer temperatures will allow the transport of volatile pollutants like POPs and Hg over greater distances though the net effect in terms of increased delivery and re-emission is difficult to predict. There is a vast store of pollutants in catchment soils and lake sediments which may be remobilised by climate-enhanced soil erosion and leaching. Warmer and wetter conditions may increase mercury methylation and transport while increased ice-free periods could increase algal scavenging of pollutants from the water column. The toxicity of trace metals and POPs is also influenced by factors such as acidity (linked to nitrate leaching above) and DOC (see above). With so many influencing factors it is very difficult to predict the net changes in deposition and impacts of trace metals and POPs in the UK. Furthermore, the lack of basic information on these substances makes the assessment of future changes in response to climate even more difficult.

Key findings and policy implications

The work completed under this contract has strengthened the evidence base for the adverse effects of N deposition as an agent of both acidification and nutrient N enrichments in sensitive water bodies of the UK.

Assessment of the role of N in contributing to acidification and critical load exceedance has shown that all impacted sites are at least partly affected by N deposition and more than half would exceed critical loads on the basis of N deposition alone, even following implementation of the EU NECD in 2010. Emissions policies relating to sulphur alone are clearly insufficient to protect sensitive UK freshwaters from acidification in many cases. Further reductions in emissions targets for total N would be required to prevent critical load exceedance in the majority of sensitive freshwaters.

The role of N deposition in causing changes to lake nutrient cycles and productivity has been demonstrated through a review of the recent literature and through direct measurement of phytoplankton responses to nutrient additions in laboratory bioassay studies. N limitation is almost as frequent as P limitation in upland lakes but co-limitation of growth by N and P is the most common status. Independent evidence for historical changes in lake nutrient inputs and productivity has been found through studies of N stable isotopes in lake sediments. A steady depletion in sediment $\delta^{15}N$ over the industrial period is found in most studied lakes, indicating that N deposition inputs have increased and have been utilised in upland catchments for many decades. The potential impacts of N deposition in increasing lake productivity are highly relevant to N emissions policy with respect to several international directives:

1. oligotrophic lakes in the UK uplands designated under the EU Habitats Directive may be particularly sensitive to the effects of N deposition, with possible changes to phytoplankton species and productivity and changes to macrophyte flora;
2. changes in the productivity and natural nutrient limitation status of upland lakes may be considered a deviation from the good ecological status required under the EU Water Framework Directive; and
3. there is a strong case for calculating nutrient N critical loads to feed into the integrated assessment modelling work under the UN-ECE Convention on Long-Range Transboundary Air Pollution, including the Gothenburg Protocol.

Confirmation that N deposition may lead to both acidification and nutrient enrichment highlights the increasing need to understand the processes that determine whether N deposition causes enhanced nitrate leaching over the short- or longer term. Results from this project have for the first time allowed the major controls on nitrate leaching to be separated and quantified at specific sites. Hydrological tracer experiments have proven that rapid flowpaths exist that can transport deposition through soils into surface waters in minutes to hours, but a large proportion of nitrate is still retained in soils. The nitrate dual isotope approach has further demonstrated that only 20-30% of leached nitrate is rapidly transported from NO_x deposition; the remainder is generated within soils by microbial processes. Hence a fraction of leached nitrate will respond rapidly to changes in NO_x deposition. However, a larger proportion of leached nitrate is generated in soils from N pools that may consist of accumulated N deposition (both NO_x and reduced N) as well as recently deposited N. Therefore a large proportion of nitrate leaching may respond very slowly to changes in N deposition while current levels of nitrate must indicate advanced terrestrial N saturation.

Understanding the balance of these nitrate sources is essential for predicting timescales of response to changes in N deposition and for calculating target loads to achieve a given water quality target within a specified timescale. This programme has shown that nitrate leaching models will also need to incorporate catchment scale attributes such as soil C:N ratio and mean bryophyte biomass which explain part of the between site variation in leaching relative to N deposition.

Literature reviews suggest that climate change will have a major effect on both nitrate and DOC leaching. Higher temperatures will lead to higher production of both although the net balance between production and retention is harder to predict and they may be leached under differing conditions. Increased storminess and more frequent droughts will probably lead to lower leaching throughout the summer but an increased susceptibility to episodic leaching events, which for nitrate may be associated with severe acid episodes. Winter fluxes of both nitrate and DOC may increase with greater episodicity, although for nitrate there may be a reduced peak value in sites affected by snowmelt since snow cover will be reduced. If DOC concentrations increase more generally or during lower flow summer rainfall events, surface water acidity will increase, potentially restricting biological recovery from acidification. Future deposition levels of trace metals and persistent organic pollutants are unknown and therefore possible effects of climate change are very hard to predict. Furthermore there are strong links between the leaching and toxicity of trace metals and chemical variables like acidity and DOC which are also predicted to change in response to climate and deposition. While these interactions make it very difficult to model or predict future changes in concentrations and impacts of these pollutants they do demonstrate the intrinsic links between climate change, air quality and water quality policies.

Success in meeting project objectives and priorities for future work

The Freshwater Umbrella programme employed many new techniques to determine the actual and potential extent of upland water quality problems stemming from N deposition. The potential problem of nutrient N impacts in upland lakes which was first proposed in a NERC funded study under the GANE programme has been corroborated by the three approaches of literature review, nutrient bioassays and isotopic analysis of sediment $\delta^{15}N$, in the latter case for the first time in the UK. There is now a wealth of evidence to support the hypothesis that N deposition must be impacting nutrient cycles and productivity of upland waters. The case for development of nutrient critical loads for UK freshwaters has been convincingly demonstrated in this programme.

However the nature of these pilot studies means that only a limited number of sites have been assessed and there are too few to upscale more widely to the national level. Attempts to upscale catchment models of N limitation were largely unsuccessful, probably due to several factors including the small number of survey sites classified for N or P limitation status, insufficient catchment scale data and the over-simplistic view that N limitation best defines sites most likely to be impacted by N deposition. In fact it became apparent during this programme that one of the indicators of the most severe N impacts (e.g. at Scoat Tarn) could be the inducement of P limitation because of a large excess nitrate availability. Hence the classification of changed or impacted nutrient status needs better definition than simply N limited under elevated N deposition.

Major progress was made in understanding nitrate leaching mechanisms using techniques new to the UK. The hydrological tracer method was successfully employed to show rapid leaching pathways for deposition at the Afon Gwy while the nitrate dual isotope method largely developed in alpine lakes of the Rocky Mountains in the USA was applied with great success to four AWMN sites under this project. The isotopic signatures of N and oxygen in leached nitrate provided very clear evidence that a large proportion could not have come directly from the atmosphere and enabled the characterisation of all four sites in terms of hydrological versus microbial nitrate contributions. The potential of this method for characterisation of catchments vulnerable to rapid nitrate leaching was clearly demonstrated.

Priorities for future work to build on the pioneering studies completed under the Freshwater Umbrella should include the following:

1. further work to define "harmful effects" from nutrient N deposition for use in critical load models;
2. expansion of the nutrient bioassay and sediment isotope work to characterise more upland catchments in terms of the nutrient N impacts they have experienced;
3. investigation of the key determinants of N isotopic signatures in lake sediments, i.e. simple magnitude of input fluxes versus in-lake fractionation effects;
4. development of catchment attribute models to upscale nutrient N impact classes across upland water bodies in the UK, including collation of new datasets and clearer definition of impacted sites;
5. upscaling of the nitrate dual isotope approach to characterise catchments vulnerable to rapid impacts from hydrological nitrate leaching and those more at risk over the longer term from N saturation and microbial nitrate leaching;
6. identification of site characteristics other than soil C:N ratio and bryophyte biomass that regulate nitrate leaching and therefore dictate vulnerability to the adverse effects of N deposition.

Website and database management

Gavin Simpson

As part of this research programme, the Freshwater Umbrella website has been completely redesigned and extended to accommodate new features and additional data, plus make it easier to access and use by researchers and the general public.

The website also has a new home at the URL www.freshwaters.org.uk and has been housed on a new webserver located within University College London. The website has a fresh, new look and has been themed along the colour scheme of the DEFRA logo. In the past 12 months, the website has had over 70000 hits (200+ per day on average), serving up almost 35000 pages. It is returned in the top 10 or 15 Google search results for terms such as "freshwaters", "acidity in freshwater" and "nitrate leaching".

A screen shot of the home page is shown below.

What is the Freshwater Umbrella?

The Freshwater Umbrella research programme into the recovery of aquatic ecosystems from the effects of acidification has been funded by DEFRA (previously the DOE and DETR) and the devolved agencies since 1990. The Freshwater Umbrella undertakes 3-year applied science programmes to develop the scientific background to aid DEFRA make policy decisions concerned with air pollution effects on freshwater systems in the UK.

The main focus of the current Freshwater Umbrella research programme is the role of nitrogen and its effects on freshwater ecosystems both as a eutrophier and through the leaching of nitrate from catchment soils. Further information about the various research programmes undertaken by the Freshwater Umbrella can be found in the Research section of this website.

DEFRA and the devolved agencies fund two complementary Umbrella research programmes; the Terrestrial Umbrella and the Dynamic Modelling Umbrella.

The Future of Britain's Upland Waters

Some of the UK's most environmentally sensitive upland lakes and streams are starting to recover from the effects of acid rain. According to new research the amount of acidic sulphur in UK waters has generally halved in the last 15 years, in turn acidity is declining and wildlife is beginning to recuperate.

The Future of Britain's Upland Waters details the proceedings of a one-day workshop held at UCL in a series of papers that review the current status of research in the ecology of upland waters in the UK. These paper stress the importance of upland waters and the threats they face, such as atmospheric pollutants and changes in land-use, and report the results of recent research on the chemistry and biology of upland waters in the UK.

In particular the report contains a summary of the main findings of 15 years of monitoring as part of the UK Acid Waters Monitoring Network (UK AWMN), a DEFRA-funded network of 22 lakes and streams established to study the success international emissions reductions and their effects. The full results of the analysis of the UK AWMN data have recently been published in a special issue of the scientific journal Environmental Pollution.

Ben Bradshaw, Fisheries and Local Environmental Quality Minister, today welcomed the research and highlighted how measures brought in by Government were starting to bear fruit. **"It will take time for these sensitive waters to recover from the devastating effects of acid rain. So it is extremely encouraging that today's research suggests that they are starting to recover,"** he said.

News

3rd October, 2006:

Oral and poster presentations on Freshwater Umbrella research now available

8th September, 2006:

Journal article on the importance of nitrous oxide in removing atmospheric nitrogen from moorland catchments published

15th November, 2005:

Two new research reports, launched today, indicate that UK waters are recovering from acid rain

27th April, 2005:

RAW-UK Final Report now available for download

17th January, 2005:

Defra Workshop on 2004 CCE Data Submission

[More news items]

Project news is displayed prominently and we use the home page to deliver relevant and important information, such as the release of the report on "The Future of Britain's Upland Waters".

Throughout, open source tools have been used to both produce and serve the website. The Apache webserver is used to server the web pages to users' browsers, and the advanced functionality of the website is driven by the PHP scripting language. The site maps are currently drawn using Mapserver, an open source web mapping tool. The data driving the web site is held on a Mysql database, which stores all the user data as well as the Freshwater Umbrella data holdings, including the national freshwater critical loads mapping data sets.

An important concern that has driven the design of the web site from the very beginning is adherence to web standards and accessibility rules. The site is coded to the World Wide Web Consortium (W3C) XHTML 1.0 standard using compliant Cascading Style Sheets (CSS) rules to separate the look and feel of the site from the actual content. This is important for access by disabled users who might be using alternative technology to access the site, such as screen readers. In addition, we have endeavoured to make each page of the site compatible with Priority 3 of the W3C Web Content Accessibility Guidelines to achieve the AAA rating. Where the AAA rating is not possible, we have made every effort to eliminate as many non-compliant elements as possible. Most other pages have AA approval.

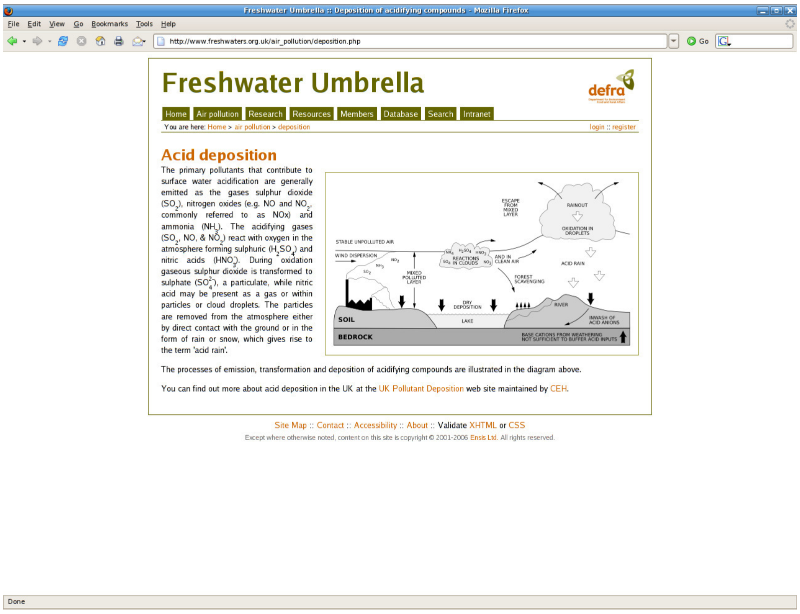
Users can register an account on the website, which provides them with a user ID and password. Different levels of access to the site are provided via the user ID, such that the project intranet resources are only available to DEFRA's project managers and the project consortium. The user accounts can also be used as a mailing list, so that when important project information is available, we can contact those interested users with details. We intend to use this facility to announce the availability of this final project report following approval from DEFRA, for example.

The web site is broken into several sections, each accessed from the main menu at the top of the screen. These sections are:

1. The **Air pollution** section contains useful and relevant background information pertinent to the project, such as the various critical loads models, as well as information on acid deposition and surface water acidification for example.
2. The **Research** section contains information on the previous Freshwater Umbrella contract as well as the work plan for the current research programme.
3. The **Resources** section provides links to useful web pages with relevant information. Access to project reports and poster and oral presentations given by the Umbrella participants is also gained through this section.
4. Information on the current research participants and their institutions can be found in the **Members** section.
5. The **Database** section provides access to the Freshwater Umbrella data holdings, particularly the extensive water chemistry data holdings.
6. An extensive web site search facility is provided in the **Search** section.
7. Project related materials for the consortium, such as the minutes of project meetings and the period status reports provided to DEFRA, are available via the **Intranet** section of the site. Access to this section is restricted to the current project team and DEFRA's project managers.

To illustrate the web site features, we now present a series of screen shots of various sections of the site.

The site was intended to be accessible to both researchers and the informed lay person. As such we provide useful background information on the problems of acid deposition and surface water acidification. The screen shot below shows the page describing acid deposition.



Freshwater Umbrella

You are here: Home > air pollution > deposition

Acid deposition

The primary pollutants that contribute to surface water acidification are generally emitted as the gases sulphur dioxide (SO_2), nitrogen oxides (e.g. NO and NO_2, commonly referred to as NOx) and ammonia (NH_3). The acidifying gases (SO_2, NO, & NO_2) react with oxygen in the atmosphere forming sulphuric (H_2SO_4) and nitric acids (HNO_3^-). During oxidation gaseous sulphur dioxide is transformed to sulphate (SO_4^{2-}), a particulate, while nitric acid may be present as a gas or within particles or cloud droplets. The particles are removed from the atmosphere either by direct contact with the ground or in the form of rain or snow, which gives rise to the term 'acid rain'.

The processes of emission, transformation and deposition of acidifying compounds are illustrated in the diagram above.

You can find out more about acid deposition in the UK at the UK Pollutant Deposition web site maintained by CEH.

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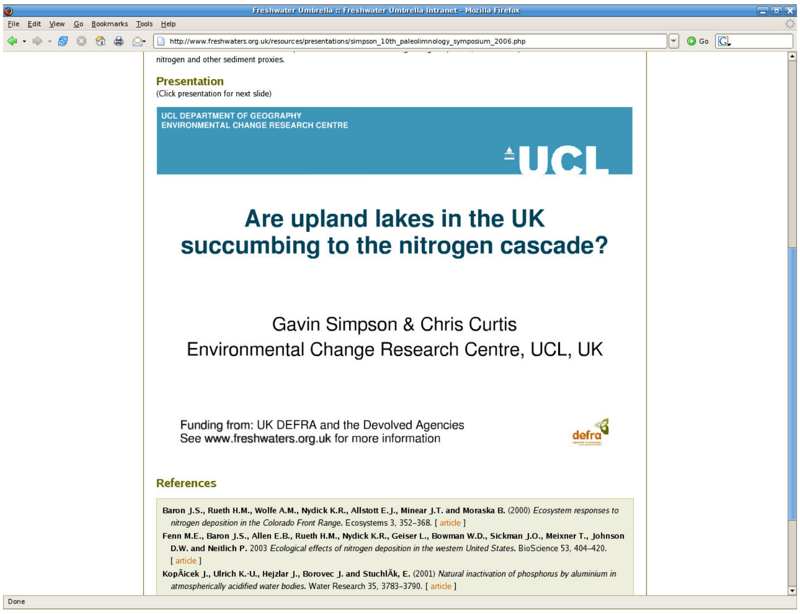
With the advent of electronic presentations at conferences and means to display these as Flash movies in web browsers, we have begun adding presentations given by Freshwater Umbrella members at international conferences to the website. Each presentation is converted from the original PowerPoint file into a Flash movie, which is then embedded in a web page. The user can then click through the slides of the presentation. The screen shot below shows a presentation given by Dr. Gavin Simpson on palaeoecological work undertaken in the current research programme on changes in nitrogen isotopes in sediment cores over the past 200 or so years as an indicator of changes in the biogeochemistry of upland UK lakes, thought to be the result of anthropogenic inputs of nitrogen via deposition.



nitrogen and other sediment proxies.

Presentation

(Click presentation for next slide)

UCL DEPARTMENT OF GEOGRAPHY
ENVIRONMENTAL CHANGE RESEARCH CENTRE

Are upland lakes in the UK
succumbing to the nitrogen cascade?

Gavin Simpson & Chris Curtis
Environmental Change Research Centre, UCL, UK

Funding from: UK DEFRA and the Devolved Agencies
See www.freshwaters.org.uk for more information

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Fenn M.E., Baron J.S., Allen E.B., Rueth H.M., Nydick K.R., Geiser L., Bowman W.D., Sickman J.O., Meixner T., Johnson D.W. and Neitlich P. 2003 *Ecological effects of nitrogen deposition in the western United States.* BioScience 53, 404–420. [article]

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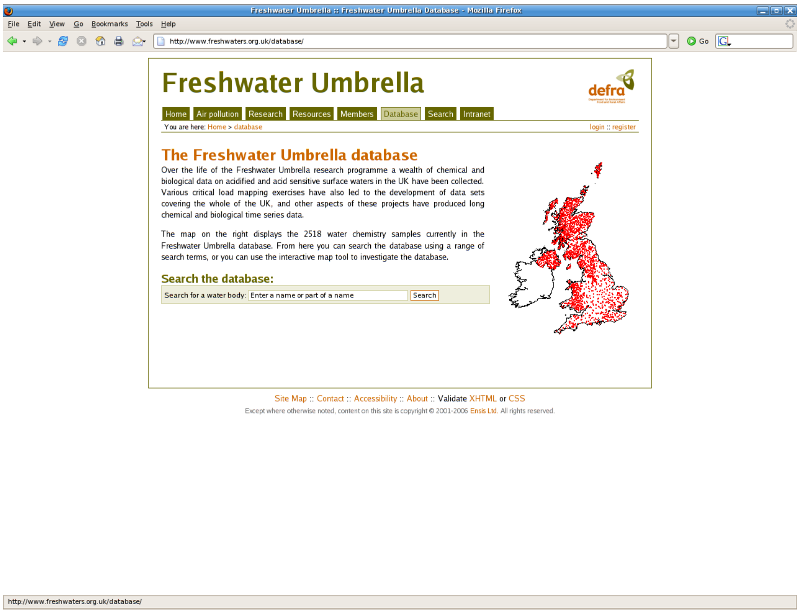
As mentioned above, the database section of the web site provides access to the data holdings. The main entry page for the database is shown below.



The Freshwater Umbrella database

Over the life of the Freshwater Umbrella research programme a wealth of chemical and biological data on acidified and acid sensitive surface waters in the UK have been collected. Various critical load mapping exercises have also led to the development of data sets covering the whole of the UK, and other aspects of these projects have produced long chemical and biological time series data.

The map on the right displays the 2518 water chemistry samples currently in the Freshwater Umbrella database. From here you can search the database using a range of search terms, or you can use the interactive map tool to investigate the database.

Search the database:

Search for a water body: Enter a name or part of a name

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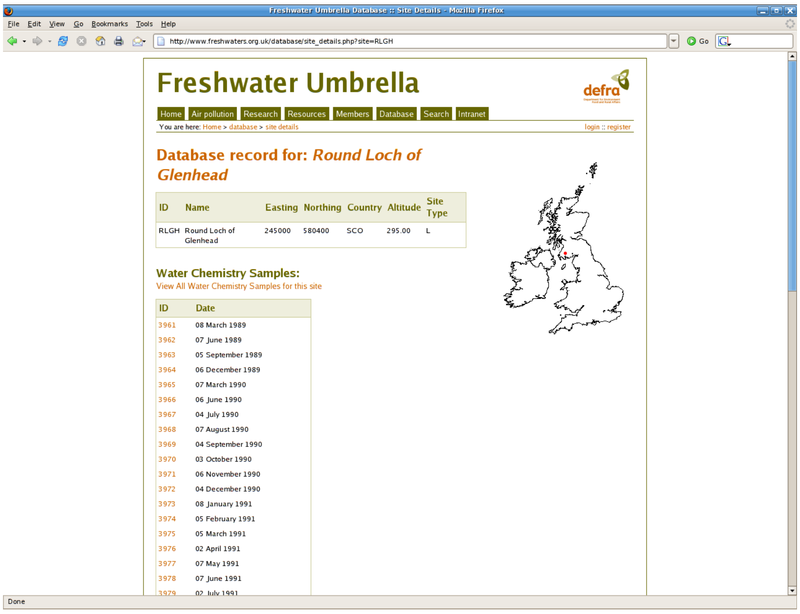
The map on the right is drawn dynamically and illustrates the locations of water chemistry samples held in the Freshwater Umbrella database. This page also provides a simple search facility, where the user can enter the name of a surface water or a partial name and the database will search for sites that match those criteria.

A list of sites that match the searched term are displayed, providing access through to the site details held in the database. Below is a screen shot of the page for the Round Loch of Glenhead, an historically important site in the study of surface water acidification and a site on the UK Acid Waters Monitoring Network.



Database record for: *Round Loch of Glenhead*

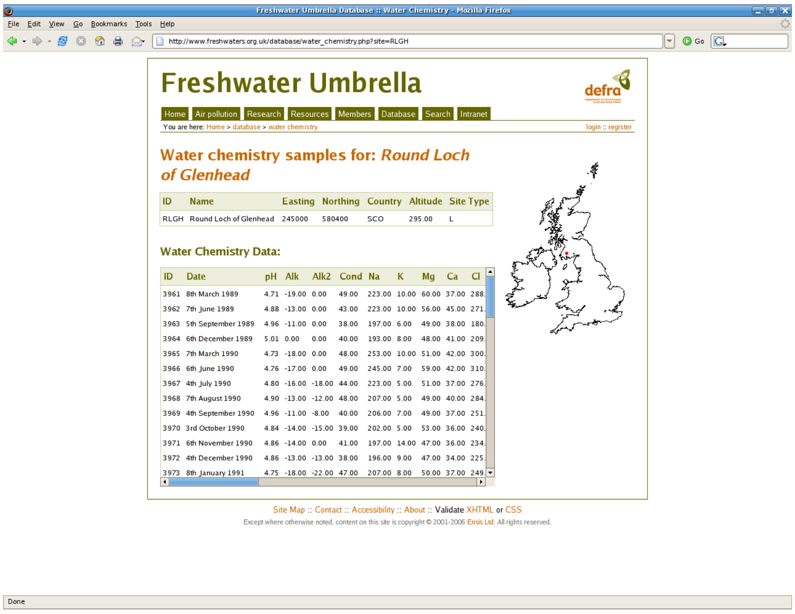
ID	Name	Easting	Northing	Country	Altitude	Site Type
RLGH	Round Loch of Glenhead	245000	580400	SCO	295.00	L

Water Chemistry Samples:

View All Water Chemistry Samples for this site

ID	Date
3961	08 March 1989
3962	07 June 1989
3963	05 September 1989
3964	06 December 1989
3965	07 March 1990
3966	06 June 1990
3967	04 July 1990
3968	07 August 1990
3969	04 September 1990
3970	03 October 1990
3971	06 November 1990
3972	04 December 1990
3973	08 January 1991
3974	05 February 1991
3975	05 March 1991
3976	02 April 1991
3977	07 May 1991
3978	07 June 1991
3979	02 July 1991

Basic site information is displayed along with a list of water chemistry samples for this site. The map on the right has again been drawn dynamically and shows the location of the site, indicated by a red dot. The user can then select and individual sampling date to view the data for that date, or choose to view all the water chemistry records for the site, as shown below:



Water chemistry samples for: *Round Loch of Glenhead*

ID	Name	Easting	Northing	Country	Altitude	Site Type
RLGH	Round Loch of Glenhead	245000	580400	SCO	295.00	L

Water Chemistry Data:

ID	Date	pH	Alk	Alk2	Cond	Na	K	Mg	Ca	Cl
3961	8th March 1989	4.71	-19.00	0.00	49.00	223.00	10.00	60.00	37.00	288.
3962	7th June 1989	4.88	-13.00	0.00	43.00	223.00	10.00	56.00	45.00	271.
3963	5th September 1989	4.96	-11.00	0.00	38.00	197.00	6.00	49.00	38.00	180.
3964	6th December 1989	5.01	0.00	0.00	40.00	193.00	8.00	48.00	41.00	209.
3965	7th March 1990	4.73	-18.00	0.00	48.00	253.00	10.00	51.00	42.00	300.
3966	6th June 1990	4.76	-17.00	0.00	49.00	245.00	7.00	59.00	42.00	310.
3967	4th July 1990	4.80	-16.00	-18.00	44.00	223.00	5.00	51.00	37.00	276.
3968	7th August 1990	4.90	-13.00	-12.00	48.00	207.00	5.00	49.00	40.00	284.
3969	4th September 1990	4.96	-11.00	-8.00	40.00	206.00	7.00	49.00	37.00	251.
3970	3rd October 1990	4.84	-14.00	-15.00	39.00	202.00	5.00	53.00	36.00	240.
3971	6th November 1990	4.86	-14.00	0.00	41.00	197.00	14.00	47.00	36.00	234.
3972	4th December 1990	4.86	-13.00	-13.00	38.00	196.00	9.00	47.00	34.00	225.
3973	8th January 1991	4.75	-18.00	-22.00	47.00	207.00	8.00	50.00	37.00	249.

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Summary and recommendations for future work.

Here we have outlined the work undertaken as part of the current project to expand and update the web presence of the Freshwater Umbrella and to improve access to results, reports and the research findings of the Umbrella, resulting in the new Freshwater Umbrella website.

The new site has a fresh, modern look and has been designed to meet web standards and allow access to as wide a range of users as possible.

Whilst significant progress has been made, further work under future Freshwater Umbrella contracts should continue to maintain the current site and add to the existing feature set. In particular, providing summary results from the current project would allow users to access the research findings, without having to delve into the technical project reports. By providing this information in a web page rather than only in the project reports, it allows indexing of the results by search engines such as Google, widening access to the results of the Umbrella.

Much more could be done with the dynamic mapping facilities of the website, including illustrations and presentations of critical loads and exceedance maps for the UK, for example.

As many people now access scientific work via the internet, the Freshwater Umbrella web site provides an excellent resource and means to widen access to the work of the Umbrella and DEFRA as a whole, and to the problems of air pollution, surface water acidification and nitrogen enrichment.

Work package 1: Critical loads for acidity

Task 1.1: Watching brief on critical loads methodology and new datasets

Chris Curtis

Several members of the Freshwater Umbrella (Chris Curtis, Gavin Simpson, Rick Battarbee, Chris Evans, Bridget Emmett, Martin Kernan and Don Monteith) attended the Acid Rain 2005 Conference in Prague, where there were parallel sessions devoted to critical loads, acidification modelling and many other relevant topics. Papers and posters relevant to UK freshwater critical loads were presented on FAB model (Henriksen & Posch, 2001) applications in Canada and Norway, linking critical loads and dynamic models within the European scale work of the CCE, and uncertainty in critical loads modelling.

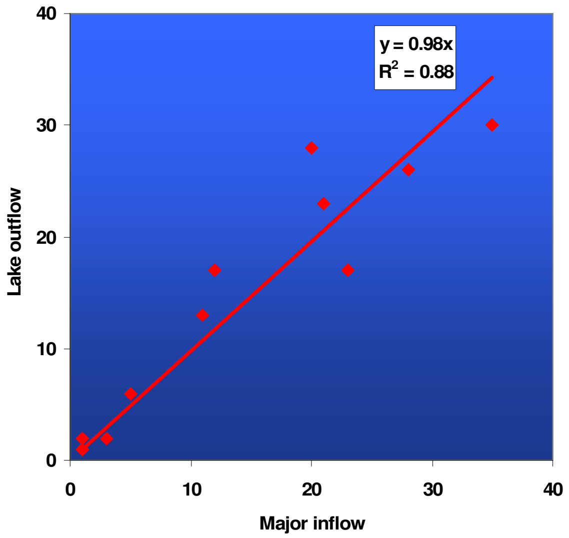
Two specific aspects of FAB model methodology were discussed in Prague. First, following discussions with Canadian and Norwegian scientists it is intended to submit a manuscript on parameterising the in-lake retention process within FAB to a journal. This aspect of the model was questioned during previous consultation exercises with DTI and other stakeholders. Their concern was the possibility that in-lake sinks for acid deposition were being underestimated due to the use of mass-transfer coefficients derived for North American lakes that may be inappropriate for UK lakes. However, data collated under this programme from previous DEFRA funded projects (CLAG Nitrogen Network, CLAM) have shown little difference in acid anion concentrations between lake inflows and outflows measured at the same time, strongly suggesting that if anything, the mass-transfer coefficients used over-estimate in-lake retention (Fig. 1.1). This relationship was shown for the first time at the Acid Rain 2005 Conference.

Second, during the Critical Loads and Dynamic Modelling Umbrella annual meeting held in Prague, the issue of catchment areas in static model applications was raised. It was agreed that the use of catchment areas to represent critical loads was problematic. Small upland lakes may have small catchment areas but be of high conservation value and are therefore under-represented in national critical loads submissions. A separate issue relates to the problem of "double accounting" catchment areas if terrestrial ecosystem critical loads are applied in the same area. These questions have not yet been resolved by the NFC and the CCE.

The UK freshwater critical loads dataset has been further expanded by the provision of a streams dataset for the North Yorkshire Moors, collected in March 2005 under the auspices of additional DEFRA funding for the Critical Loads and Dynamic Modelling Umbrella by Chris Evans. While collection of the necessary catchment attribute data has not been done yet, it is intended to apply the FAB model to this new regional dataset when these data become available, prior to the next CCE call for data.

Finally, the justification for the adoption of empirical, soil-specific values of denitrification in the FAB model, contrary to the recommendations of the CCE Mapping Manual (UBA, 2004) has been published in the journal Soil Biology and Biochemistry (Curtis *et al.*, 2006), based on work done under the DEFRA CLAM project (Curtis & Simpson, 2001).

Figure 1.1: Comparison of mean nitrate concentration (μeq l^{-1}) in lake outflow and major inflow streams (CLAG Nitrogen Network sites)



Status of UK critical load maps

The updated UK critical loads of acidity maps for freshwaters (April 2004) have not yet been published other than in the previous Freshwater Umbrella Final Project Report (Curtis & Simpson, 2004). A journal manuscript is in preparation to include updates to the mapping dataset, the choice of ANC_{crit} and critical load exceedances using the latest deposition data, relative to the previous published version of the FAB model in the UK (Curtis *et al.*, 2000).

One relatively recent adaptation to the FAB model which arose from work done by Chris Curtis under the DEFRA CLAM programme was a reformulation to allow for direct deposition to lake surfaces (Henriksen & Posch, 2001). Previously the FAB model could calculate zero NO_3^- leaching to lakes where total N deposition was lower than the catchment's average ability to retain it ($CL_{min}N$). Under the new model formulation, direct deposition to lake surfaces is recognised which means that some NO_3^- presence in the lake must result from N deposition. In exceeded sites, this means that N deposition to lakes always makes a contribution to exceedance. Theoretically, given the negligible surface area of streams for direct deposition, it is still possible to get complete retention of deposited N where N deposition is lower than $CL_{min}N$ for stream catchments. In such cases, N deposition makes no contribution to critical load exceedance for the stream.

The crucial importance of N deposition in contributing to critical load exceedance in UK freshwaters is evident in a re-analysis under this contract of the previous 2004 submission to CCE. Of the 1722 mapping sites, FAB model critical loads were exceeded at 659 (38.3%) according to annual mean deposition data for 1999-2001 (Table 1.1). Total N deposition was greater than $CL_{max}N$ at 314 lakes and 56 streams, i.e. at 56.1% of all exceeded sites. This means that N deposition alone is sufficient to cause critical load exceedance at more than half of exceeded sites for 1999-2001. At the remaining exceeded sites (223 lakes, 66 streams) N deposition alone is not sufficient to cause critical load exceedance but it does contribute to the total acid load along with S deposition which results in critical load exceedance. There are no exceeded sites where N deposition does not contribute to critical load exceedance. Hence reductions in total N deposition from 1999-2001 levels will result in reduced critical load exceedances at all impacted sites.

Even following implementation of the EU National Emissions Ceiling Directive (NECD), 521 sites (30.3% of the total) are still exceeding critical loads for acidity by 2010 (Table 1.1). Total N deposition alone is still sufficient to cause critical load exceedance (i.e. is $>CL_{max}N$) at 265 lakes and 39 streams, which make up 58.3% of remaining exceeded sites. As in 1999-2001, N deposition contributes to critical load exceedance in all sites; there are no sites where predicted NO_3^- leaching does not occur.

Table 1.1: Critical load exceedance statistics for contribution of N deposition

Description	1999-2001	%	NECD 2010	%
Lakes with N deposition > $CL_{max}N$	314	47.6	265	50.9
Lakes with N deposition < $CL_{max}N$	223	33.8	166	31.9
Streams with N deposition > $CL_{max}N$	56	8.5	39	7.5
Streams with N deposition < $CL_{max}N$	66	10.0	51	9.8
Total:	**659**	**100.0**	**521**	**100.0**

Hence N deposition and NO_3^- leaching still play a critical role in causing acidification in lakes and streams in the UK and this role increases in relative terms by 2010 following implementation of the NECD. Therefore it is impossible to protect exceeded freshwaters in the UK from acidification without reducing N as well as S deposition.

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Work package 2: Nitrogen as a nutrient

Task 2.1: Literature review on evidence for eutrophication effects of N deposition in upland waters

EVIDENCE FOR EUTROPHICATION EFFECTS OF N DEPOSITION IN UPLAND WATERS

Chris Curtis

Introduction

The term "eutrophication" is widely used in national and European scale policies linked to the protection of drinking water supplies, natural water bodies and the treatment of polluting discharges to inland and coastal waters. It is defined in the EU Urban Waste Water Directive of 1991 (91/271/EEC) as "*the enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned*".

Following the work of Schindler (1977) and others in the 1970s it was long assumed that in the great majority of lakes, phosphorus (P) was likely to be the key limiting nutrient. This assumption was thought to be particularly true for upland lakes remote from direct catchment sources of pollution. In the 1980s and 1990s the focus of pollution research in these systems was on acid deposition, first on sulphur (S), and later on nitrogen (N). Some naturally P rich lowland lakes had been found to be nitrogen (N) limited (e.g. the West Midland Meres; Moss *et al.*, 1994) but these lakes are uncommon in the UK. Even with the knowledge that N is a major nutrient in freshwater ecosystems, the major impact of anthropogenic N deposition was widely assumed to be surface water acidification. An early literature review on the subject by Elser *et al.* (1990) found that in fact the potential role of N as an agent of enrichment had often been overlooked, and that in reality, inputs of both P and N in combination generally had much greater effects on algal growth responses than individual inputs of either nutrient. However, for the rest of the 1990s there was very little attention given to the potential effects of N deposition on lake trophic status. Even a very recent review of the effects of anthropogenic N sources on aquatic ecosystems in Canada (Schindler *et al.*, 2006) made little mention of potential nutrient N impacts from deposition, instead focussing on acidification and eutrophication due to catchment-based activities. However, Schindler (2006) in another review on eutrophication did point out a possible contribution from N deposition in some systems.

It has only been in the last five years that this issue has achieved a momentum in the literature, moving from speculative effects of N deposition as a nutrient in remote Rocky Mountain lakes in the early part of the decade to the May 2005 edition of Limnology and Oceanography, where the Editorial accompanied a paper by Bergström *et al.* (2005) on the clear effects of N deposition on nutrient limitation in Swedish lakes.

There is still relatively little published on the non-acidification effects of N deposition but related research may be divided into four categories which are considered separately below:

1. nutrient addition studies
2. studies directly linking N deposition with observed ecological change
3. palaeolimnological studies showing possible N deposition responses, and
4. the confounding factors of concurrent acidification and climate change.

Nutrient addition studies

The few published nutrient addition studies employed various experimental approaches in terms of magnitude of additions, and biological effects were not necessarily related to observed increases in concentrations of inorganic N species.

Evidence of the importance of N in lakes was apparent in some of the nutrient additions studies done in the 1990s. Attempts to increase food resources for salmon in Kootenay Lake, British Columbia, Canada through N and P additions led to significant changes in the planktonic diatom flora, with diatom abundance being significantly correlated with dissolved inorganic N (Yang *et al.*, 1996). In another Canadian nutrient enrichment study, the whole of the pre-Alpine Chilko Lake was fertilized, leading to a doubling of autotrophic picoplankton numbers within three weeks despite no measurable increase in NO_3^- concentration from the baseline value of c. 1 μeq l^{-1} (Stockner & Shortreed, 1994). Community composition and abundance were controlled by scarce nutrient supplies during the early growth phase, although grazing became the most important control as N and P co-limitation occurred later in the season. More extreme enrichment experiments with N (+2 mg l^{-1} = 143 μeq l^{-1}) and P (+100 μg l^{-1}) in Lake Orträsket (northern Sweden) demonstrated that primary productivity in humic lakes may be N limited, possibly induced by mixotrophic phytoplankton grazing on P-rich bacteria (Jansson *et al.*, 1996).

Experimental acidification and nutrient additions in the Experimental Lakes Area of Canada (Findlay *et al.*, 1999) found no responses in the phytoplankton community to two years of N additions which increased NO_3^- from <10 to c. 30 μeq l^{-1}. This lack of response could have been due either to P limitation of phytoplankton or to the low pH (<5.4) limiting algal responses that might otherwise have occurred.

Nutrient addition experiments to seepage and drainage lakes in the Adirondack mountains of New York state, USA demonstrated that the phytoplankton of clearwater drainage lakes were P-limited while both clear- and brown-water seepage lakes responded to additions of N (×10 ambient, with ambient = 1-37 μeq l^{-1}) or N+P (Saunders *et al.*, 2000).

The diatoms *Asterionella formosa* and *Fragilaria crotonensis* were found to be abundant in alpine lakes of the Beartooth Mountains with low P but elevated N availability, and both taxa responded strongly to N (initial concentration of 1 μeq l^{-1} increased by +18 μeq l^{-1} as NO_3^-) but not P or Si additions (Saros *et al.*, 2005). Increasing abundance of these species has been linked to atmospheric N deposition in various studies of alpine lakes (see below).

Evidence for N deposition effects - North America

Some North American studies in the 1990s found that the incidence of P limitation in lakes could be increasing because of N deposition when in fact the lakes may have originally been N limited or co-limited by N and P. Since the 1960s, increased primary productivity and a shift from N-P co-limitation to P limitation in Lake Tahoe (California-Nevada) has been attributed to atmospheric deposition of N (Jassby *et al.*, 1995). In a study of three large lakes in the Yellowstone National Park, N limitation of phytoplankton was found to be most common but N deposition was leading to greater incidence of both P and Si limitation, with changes to natural species assemblages (Interlandi & Killham, 1998).

Much recent evidence has emerged from the Rocky Mountains of Colorado and Wyoming and the Sierra Nevada of California, suggesting that very remote, base poor upland/mountain aquatic ecosystems are demonstrating a response to atmospheric nitrogen deposition even at very low inputs (e.g. Baron *et al.*, 2000; Wolfe *et al.*, 2001; Fenn *et al.,* 2003; Sickman *et al.*, 2003; Saros *et al.*, 2005), although some studies have been inconclusive (Burns, 2004). Studies of ponds in Banff National Park in the Canadian Rockies found that found that phytoplankton abundance and community composition were best explained by total phosphorus (TP), pH and conductivity but inorganic N best explained epipelon (sediment living species; McMaster & Schindler, 2005).

In a study of Colorado Rocky Mountain lakes, Nydick *et al.* (2003) found only temporary responses of phytoplankton chlorophyll *a* to early season NO_3^- peaks in rocky watersheds. In most lakes, P was generally limiting to phytoplankton growth, but N deficiencies were more important in lakes with forested watersheds and fringing wetlands. In later work, Nydick *et al.* (2004) found that while phytoplankton are most sensitive to nutrient N additions, benthic processes are important for NO_3^- uptake in shallow, oligotrophic lakes. Lafrancois *et al.* (2004) found that the most striking changes in phytoplankton species composition in mountain lakes occurred with both nutrient enrichment (N and P) and acidification.

Related studies of benthic invertebrates in 22 Colorado mountain lakes found that NO_3^- was unrelated to benthic invertebrate distribution (Lafrancois *et al.*, 2003), with altitude and presence of fish best explaining presence/absence of key taxa.

Studies of nutrient N enrichment in these Rocky mountain lakes are so far advanced that even remote-sensing (reflectance spectroscopy) has been proposed as a method of detecting changes in lake sediment chlorophyll *a* as a proxy for trophic status (Das *et al.*, 2005).

The occurrence of N limitation in North American lakes has also been recorded in the extreme Arctic north of the continent. In a study of 16 major Arctic lakes in Alaska, LaPerriere *et al.* (2003) found relationships between catchment characteristics, in particular elevation, and P or N limitation. N limitation increased in importance in lakes at higher altitude.

Evidence for N deposition effects - other regions

Outside of North America, another region with increasing evidence in the recent literature for lake N limitation is north-west Europe. Declining N deposition in Finland has been associated with decreasing trends in dissolved inorganic N (Rekolainen *et al.*, 2005) to the extent that the authors speculated on an increase in the proportion of lakes that were becoming N limited. Studies in the UK uplands used phytoplankton bioassays to show that around three quarters of 30 study lakes are either N limited or co-limited by N and P (Maberly *et al.*, 2002).

Two of the most extensive studies to date on the nutrient effects of N deposition have very recently been published. The first looked at the relationship between phytoplankton biomass, N and P concentrations and N deposition in 225 Swedish lakes (Bergström *et al.*, 2005). The study speculated that in unproductive Swedish lakes, increased lakewater NO_3^- concentrations due to N deposition had resulted in a shift from natural N limitation to P limitation. Furthermore, a clear eutrophication effect was found in high N deposition areas, with higher phytoplankton biomass relative to total P concentration than in low N deposition areas. The later, wider-ranging study from two of the same authors collated data from oligotrophic lakes in 42 regions of Europe and North America and again concluded that N deposition had not only increased NO_3^- concentrations but had also caused eutrophication and increased biomass of phytoplankton in naturally N limited lakes (Bergström & Jansson, 2006). Phytoplankton distributions in Alpine lakes have also been associated with NO_3^- concentrations, affected by deposition inputs (Tolotti *et al.*, 2006).

Published studies on N limitation in remote lakes from other parts of the world are sparse but geographically wide-ranging. Camacho *et al.* (2003) used bioassays to demonstrate a seasonal pattern of N limitation to phytoplankton growth in a Spanish karst lake where atmospheric deposition was suggested to be a possible key factor in controlling nutrient deficiency. Evidence of both N and P limitation has been found in the ultraoligotrophic Lake Puma Yumco, located at 5030m altitude in the pre-Himalayas of Tibet (Mitamura *et al.*, 2003). N was found to be the main limiting nutrient for phytoplankton production in a eutrophying high mountain lake in Ecuador (Gunkel & Casallas, 2002) and in the naturally acidic lake Caviahue in Patagonia, Argentina (Beamud *et al.*, 2007). A wider study of 39 Patagonian lakes found that N rather than P was the key limiting nutrient (Diaz *et al.*, 2007). Hence it seems likely that the incidence of N limitation and effects of N deposition on trophic status will increasingly be reported in the literature as the problem becomes more widely recognized and studied.

Palaeolimnological analysis for evidence of biological response to N deposition independent of any acidification response

Palaeoecological analysis of sediment records from many lakes in the boreal and sub-arctic zones reveal significant ecological changes over the past 200 years, following several hundred years of relative stability. The onset of change often coincides with the first appearance of spheroidal carbonaceous particles (SCPs), thereby implicating atmospheric contamination as a likely trigger. Recent work on a core from the UK Acid Waters Monitoring Network site, Loch Coire Fionnaraich, in north-west

Scotland, provides a particularly striking example of this behaviour. While the ecological response is not indicative of acidification the mechanism is not yet understood.

There are very few published palaeolimnological studies linking biological change specifically to N deposition effects. Chrysophyte cysts in surface sediments of 105 Pyrenean lakes were found to show independent relationships with nitrate concentrations as well as alkalinity and pH (Pla *et al.*, 2003). This study suggested that chrysophytes preserved in sediment cores could have potential as a tool for reconstructing past changes in NO_3^- concentrations and hence nutrient N effects due to anthropogenic deposition.

Changes in the last decade of a 400 year old sediment diatom record from Beartooth Lake in the Rocky Mountains have been attributed to the effects of increased N loading and thermal stratification by Saros *et al.* (2003).

Wolfe *et al.* (2001; 2003; 2006), working on cores from remote lake ecosystems in the Rocky Mountains of Colorado and in the Canadian Arctic have demonstrated a link between apparent eutrophication and a change in $\delta^{15}N$ which is indicative of an increased supply of N from the atmosphere. While N deposition in this region is relatively high, it has been proposed that a similar process may be operating more widely. Recently reported work of Jones *et al.* (2004) demonstrates that the analysis of $\delta^{15}N$ in lake surface sediments might be used as a measure of the degree of N limitation in lakes.

In most of these studies, it has proven difficult to separate the potential effects of N deposition on lake nutrient status from other confounding factors that have resulted in changes occurring over similar timescales, often linked directly to the activities that generate anthropogenic N deposition. The two main confounding factors are acidification and climate change.

Confounding factors - acidification

It has already been mentioned above that nutrient additions in combination with acidification have the most dramatic impact on lake biota (Findlay *et al.*, 1999; Lafrancois *et al.*, 2004). Acidification has, however, also been linked to the process of oligotrophication whereby nutrient supply is reduced.

Schindler (1994) observed that the overall productivity of acidified lakes does not appear to decline unless the P supply is reduced. Later work in the Czech Republic suggested a mechanism linking acidification with reduced P supply. Abiotic P immobilization by colloidal aluminium contributed to severe P limitation of biomass in a strongly acidified mesotrophic lake in the Sumava Mountains of the Czech Republic, despite very high N deposition loads (Kopacek *et al.*, 2001; 2004; 2007). Hence the interactions between acidification and eutrophication or oligotrophication are complex.

Confounding factors - climate change

Early work on the potential effects of climate change on primary productivity in the sub-alpine Castle Lake (northern California) predicted that increased temperatures would lead to earlier spring ice-out and longer growing seasons, resulting in enhanced productivity (Byron & Goldman, 1990).

Kolesar *et al.* (2002) found that autumn phytoplankton populations in three Rocky Mountain lakes were influenced most by changes in water temperature and incident solar radiation, suggesting that climate change effects could be significant. The potential effects of climate change on fishless alpine ponds were assessed by Strecker *et al.* (2004), working with mesocosm experiments in Banff National Park. They found that moderate warming destabilized plankton dynamics without significantly increasing dissolved N and P concentrations.

Changes in the biological communities of remote Arctic lakes since 1850 have been attributed to climate change by Birks *et al.* (2004) and Smol *et al.* (2005). Other potential drivers of change such as N deposition were thought to be less important because of the remoteness of these sites and the early onset of change, although this issue is still being debated in the literature. More recently, Wolfe *et al.* (2006) concluded that climate change and N deposition were synergistically causing changes in lakes of the eastern Canadian Arctic. Furthermore, changes in diatom assemblages across ecoclimatic zones (correlated with differing total N concentrations) in the Canadian Arctic have been used to derive a diatom-total N transfer function on the premise that palaeolimnological changes in diatom-inferred total N might usefully be used to determine climate-related changes (Lim *et al.*, 2007).

Given the strong links between terrestrial and aquatic nutrient cycles and climate (e.g. mineralization and nitrate production in soils), the separation of direct climatic effects (e.g. temperature, precipitation, ice-out) and N deposition (nutrient) effects is likely to remain a major challenge for the future.

Synthesis

The long-prevailing assumption that lakes are universally P limited has been shown in many studies over the last 10 years to be incorrect. Nutrient addition experiments to whole lakes or in mesocosm studies have shown mixed results with both P and N limitation found, as well as limitation by other factors. Wider-ranging spatial studies of nutrient limitation, often employing direct bioassay measurements, have shown that phytoplankton and in some cases benthic algae are frequently N limited in upland, alpine and arctic lakes. Published evidence is available from the UK, several studies in the USA and Canada, Sweden, Finland, the Alps, Spain, Patagonia, Ecuador and the Himalayas. More detailed palaeolimnological studies, mostly from North America and the Arctic, have shown changes towards increasing dominance of mesotrophic and planktonic algae which are consistent with increasing N deposition over the last 50-150 years.

Attempts to make direct links between palaeolimnological changes and N deposition are however complicated by the two major confounding factors of acidification and climate change, which may have occurred over very similar timescales to the global increase in N deposition. The causes of changes in preserved algal remains may therefore be very difficult to separate. However, given the direct evidence from nutrient addition and bioassay studies that the phytoplankton of some lakes respond to N additions, it must be concluded that N deposition to these systems has to cause some change in productivity and probably also in species assemblages. As yet there is little evidence for the direct effects of N deposition on other organisms in upland lakes, although work in shallow oligotrophic lakes in the Netherlands has shown an adverse effect on the macrophyte communities adapted to low nutrient availability which are widely distributed in upland lakes of the UK (see Task 2.4 below).

The review of the literature described above may be compared with an earlier review with a broader but overlapping remit, prepared by Maberly *et al.* (2004) for the Scottish Executive to determine the importance of nitrogen in freshwater eutrophication. The wider scope of this review included lowland lakes and rivers impacted by agriculture but included an assessment of the importance of N deposition in upland and semi-natural catchments. It was motivated by the need to distinguish between waters where eutrophication is driven by phosphorus and those where N is the primary control, to assist in policy formulation and compliance monitoring under the EU Urban Waste Water Directive, the Nitrates Directive and the Water Framework Directive. As in the present review, it was concluded by Maberly *et al.* (2004) that there is growing evidence globally that N may be the primary or co-limiting nutrient in certain types of lakes, especially in the uplands.

The policy relevance of N limitation in upland lakes is that N deposition must be affecting the structure and function of these natural ecosystems, with possible implications for the protection of designated habitats under the EU Habitats Directive. Furthermore, it is likely that in the most N impacted systems there may be a significant departure from the good ecological status required under the EU Water Framework Directive. For these reasons, there is an urgent need to review the case for the development and application of nutrient N critical loads in UK upland waters (see Task 2.4) with a major requirement being the identification and definition of the "harmful effects" inherent in the critical loads concept.

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Task 2.2: Analysis of existing datasets (deposition, soils, land-cover, topography) to determine relationships between N leaching, N limitation and landscape-scale predictors

Martin Kernan, Gavin Simpson, Chris Curtis and Stephen Maberly

I) Prediction of N limitation from catchment characteristics

Introduction

The potential importance of N deposition in causing eutrophication in N limited lakes has been demonstrated under the current contract through experimental bioassay work, palaeolimnological studies and literature review. Changes in algal communities and possibly macrophytes in N impacted upland lakes may adversely affect the conservation value and good ecological status required under the EU Habitats Directive and Water Framework Directive. Hence it is essential to determine the potential spatial extent of the problem in sensitive waters of the UK uplands.

Recent publications arising from the NERC *GANE* programme have shown that landscape scale datasets may be used to predict N limitation in surface waters where N deposition is a major source of N (Maberly *et al.*, 2002).

This Task represents attempt to upscale this approach to the national level using existing critical loads databases of water chemistry and land-cover for over 2000 water bodies. The work includes GIS based characterisation of catchment slope and multivariate statistical analysis of diverse datasets.

Nutrient limitation in upland lakes

Phosphorus has traditionally been seen as the primary nutrient limiting the productivity of unproductive lakes in upland areas or where there is no significant catchment nutrient source (Maberly *et al.,* 2002). However, the potential for nitrogen limitation has been identified across a variety of lakes (Elser *et al.,* 1990; Moss *et al.,* 1994; Jannson *et al.,* 1996). More recently, Maberly *et al.* (2002) found that both phytoplankton and periphyton were limited as much by nitrogen as phosphorus in unproductive upland lakes and that co-limitation occurred most frequently. It was suggested that the importance of nitrogen in these systems was a result of low P concentrations, low pH and high flushing rates, each of which can lead to restricted cyanobacteria development. The high lake to catchment ratio of many of the study sites suggested that these systems were characterised by rapid flushing and thus exhibited a close coupling of lake and catchment. A subsequent study (Maberly *et al.,* 2003) examined the relationship between catchment characteristics and later water chemistry, phytoplankton and periphyton biomass, and phytoplankton and periphyton nutrient limitation for the 30 upland lakes used in the earlier study on nutrient limitation (Maberly *et al.,* 2002).

Nutrient limitation and phytoplankton were estimated *in situ* and experimentally, respectively. For each site, mean P, N and co-limitation was calculated as a percentage. For Great Britain, the land cover for each catchment was determined (on a percentage cover basis) by overlaying digital catchment outlines onto the 25m resolution LCM 1990 digital land cover map (Fuller *et al.*, 1994). Mean slope values for GB sites were obtained from the Flood Estimation Handbook (FEH) CD-Rom (NERC AA, 1999). For catchments in Northern Ireland LCM2000 digital data (Fuller *et al.*, 2001) were used to derive land cover information and mean slope was obtained from a digital elevation model (DEM) from the Ordnance Survey of Northern Ireland.

Stepwise linear regression was used to identify significant relationships between the nutrient limitation measures and percent land cover. Multiple regression was used subsequently to generate a predictive equation allowing nutrient limitation to be predicted using catchment attributes. This accounted for 42% of the variation in P limitation and 29% of the variation in N limitation. P limitation was positively related to shrub heath and bracken coverage and negatively related to pasture. N limitation exhibited positive relationships with grass shrub heath and deciduous woodland and negative relationships with pasture, shrub heath and inland bare ground. No statistically significant relationships were identified between land cover and co-limitation. P limitation increased with catchment slope while the converse was true for N limitation. The latter relationship was not significant and variance ratio tests showed that including slope in the predictive models did not improve the fit significantly. The regression models generated are shown in Table 2.1.

Table 2.1: Results of regression analysis relating nutrient limitation measures to land cover

Variable	Constant	Coefficients	*Adj* R^2	P
P-limitation	16.282	-0.4395 PMG +0.3068 SHe + 1.375 Bra	41.8	0.001
%	(4.717)	(0.2731) PMG (0.1616) SHe (0.328) Bra		
N-limitation	25.371	-0.2927 Rpa + 1.146 MRG - 0.3236 SHe + 2.636 DMW - 0.7763 IBG	28.6	0.02
%	(6.887)	(0.1414) Rpa (0.7) MRG (0.1728) SHe (0.936) DMW (0.39421) IBG		

Land Cover Types (PMG- Pasture / meadow /amenity grass; She - Shrub heath; Bra - Bracken; Rpa- Rough pasture / grass moor; MRG- Marsh / rough grass; DMW- Deciduous/Mixed Woodland; IBG- Inland bare ground.

Selection of additional sites for sampling

In order to expand the bioassay database, 13 additional sites were sampled (Task 2.3.2). Where possible these coincided with the sediment isotope work being undertaken in Task 2.3.1. However, the main criteria for site selection was to ensure that a gradient of modelled N and P limitation was represented, expressed as % limitation.

The regression model (Maberly *et al.*, 2003) was applied to the UK freshwater database. This comprises *c.* 1600 sites for which land cover data have been generated and these were used to parameterise the model. Predicted %N and %P limitation values were derived, based on the land cover characteristics of each site. This resulted in a large gradient for both N and P limitation. Sites for bioassay investigation were selected along a primary gradient of predicted %N limitation and a secondary gradient of %P limitation. Site selection also encompassed a geographical gradient. Table 2.2 lists the additional sites for bioassay analysis.

Table 2.2: Additional sites selected for bioassay sampling with modelled %N and %P values

Code	Site	Country	%N	%P
SCOATT	Scoat Tarn	England	36.1	16.7
BURNMT	Burnmoor Tarn	England	30.5	3.1
VNY4101	Small Water	England	86.3	18.6
CZTQ32	Hammer Pond	England	0.8	92.3
NAGA	Lochnagar	Scotland	17.2	27.9
VNG9402	Loch Coire Fionnaraich*	Scotland		
LNEI	Loch nan Eion*	Scotland		
CZNG96	Loch Coire Mhic Fhearchair*	Scotland		
EDNO	Llyn Edno	Wales	35	8.8
MAIR	Llyn Mair	Wales	17.4	120.1
GAM	Llyn Gamallt Fawr	Wales	21.5	64.9
WSH7301	Llyn Hiraethlyn	Wales	7.2	23

*Not modelled but being used for isotope work

Application of the predictive model to national datasets

The primary aim of Task 2.2 was to apply models for N and P limitation to the national datasets to produce a map of likely N and P limitation which could be used to assess the extent of potential effects of nutrient N pollution.

A preliminary exercise at applying the models of Maberly *et al.* (2002) to the national data sets raised some issues that need to be addressed before the first maps of N and P limitation are produced.

The main issue encountered was related to the specification of the regression models in Maberly *et al.* (2002). Here the authors treated the predictor variable (y) in their regression models as a continuous variable that can take values ranging from $+\infty$ to $-\infty$. As y is a proportion (the number of bioassays exhibiting a particular response over the total number of bioassays), it takes values from the range 0-1.

The model formulation used by Maberly *et al.* (2002) did not appear to produce values outside this range (expressed in the paper as a percentage = proportion x 100) and as such did not produce any implausible results. However, when applying this to the national data sets using landcover data and lake catchment information derived from the GB Lakes database (Hughes *et al.*, 2004), values for N and P limitation for a considerable number of sites were predicted to be greater than 100% and less than 0% - which are clearly nonsensical.

Methods

As a result we attempted to re-apply the models of Maberly *et al.* (2002) using updated land cover data from LCM2000 and a model formulation that accounts for the restrictions on the range of values that y can take. One suitable form of model is a logistic regression model:

$$logit\ p = \log[p(1-p)] = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_k x_k + \epsilon_k$$

in which *logit p* is the log odds. This model is linear when expressed on the logit scale, as demonstrated above and can be fitted under the Generalized Linear Model (GLM) framework with a binomial error distribution using a logit link function. This formulation has the desired properties of restricting the fitted values *y* to lie between 0 and 1.

For the logistic regression, it was appropriate to transform the predictor variables (the land cover variables) using an arcsine transformation. This transformation was applied to try to deal with the closed compositional nature of the variables where each variable is sum constrained to 1 and is not independent of the values for the other variables within a site. The transformed variable x' is given by:

$$x' = \arcsin(\sqrt{x})(360(2\pi))$$

except where x = 0, in which case x = 1 / (4*n*) and where x = 1, in which case x = (*n* - 0.25) / n before applying the arcsine transformation, where *n* is the number of observations (*n* = 27 in this analysis). This adjustment to the x was applied to improve the equality of the variances in the angles calculated in the arcsine transformation step. The arcsine transformation above contains an explicit transformation of the variables from radians to degrees.

Following preliminary modelling it was decided that instead of trying to model the absolute proportions of tests that are P or N limited, we would restrict this approach to modelling the probability of P or N limitation based on the presence/absence of limitation, i.e. the proportion p was assigned a value of 0 if $p = 0$ and 1 if $p > 0$. This leads to a transformation of the response *y* to a binomial variable with values 0, 1. This transformation was required as the data for the 27 sites are very much over-dispersed (i.e. exhibiting more variance than expected under the binomial model), probably the result of the small data set size.

An alternative approach is to use tree-based models. Tree-based models are used routinely in machine learning problems as they provide a robust way of implementing regression or classification models. They are invariant to transformations of the variables used in the model for example. Because of the transformation to the response *y* to 0, 1 values, we chose to fit a classification tree to the binary response data. The classification tree aims to find a decision tree or rules that allow the prediction of N or P limitation, based on the known relationships between the two groups (limited/not-limited) and the predictor variables in the training set.

Prior to modelling using the logistic regression and the classification tree, one site (CZSD59) was removed as an outlier and a number of the original 27 land cover classes that took values of 0 for all site in the data set were deleted as they provided zero discriminatory power.

For the logistic regression model, all the remaining predictor variables were included in the full model and a step-wise procedure consisting of forward selection and backward elimination steps was applied to the full model, with the aim of producing a minimal, adequate model following the rule of parsimony. At each step in the procedure, the effect on model performance of eliminating or adding a variable to the current model was assessed using BIC (Bayes Information Criterion, also know as

Schwartz Information Criterion), which penalises model complexity, to guard against over-fitting. The models resulting from the step-wise procedure were further pruned to remove non-significant variables.

Results

Following this model building exercise, we had two models for predicting N and P limitation respectively. Both models contained a single explanatory variable; proportion of coniferous woodland (gb13). These models were confirmed using the classification tree models and as a further exercise, the predictor variables were standardised to account for size effects between variables, and in both cases a model with a single predictor variable (proportion of coniferous woodland) was chosen.

In Maberly *et al.* (2003) the proportion of coniferous woodland was highly correlated with total dissolved phosphorus (TDP), dissolved organic nitrogen (DON), dissolved organic carbon (DOC) and phytoplankton Chlorophyll α (Chl α), all variables that would be important in determining N or P limitation.

We did not attempt to model co-limitation in this exercise as it was not clear how best to treat the response y when the data are for co-limitation (effectively a success for both N and P limitation within the bioassay replicates).

The classification rates for the GLM and tree-based models for P- and N-limitation are shown in Table 2.3a-d. These numbers do not reflect the predictive power of the models given some new data and are overly optimistic as the power has been determined by asking the model to predict for the data set that was used to build the model. The numbers do suggest that for N and P limitation, at least, the proportion of coniferous woodland has high discriminatory power.

Summary and Conclusions

The initial application of the original regression models of Maberly *et al.* (2002) to the national data sets resulted in predicted proportions of N and P limitation of greater than 100% and less than 0% as a result of the way the authors' model was formulated. Here we address this issue and fit logistic and classification tree models to the LCM2000 land cover data set and the original P and N limitation data of Maberly *et al.* (2002). These models are restricted to producing predictions on the correct scale.

Both the logistic regression and classification tree models identified the proportion of coniferous woodland in the catchment as the single variable which significantly discriminated between limited and non-limited sites for both N and P. The regression tree models suggest that for P limitation sites with > c. 5% coniferous woodland in the catchment will be P limited. For N limitation the tree model suggests a value of > c. 0.8% coniferous woodland is indicative of N limitation.

These results should be interpreted with caution. They are based on an extremely small dataset that is itself very noisy, and as such was difficult to model using the GLM approach. As we have no independent data we have not applied a validation to these models. The additional data collected at 13 extra sites as part of the FUMBLE project will initially be used to validate the results of this modelling exercise. Subsequently these additional sites will be added to the model building training set and a new set of models will be built for N and P limitation (see below).

At this time it is not appropriate to apply these models to national data sets with a view to producing maps of N and P limitation. Further work is required before this can be done. On the basis of this work, further sites may need to be sampled in addition to the 13 sites mentioned above before we can be confident of applying these models to national data sets to produce maps of N and P limitation.

Table 2.3: Prediction performance of models

Table 2.3a: P-limitation prediction performance for the logistic regression model

	FALSE	***TRUE***	***Correct***	***% Correct***
FALSE	5	3	23	85.2
TRUE	1	18		

Table 2.3b: P-limitation prediction performance for the classification tree

	FALSE	***TRUE***	***Correct***	***% Correct***
FALSE	6	2	23	85.2
TRUE	2	17		

Table 2.3c: N-limitation prediction performance for the logistic regression model

	FALSE	***TRUE***	***Correct***	***% Correct***
FALSE	11	1	20	74.1
TRUE	6	9		

Table 2.3d: N-limitation prediction performance for the classification tree

	FALSE	***TRUE***	***Correct***	***% Correct***
FALSE	11	1	22	81.4
TRUE	4	11		

Further work

The additional 13 sites were subsequently added to the bioassay database and the model was rerun to assess whether there were sufficient sites to upscale the modelling approach in a statistically valid way. These results are presented in the next section.

II) Model development incorporating new bioassay sites under Freshwater Umbrella

Introduction

The conclusions of the previous modelling work undertaken in Task 2.2 highlighted the problems inherent in using such a small calibration dataset. A decision was taken to combine the 13 sites sampled under Task 2.3.2 with the original bioassay database (Maberly *et al.*, 2002) to give a total of 43 sites (See Fig. 2.1). A key issue was the comparability of new data with the original survey where more bioassay analyses were performed. Therefore it was necessary to recompile the original bioassay data for comparability with sites sampled under Task 2.2 (i.e. generate common dataset of bioassay results for all 43 lakes). The problem of "what to predict" was also discussed, given the seasonality of N and P limitation and water chemistry, i.e. what is a useful output from the model. It was agreed to work primarily with % N limitation but this is a proportion of bioassay tests showing a positive outcome with 4 possible results (0, 1, 2, 3). Other ways of expressing N limitation data should also be considered in future.

Preliminary analysis suggested that, even with the additional sites, the bioassay dataset was too small to generate relationships and produce maps. Therefore, rather than upscaling the modelling approach using %N and %P limitation, it was decided to examine the relationship between N limitation and other chemical parameters to examine whether a surrogate variable might be employed to reflect N limitation status. Previous work (Maberly *et al.*, 2003) identified dissolved inorganic nitrogen (DIN) as a significant factor controlling the extent of N or P limitation at a given site and the use of DIN as a surrogate for N limitation was subsequently explored. If this proved successful it would enable the UK Freshwaters database (c. 2000 sites) to be used to quantify the relationships between N limitation status and catchment attributes (such as land cover) allowing the modeling of N limitation status sites where there are no chemistry data available. The purpose would be to produce a comprehensive map of N limited sites across upland Britain.

Thus the purpose of the additional work in Task 2.2 was to develop the modelling approach by:

a) expanding the size of the calibration dataset to 43 sites;
b) examining relationships between N limitation and DIN to see if the latter can be used as a surrogate for former;
c) use of national UK freshwater database and LCM2000 land cover database to quantify DIN - land cover relationships; and
d) use this to produce map of upland sites where N is the limiting nutrient.

Expansion of calibration dataset

The original model from Maberly *et al.* (2002) was rerun using common analyses from the original GANE (n=30) and current Freshwater Umbrella (n=13) bioassay datasets (see Task 2.3.2). Thus only the phytoplankton assays were used, with the periphyton data removed from the GANE results. The results were combined with the extra 13 sites from the Freshwater Umbrella giving 43 in total. Table 2.4 shows the results of the bioassays.

Table 2.4: Nutrient limitation status at 43 upland sites based on phytoplankton bioassays (Maberly *et al.*, 2002). Percent limitation is based on whether none, one third, half, two thirds or all bioassays resulted in a particular limitation

Northing	Easting	Site	% P limited	% Co-limited	% N limited
350100	499200	Gurnal Dubs	0	67	33
349200	498800	Potter Tarn	0	100	0
337000	496800	Moss Eccles Tarn	0	33	67
326700	503700	Red Tarn (Wrynose)	33	67	0
328400	502100	Greenburn Beck Tarn	100	0	0
329200	504300	Blea Tarn (Wrynose)	67	33	0
316500	500900	Blea Tarn (Eskdale)	33	67	0
316000	497000	Devoke Water	0	100	0
331100	513600	Harrop Tarn	0	100	0
327500	516000	Watendlath Tarn	33	0	67
264500	359500	Llyn Idwal	33	67	0
264700	356100	Llyn Cwm-y-ffynon	0	0	100
264100	354800	Llyn Teyrn	0	67	33
264800	348200	Llyn Llagi	33	67	0
177300	841500	Loch Dithreabh na Cuileige	33	67	0
180900	842000	Loch Coire nan Arr	0	100	0
179200	829000	Loch Iain Oig	0	67	33
179500	816500	Loch nan Uranan	0	67	33
240500	808000	Borlum Hill Loch	33	33	33
258900	828900	Loch ceo Glais	0	67	33
262800	829200	Loch a'Choire	0	100	0
244100	813000	Loch Nan Lann	0	33	67
251300	600200	Loch Muck	0	67	33
241000	596100	Loch Skelloch	0	33	67
236500	586500	Loch Kirrieroch	0	67	33
245000	580300	Round Loch of Glenhead	0	100	0
332800	325200	Blue Lough	67	33	0
321100	417700	Loughgarve	0	100	0
202800	354700	Lough Navar	50	0	50
202900	355900	Meenameen Lough	100	0	0
315900	510400	Scoat Tarn	100	0	0
318400	504300	Burnmoor Tarn	0	67	33
345500	510000	Small Water	0	100	0
539700	128700	Hammer Pond	0	33	67
266300	349700	Llyn Edno	67	33	0
265300	341300	Llyn Mair	33	67	0
274500	343900	Llyn Gamallt Fawr	0	67	33
274300	337000	Llyn Hiraethlyn	0	33	67
194500	849800	Loch Coire Fionnaraich	0	67	33
192500	850800	Loch Coire nan Eion	33	67	0
194300	860600	Loch Coire Mhic Fhearchair	67	33	0
325200	785900	Lochnagar	67	33	0
316000	768600	Loch Beanie	67	33	0

Three phytoplankton bioassays were undertaken and % limitation is based on whether none, one third, half, two thirds or all bioassays resulted in a particular limitation. Thus, from Table 2.4, Coire nan Arr was co-limited each time, Greenbeck Burn Tarn was P limited on each occasion and Cwm-y-ffynon was N limited. For the purposes of this study, the focus was on sites at which N limitation occurred at any given time. A map (Figure 2.1) shows the location of the calibration sites. Figure 2.2 shows how P, N and N limitation varies nationally and, for Wales, the Lake District and Galloway, regionally. Nationally, sites in NE and NW Scotland do not tend to exhibit N limitation. Sites in Wales and the Lake District are more variable in terms of N limitation status. Percent P limitation is relatively high in NE Scotland but rather lower in N Wales (where co-limitation dominates) and completely absent in the Galloway region.

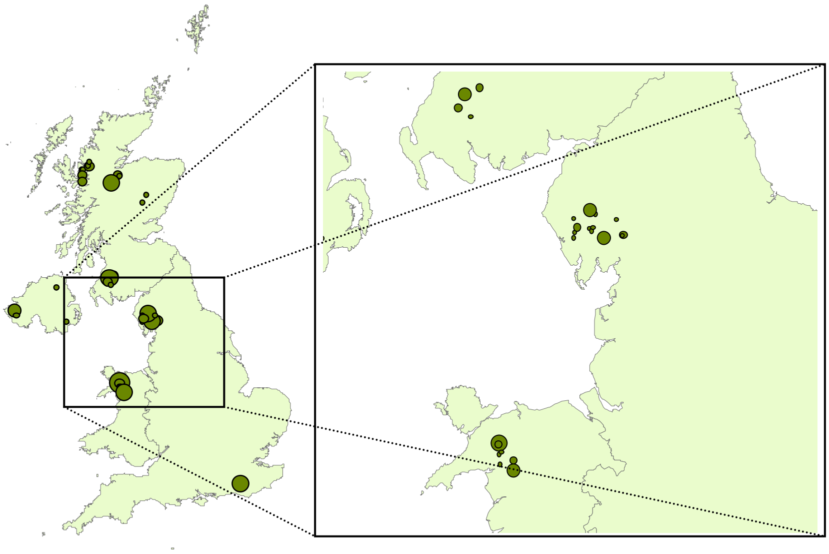
Figure 2.1: Map of 43 bioassay sites

Relationships between N limitation and dissolved inorganic nitrogen (DIN)

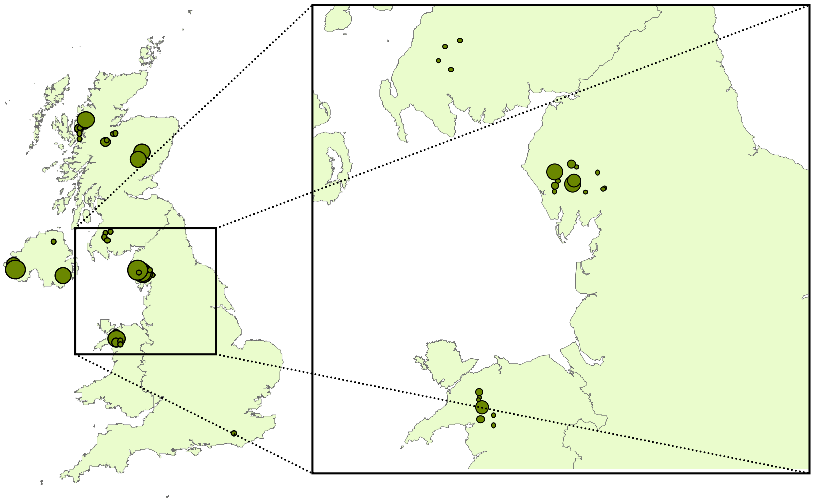
Exploratory analyses were undertaken to examine whether a strong relationship existed between N limitation and dissolved inorganic nitrogen (DIN) to assess whether the latter could be used as a surrogate for the former. DIN ranged from 1 mmol m^{-3} at Llyn Gamallt Fawr in North Wales to 22 mmol m^{-3} at Blue Lough in Northern Ireland with a median of 7.1 mmol m^{-3}. Figure 2.3 shows how DIN values are distributed spatially across the calibration dataset. There are no clear spatial patterns in the data. N and P limitation were plotted against DIN for the 43 sites (Figs. 2.4a and b, respectively). There is a lot of scatter in the data and the positive relationship between P limitation and DIN appears stronger than the negative relationship exhibited between N limitation and DIN. Correlations between % limitation and measures of nutrient concentration (together with altitude) are shown in Figure 2.5 to examine whether other surrogates may be used to obtain some estimation of N limitation. P limitation exhibits relatively strong correlations with DIN, NO_3^- and altitude. N limitation correlations tend to be weaker with the highest *r* values representing relationships with altitude, NO_3^- (negative) and DIN (positive).

Figure 2.2: Map of N (a), P (b) and Co- (c) limitation across the 43 site bioassay dataset

a) N limitation



b) P limitation



c) Co-limitation

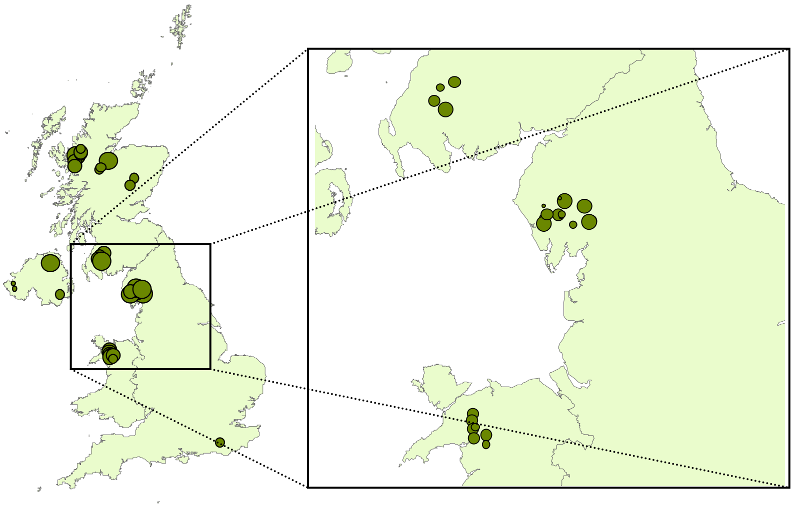


Figure 2.3: Map of dissolved inorganic nitrogen (DIN) at bioassay sites

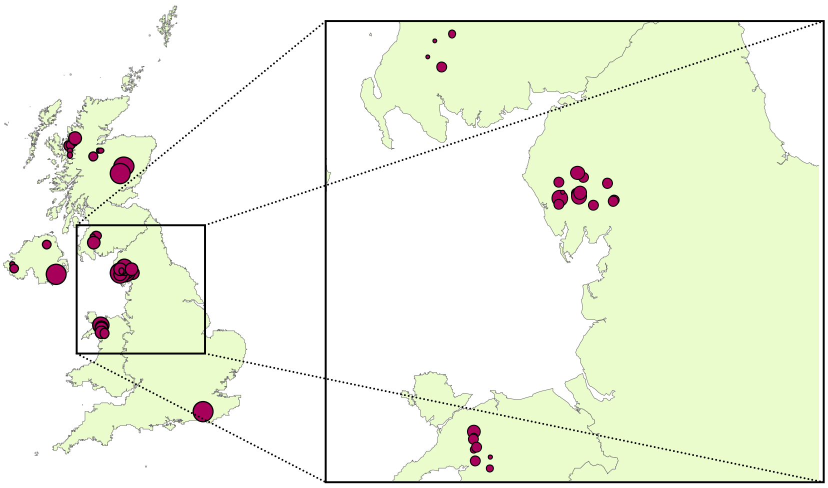
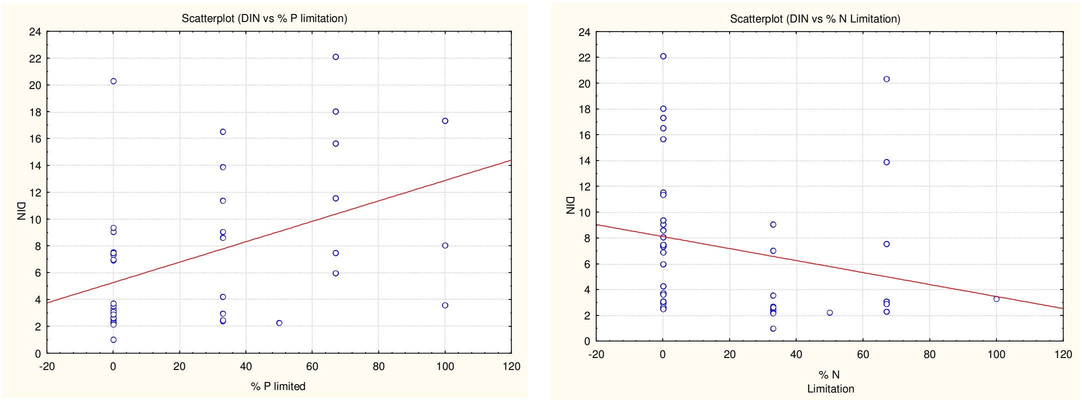


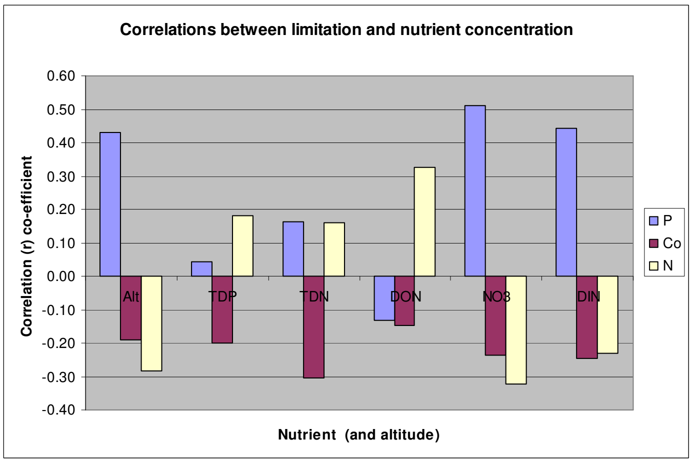
Figure 2.4: Scatterplots illustrating the relationship between N and P limitation and DIN



a) P limitation vs DIN

b) N limitation vs DIN

Figure 2.5: Correlations between % N, P and co-limitation and altitude, total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), nitrate (NO3) and dissolved inorganic nitrogen (DIN)



Use of national UK freshwater database and LCM2000 land cover database to quantify DIN - land cover relationships

DIN values are available for over 2000 lakes and streams across the UK in the UK Freshwaters database. Figure 2.6 shows how these are distributed across the UK (with all sites with an agricultural influence screened out). The highest concentrations tend to cluster in areas that have experienced elevated levels of N deposition including the Peak District, parts of Wales, the Lake District and south west Scotland. A correlation analysis was undertaken to assess whether these patterns also reflected the mitigating effects of land cover and soil type. Figure 2.7 summarises the correlation analysis showing *r* values between N limitation and:

a) catchment coverage of each of the land cover classes from the LCM2000 land cover database;
b) catchment weighted values for soil N immobilization:
c) catchment weighted values for denitrification; and
d) altitude.

The strongest correlations are with gb10 (% open shrub moor), gb 14 (improved grassland), gb19 (acid grassland), N immobilisation and N denitrification. However, of these, only the correlation with gb10 exceeds an absolute value of 0.3.

Conclusions

The final aim, to produce map of upland sites where N is the limiting nutrient, was not achieved. The weak relationships, uncertainties and errors at each stage of the modelling process preclude upscaling to national datasets at this stage. It may be possible using more sophisticated statistical techniques to improve the strength of the relationships between N limitation and DIN (or some other surrogate) and between this and land cover. However, this is a noisy data set and while improving the modelling may increase predictive power it is likely that large errors will remain. Ideally, more direct measurements of N limitation are needed from sites over wider gradients if this is to be modelled at a national scale with any degree of confidence in the results. This work should be closely linked to attempts to improve models of NO_3^- leaching using more detailed catchment scale datasets than previously available. A key issue is that of upscaling from moderately sized datasets which need to represent broad environmental gradients to the national scale. While challenging, this work is required to address the increasing need to develop national scale models for both NO_3^- leaching and nutrient N critical loads which are, as this work programme has shown, now an urgent priority for oligotrophic and mesotrophic upland waters in the UK.

Figure 2.6: Map of dissolved inorganic nitrogen concentration at non-agricultural sites in the UK Freshwaters Database

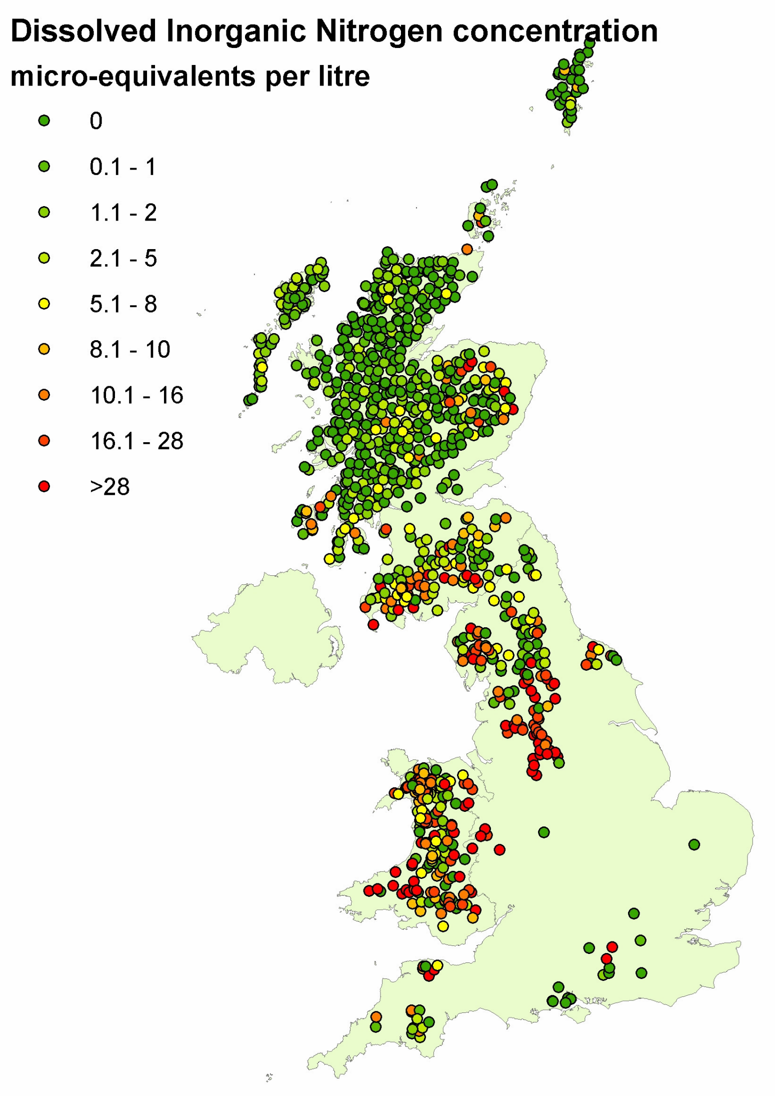
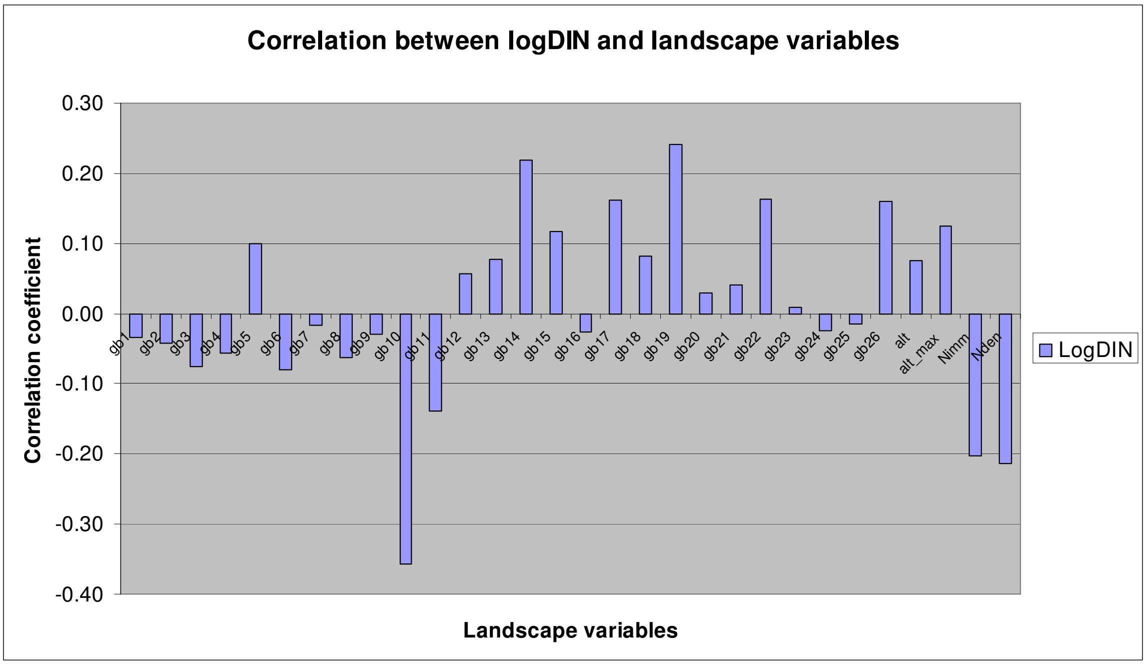


Figure 2.7: Correlation coefficients between dissolved inorganic nitrogen and the catchment coverage of each of the land cover classes from the LCM2000 land cover database, catchment weighted values for soil N immobilization, denitrification and altitude.



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Task 2.3: Design and implementation of scoping survey on basis of Task 2.2 above

2.3.1: Palaeolimnological analysis for evidence of biological response to N deposition independent of any acidification response

and

2.3.3: Comprehensive analysis of palaeolimnological evidence for nutrient N response in up to 6 lakes where existing catchment / water chemistry data indicate potential N limitation in Task 2.2

Gavin Simpson and Chris Curtis

Note

Tasks 2.3.1 and 2.3.3 are reported here together. With approval from DEFRA, following completion of Task 2.3.1 the proposed work under Task 2.3.3 was modified to provide the maximum amount of data within the available budget to complement the findings of Tasks 2.2 and 2.3.1. The major change was a substitution of some sediment core analyses for lake surface sediment analyses. Joint results are presented below.

Introduction

Recent evidence, mostly from North America, has emerged suggesting that base poor upland and mountain aquatic ecosystems are demonstrating a response to anthropogenic nitrogen deposition, despite the low inputs (Findlay *et al.*, 1999; Baron *et al.*, 2000; Wolfe *et al.*, 2001; Fenn *et al.*, 2003; Sickman, 2003). Contrary to expectations, many upland lakes in Europe and North America are N, rather than P, limited or co-limited by both N and P (Maberly *et al.*, 2002; Bergström *et al.*, 2005; Bergström & Jansson, 2006: see Tasks 2.1 and 2.3.2). It has been suggested that the natural state of many upland lakes is N-limitation and the widespread occurrence of P-limitation is a reflection of a change in the N and P balance of these lakes as a result of increased inputs anthropogenic N (Bergström & Jansson 2006).

Wolfe *et al.* (2001), working on cores from remote lake ecosystems in the Rocky Mountains, Colorado, have demonstrated a link between apparent eutrophication and a change in δ^{15}N of bulk organic matter in sediment cores from two lakes. This change in δ^{15}N of bulk organic matter to isotopically lighter nitrogen is indicative of an increased supply of N from the atmosphere to the lakes and their catchments. N deposition in this region is relatively high for alpine regions in North America, though it has been suggested that a similar process may be operating more widely. Changes in the δ^{15}N of bulk organic matter, similar to those identified by Wolfe *et al.* (2001), have been seen in remote lakes on Baffin Island (Wolfe *et al.*, 2006) and in Greenland (Simpson *et al.*, unpublished research) experiencing low but elevated inputs of anthropogenic N via long range transportation.

Furthermore, Jones *et al.* (2004) have recently reported that there is a weak but statistically significant link between the $\delta^{15}N$ of lake surficial sediments and total N deposition for a small set of upland lakes, and suggest that $\delta^{15}N$ might be used as a surrogate for the degree of lake N-limitation.

Nitrogen isotopes are good integrators of the N cycle (Robinson, 2001) and have been used extensively to track pollution and process in catchments and waters (Kendall, 1998), and whilst the exact interpretation of the changes in $\delta^{15}N$ of bulk organic matter is still being researched, it is clear that the changes in the isotopic values of nitrogen bearing compounds in lake sediments indicate a widespread and profound change in the biogeochemistry of the studied lakes.

Lake sediments contain organic matter from a range of sources. Particular amongst these is organic matter derived from aquatic macrophytes and algae, terrestrial macrophytes and soil humus. Each of these sources contains and therefore contributes varying amounts of N to sediment organic matter. Phytoplankton derived organic matter is relatively N-rich, due to the high protein and lipid content of the cells. Organic matter derived from terrestrial plants is dominated by cellulose and lignin which are N-poor, whilst soil-derived organic matter may be relatively N-rich due to N-fixation by bacteria, especially around plant roots.

Differences in N content of the various constituents mean that N-rich fractions can dominate the isotope values of bulk organic matter measured in lake sediments, even if these N-rich sources do not dominate volumetrically. Therefore, terrestrial plant material is unlikely to distort or influence the isotope values measured in lake sediment organic matter as that source is N-poor. Likewise, a new N-rich source could have a disproportionate effect on sediment N isotope values despite being at a relatively low concentration or flux (Talbot, 2001). As such, N isotope values from lake sediment organic matter can be expected to reflect the N isotope values of the N-rich sources as well as in-lake processing of that N.

The contribution to lake sediment organic matter N isotope values made by atmospheric deposition is difficult to determine without having wider knowledge of the N isotope values of sources and applying mixing and fractionation models. What is easier to conclude, is that the observed changes in lake sediment N isotope values from North America (e.g. Wolfe *et al.*, 2001) indicate a change in the biogeochemical cycling of these lakes. Because the sediment core isotope values are reasonably stable or constant prior to the switch to gradually lower proportions of ^{15}N, we can hypothesize that the lakes had reached some form of stable state and that the N isotope values of the lake sediment were in steady state with inputs. The observed change in $\delta^{15}N$ indicates that sources of N to these lakes have altered or that the processing of N within the lake and/or its catchment has changed. Given the timing of these changes and the switch to lower $\delta^{15}N$ values of lake sediment organic matter, a prime candidate that could be associated with these changes is the increase in deposited N observed through the northern hemisphere since the early to mid 1800s.

One characteristic shared by both the Colorado Rocky Mountain lakes and those in the Arctic is their high degree of sensitivity to change. There is significant evidence that the effects of N deposition on mountain and Arctic lakes is widespread and changes in the $\delta^{15}N$ of bulk organic matter have been observed even in areas receiving low levels of N deposition. The extent to which less sensitive upland lakes in Europe and North America have also been affected by anthropogenic atmospheric N deposition is not known.

Aims and objectives

Here we investigate the palaeolimnological N isotope record for a series of upland lakes in the UK receiving a range of anthropogenic N inputs from atmospheric deposition, to determine whether the patterns of change associated with N enrichment from deposition observed in North America are also found in the UK. We also conduct a study of $\delta^{15}N$ of lake surficial sediments in relation to total N deposition on a larger data set than that originally used by Jones *et al.* (2004) to investigate whether the proposed link between $\delta^{15}N$ and N deposition holds over a larger spatial gradient. A link between $\delta^{15}N$ and N deposition would support the conclusion that patterns observed in sediment cores reflect historical increases in deposition and would provide an independent proxy for historical N deposition for use in dynamic catchment hydrochemical models such as MAGIC.

Methods

Sediment core analysis was undertaken at 12 sites across the UK. (Table 2.5). Bulk organic matter sub-samples from sediment cores from each lake were air dried at 40 °C or below. These sub-samples were then milled to a fine powder using a Retsch mixer mill. Approximately 0.001g of milled sediment was transferred to pre-weighed tin capsules, which were then sealed. The amount of dried sediment in each capsule was recorded.

The samples were analysed for total N and C, and $^{14}N/^{15}N$ and $^{12}C/^{13}C$ at the UC Davis Stable Isotope Facility, California, USA via isotope ratio mass spectrometry on Hydra 20-20 or Anca-GSL isotope ratio mass spectrometers.

The concentration of N and C in the samples is expressed as grammes N or C per gramme dry weight of sediment. The isotopic ratio of $^{14}N/^{15}N$ and $^{12}C/^{13}C$ is expressed using the delta (δ) notation in parts per thousand (or per mille, ‰), where $\delta^{15}N$ (‰) and $\delta^{13}C$ (‰) = $[(R_{sample} / R_{standard}] - 1] \times 1000$, where R is the $^{14}N/^{15}N$ or $^{12}C/^{13}C$ ratio in the measured sample or the appropriate standard. The standard for nitrogen is the $\delta^{15}N$ of atmospheric nitrogen (commonly referred to as AIR), and for $\delta^{13}C$ the standard is Vienna Pee Dee Belemnite (VPDB). The C/N ratio was calculated from the mass of N and C and converted to atomic ratios by multiplying the mass ratios by 1.167 (the ratio of the atomic weights of N and C).

Diatoms samples were prepared following standard methods (Battarbee *et al.*, 2001). At least 300 diatom valves were counted in each sample using a Leitz research microscope with a x100 oil immersion objective and phase contrast. Diatom taxonomy follows Krammer and Lange-Bertalot (1986-1991).

Sediment cores were dated using a combination of spheroidal carbonaceous particle (SCP) and ^{210}Pb radiometric dating, or by correlation of new cores with existing dated cores. Not all cores presented in the results section were dated, since additional sites were analysed as part of changes to the work programme agreed with DEFRA.

NO_x, NH_y and Total N deposition data were derived from national 5x5km gridded data (annual mean values for 1995-97) provided by CEH Edinburgh. The relationship between N deposition and surface sediment $\delta^{15}N$ was investigated using least squares regression techniques using R version 2.5.1 (R Core Development Team, 2007). NO_x and Total N deposition were log transformed prior to analysis as preliminary modelling showed non-Gaussian, and non-constant variance in, model residuals. After log transformation, these problems disappeared. The resulting plots were drawn on the original (non-logged) scale of the predictor.

Table 2.5: Isotope sediment core sampling locations

Site	WBID	Altitude (m)	Area (ha)	Grid Reference	Country
Lochnagar	21723	788	9.9	N0252859	Scotland
Loch nan Eion	17147	356	28.6	NG924511	Scotland
Loch nan Eun	7824	166	3.5	NG231298	Scotland
Round Loch of Glenhead	27927	298	12.7	NX449803	Scotland
Scoat Tarn	29156	598	4.3	NY159103	England
Wast Water	29183	64	278	NY162059	England
Burnmoor Tarn	29215	253	23.9	NY183043	England
Llyn Gwngu	38163	438	3.1	SN838729	Wales
Llyn Nadroedd	34061	539	1.0	SH594543	Wales
Loch Coire Fionnaraich	17334	236	9.3	NG945498	Scotland
Loch Coire Mhic Fhearchair	16140	592	10.1	NG941608	Scotland
Loch Enoch	2708	498	50.2	NX445851	Scotland

Stratigraphic Results

A summary diagram of the changes in $\delta^{15}N$ for each of the 12 sediment cores analysed is shown in Figure 2.8. With the exception of two sites (Llyn Nadroedd and Loch nan Eun) there is a trends towards isotopically lighter bulk organic matter in the upper levels of the analysed sediment cores, illustrated by a reduction in measured values of $\delta^{15}N$.

With the exception of Llyn Nadroedd and Loch nan Eun, the observed results are consistent with the patterns observed elsewhere in the USA and the Arctic (Wolfe *et al.*, 2001, 2006; Simpson *et al.*, unpublished work). Subsequent discussion is restricted to those sites that exhibit the decline in $\delta^{15}N$, unless specifically indicated.

Stratigraphic plots of the isotope measurements, total N and C and atomic C/N ratio for each of the sites are shown in Figures 2.9-2.20 below.

For the sites that show a decrease in $\delta^{15}N$ in the upper section of the core, we find that prior to this decline, relatively stable $\delta^{15}N$ values are observed in the range +2 to +3.5‰, although there is a degree of scatter between data points. The main exception to this is Loch Coire Mhic Fhearchair, which exhibits a shift of +4‰ around 10cm which occurs over several samples. This suggests a rapid change in the biogeochemistry of the loch at this time point, although without further investigation it is difficult to suggest a plausible mechanism for this change.

Figure 2.8: Summary diagram of δ^{15}N measurements for each of the 12 study sites. Data are arranged on the y-axis by depth down the sediment core, with top equivalent to present day.

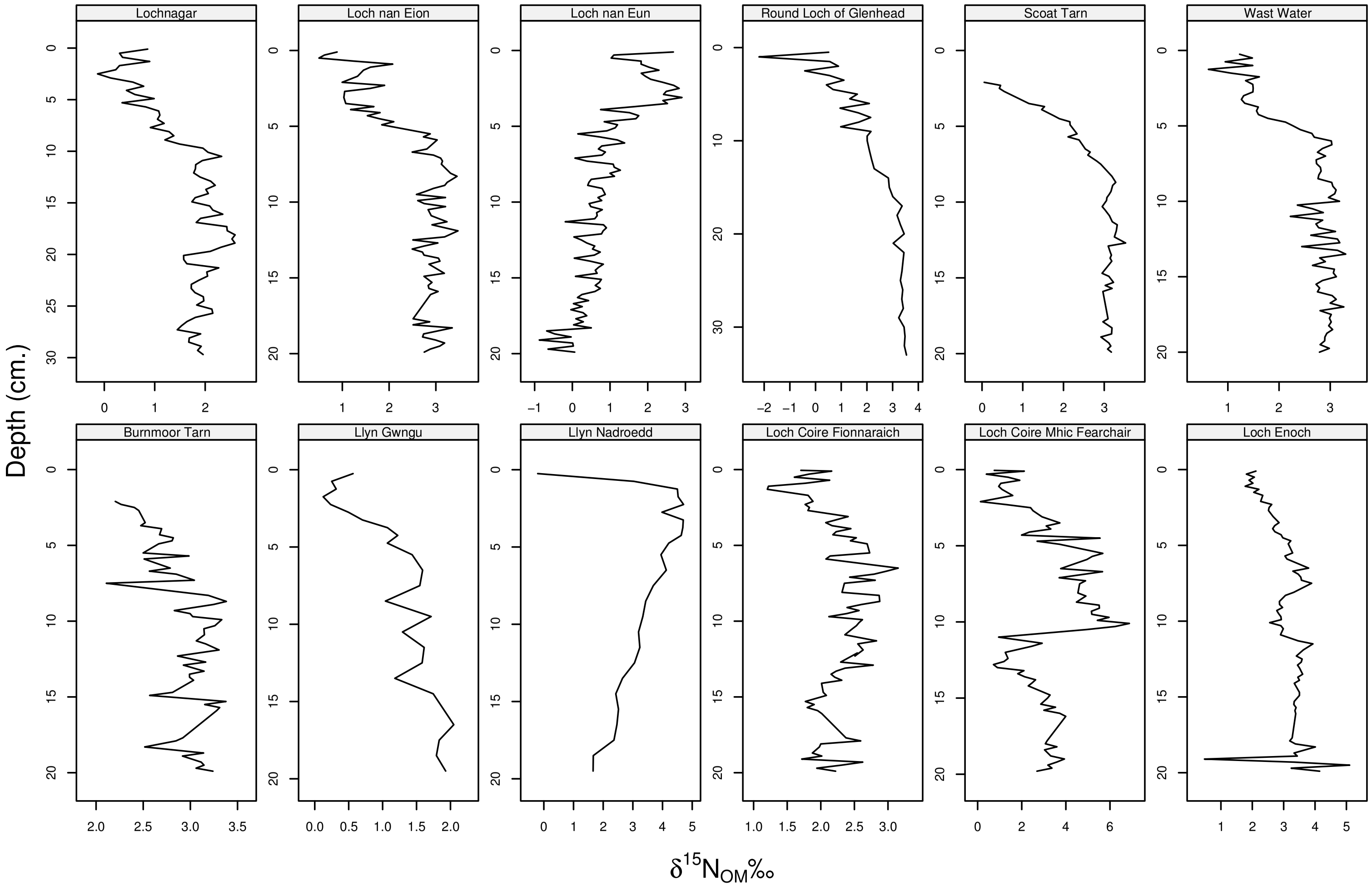


Figure 2.9: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Lochnagar

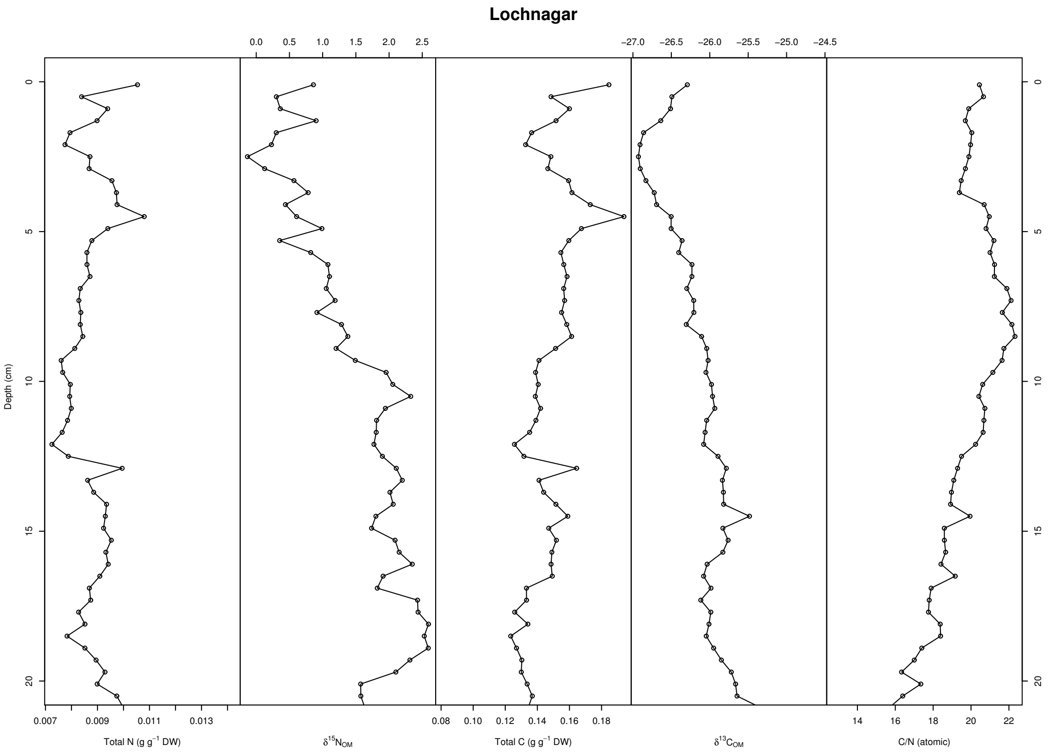


Figure 2.10: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Loch nan Eion

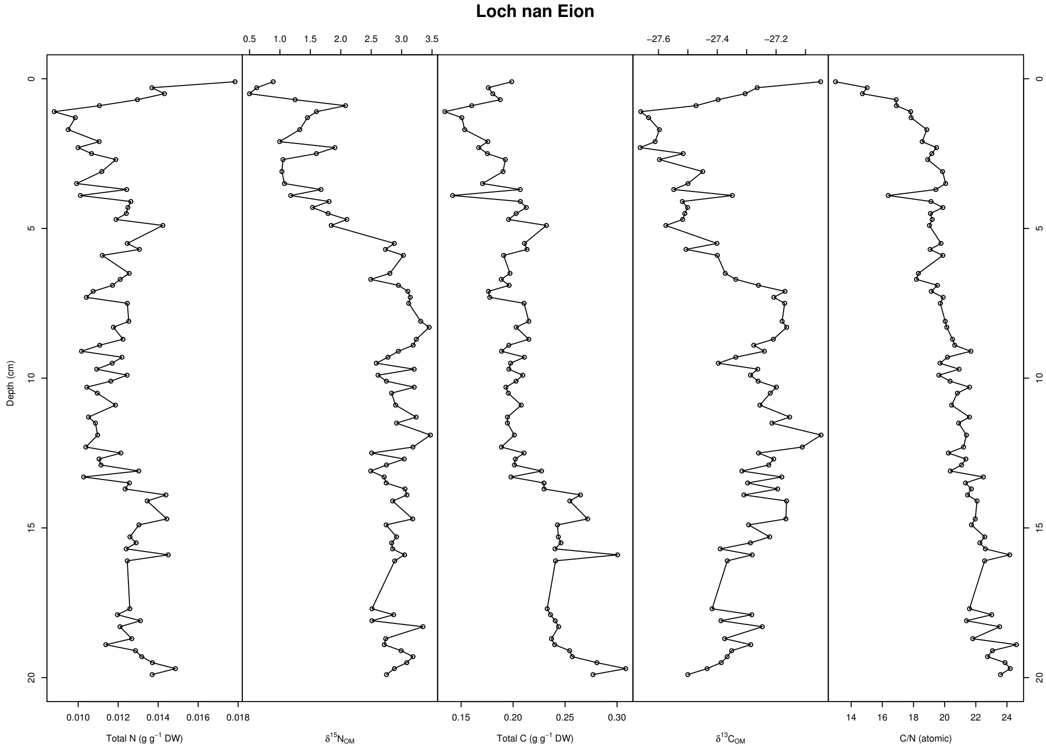


Figure 2.11: Stratigraphic plot of δ^{15}N and δ^{13}C, total N & C and atomic C/N ratio for Loch nan Eun

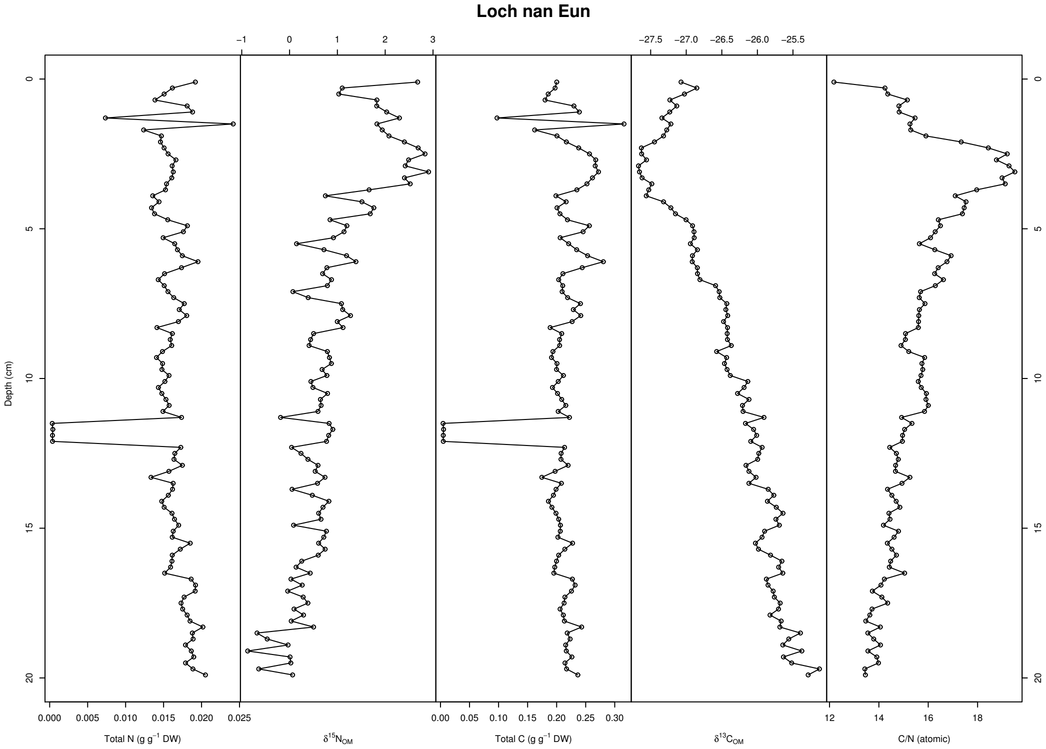


Figure 2.12: Stratigraphic plot of δ^{15}N and δ^{13}C, total N & C and atomic C/N ratio for Round Loch of Glenhead

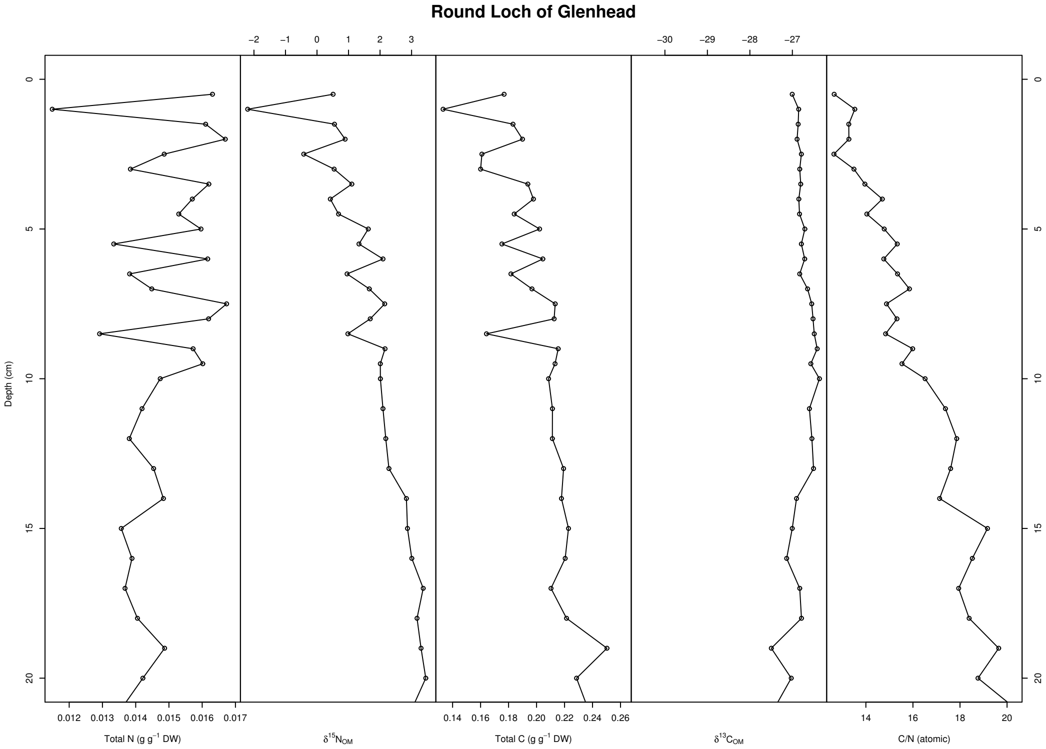


Figure 2.13: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Scoat Tarn

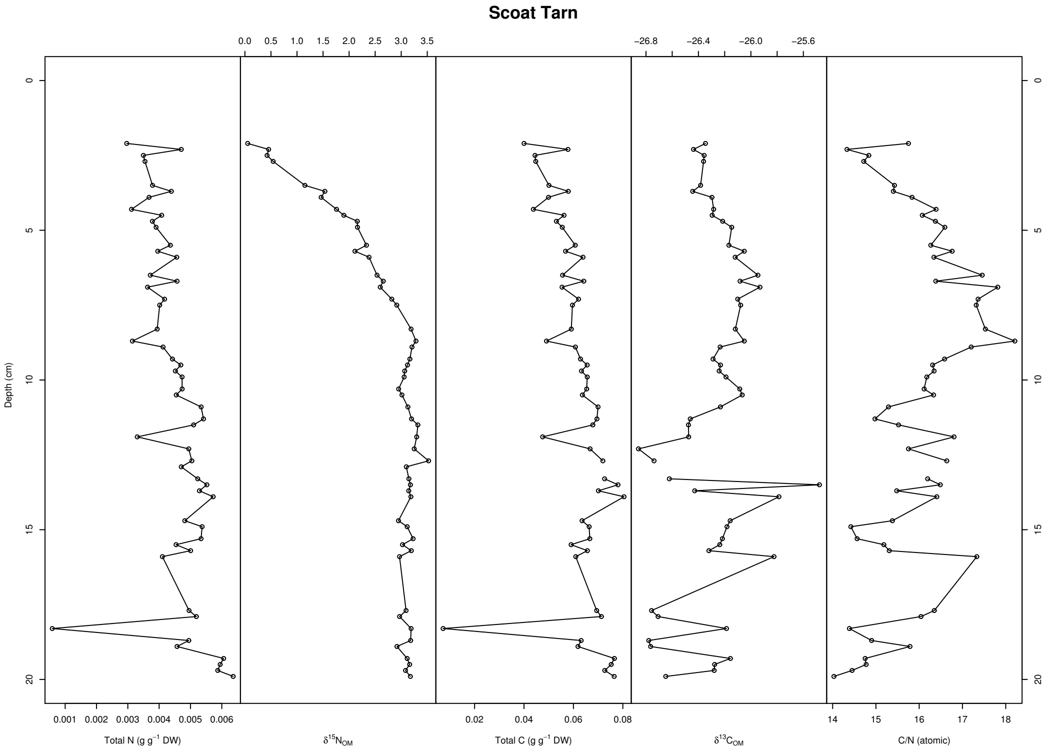


Figure 2.14: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Wast Water

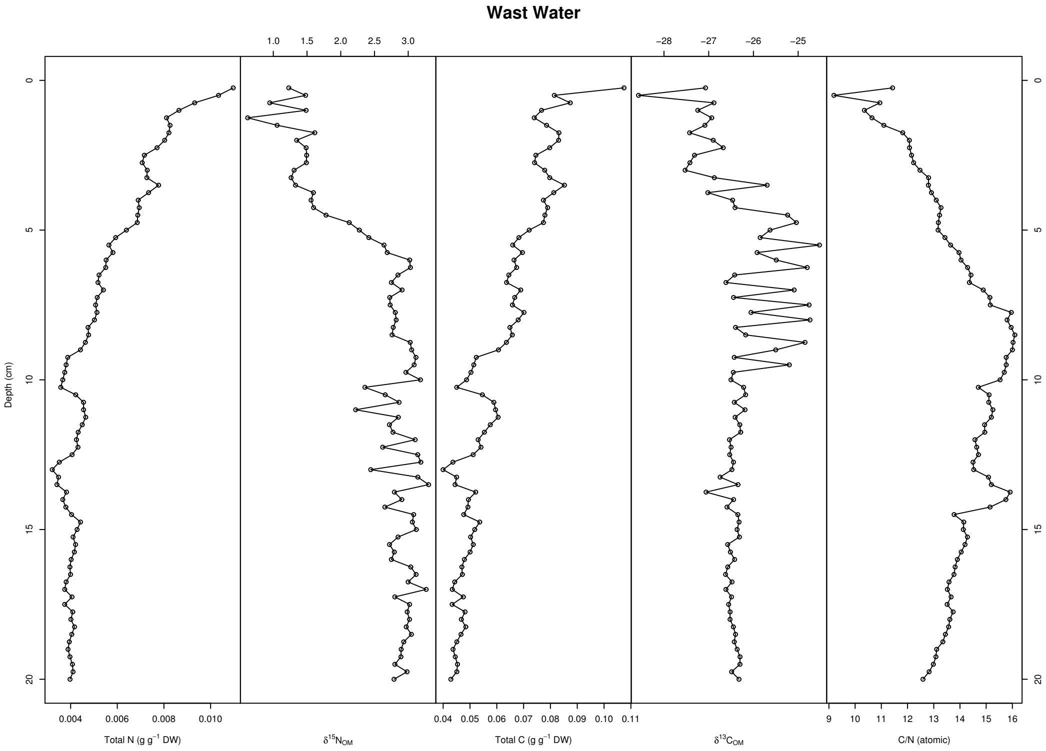


Figure 2.15: Stratigraphic plot of δ^{15}N and δ^{13}C, total N & C and atomic C/N ratio for Burnmoor Tarn

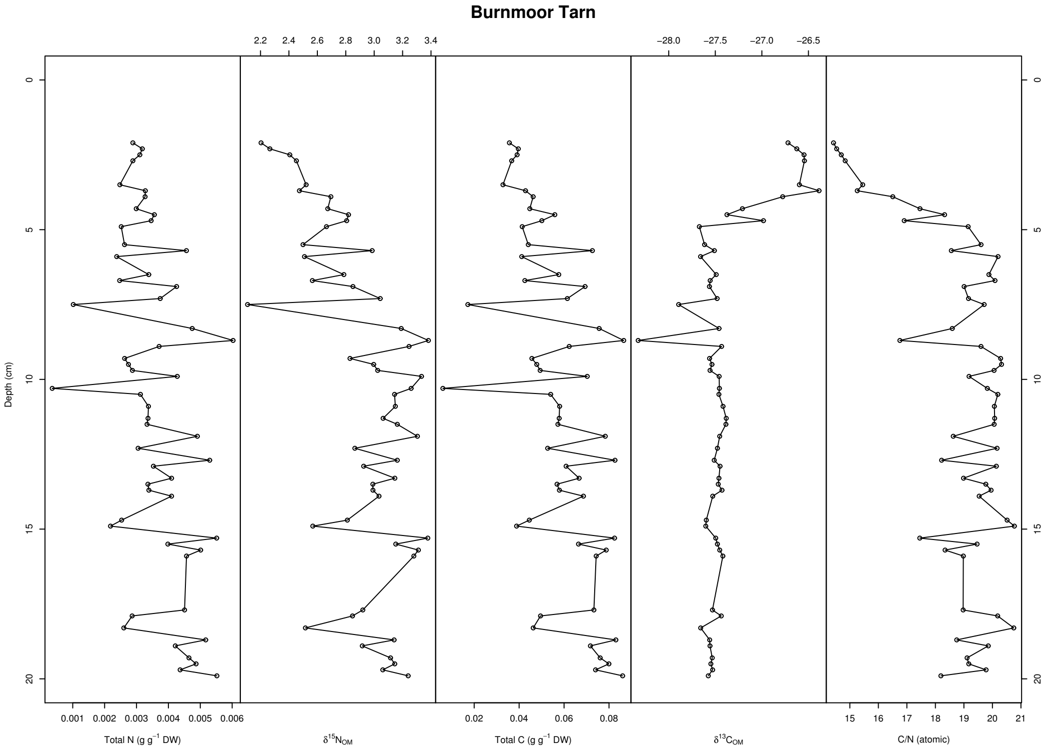


Figure 2.16: Stratigraphic plot of δ^{15}N and δ^{13}C, total N & C and atomic C/N ratio for Llyn Gwngu

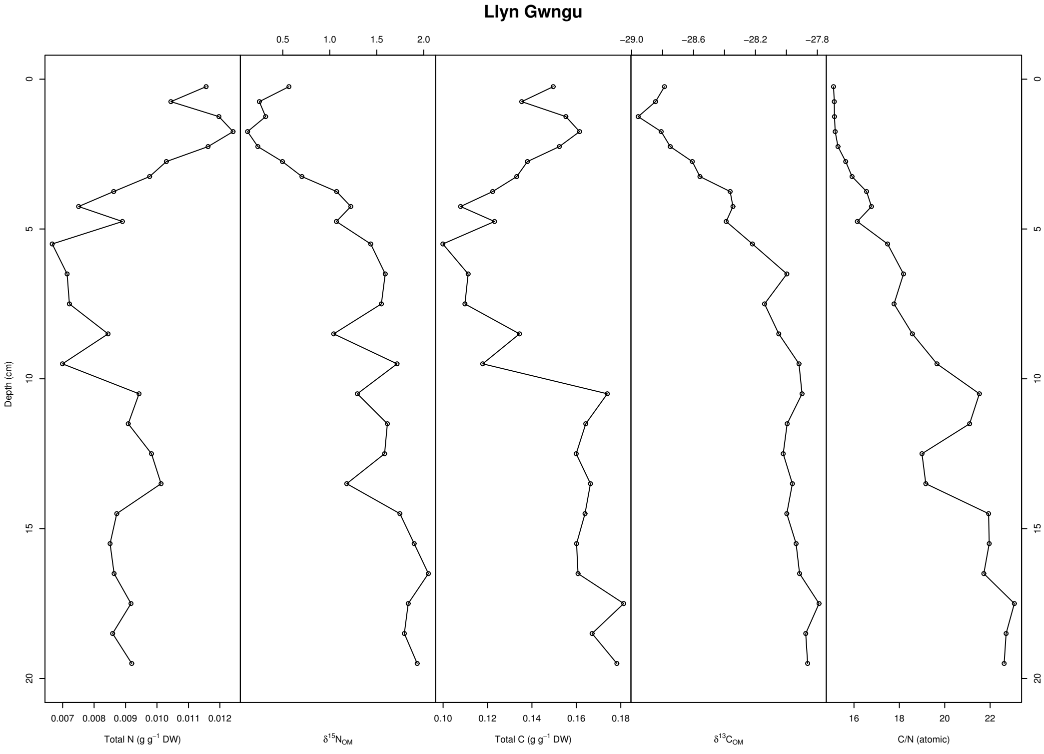


Figure 2.17: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Llyn Nadroedd

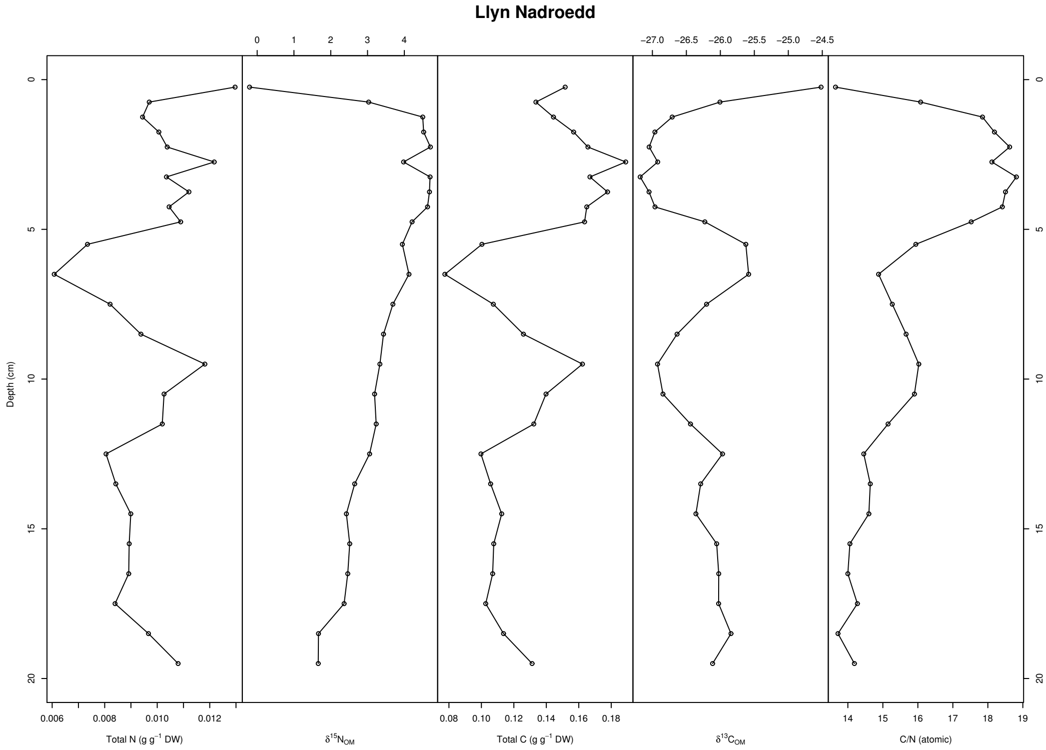


Figure 2.18: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Loch Coire Fionnaraich

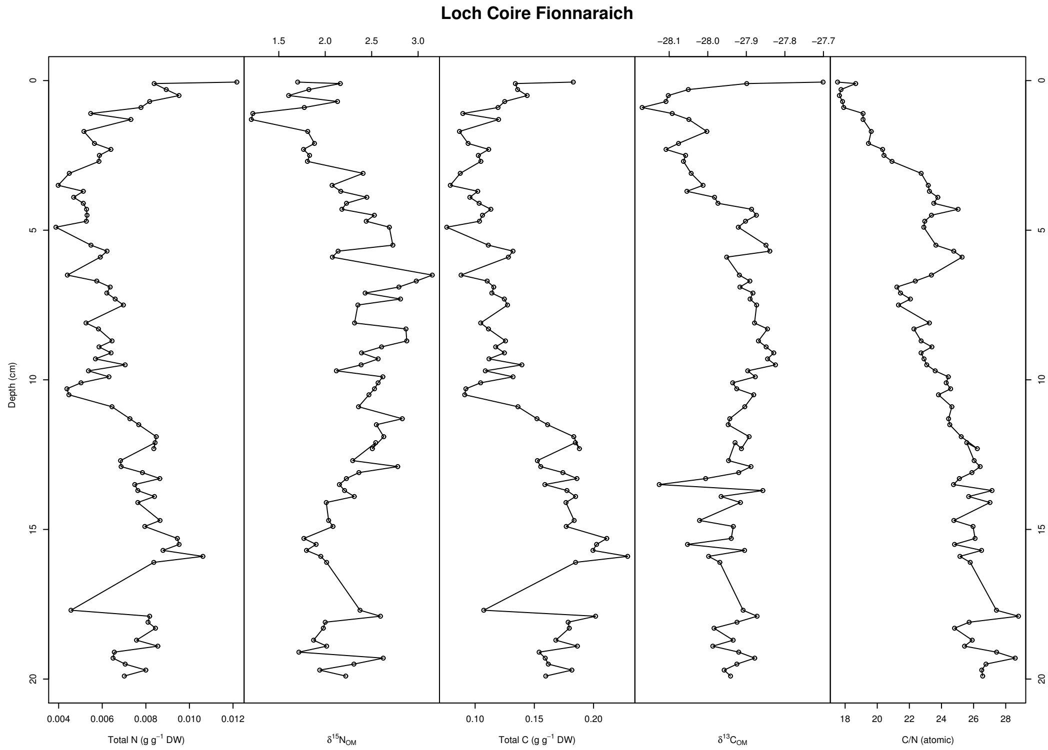


Figure 2.19: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Loch Coire Mhic Fhearchair

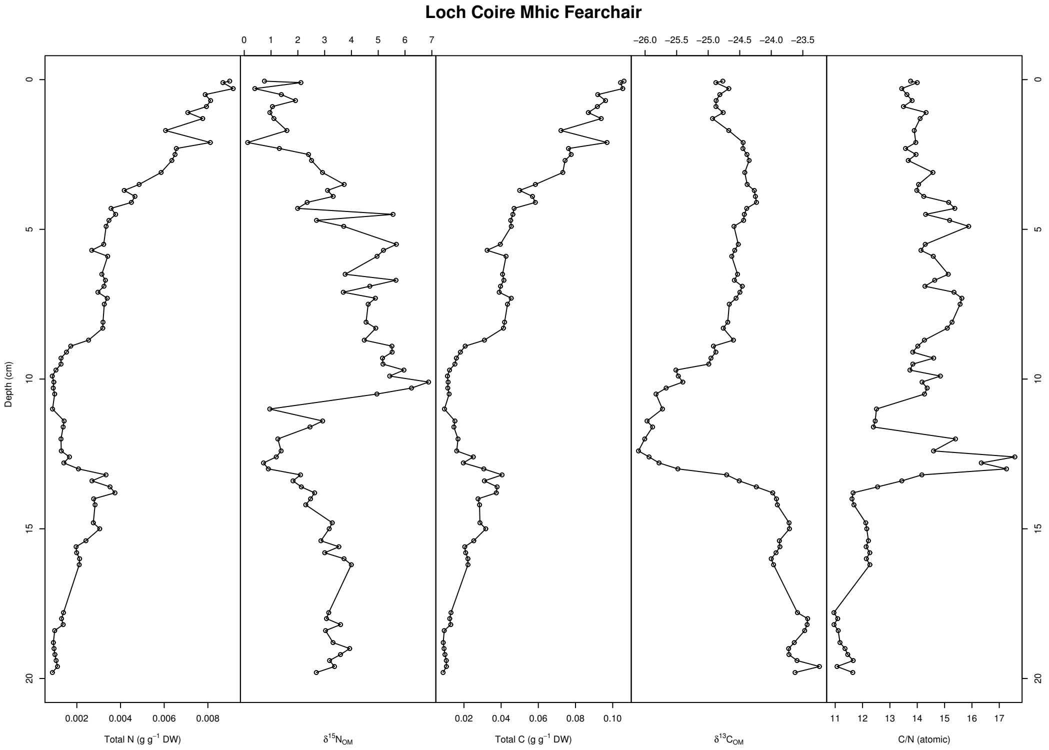
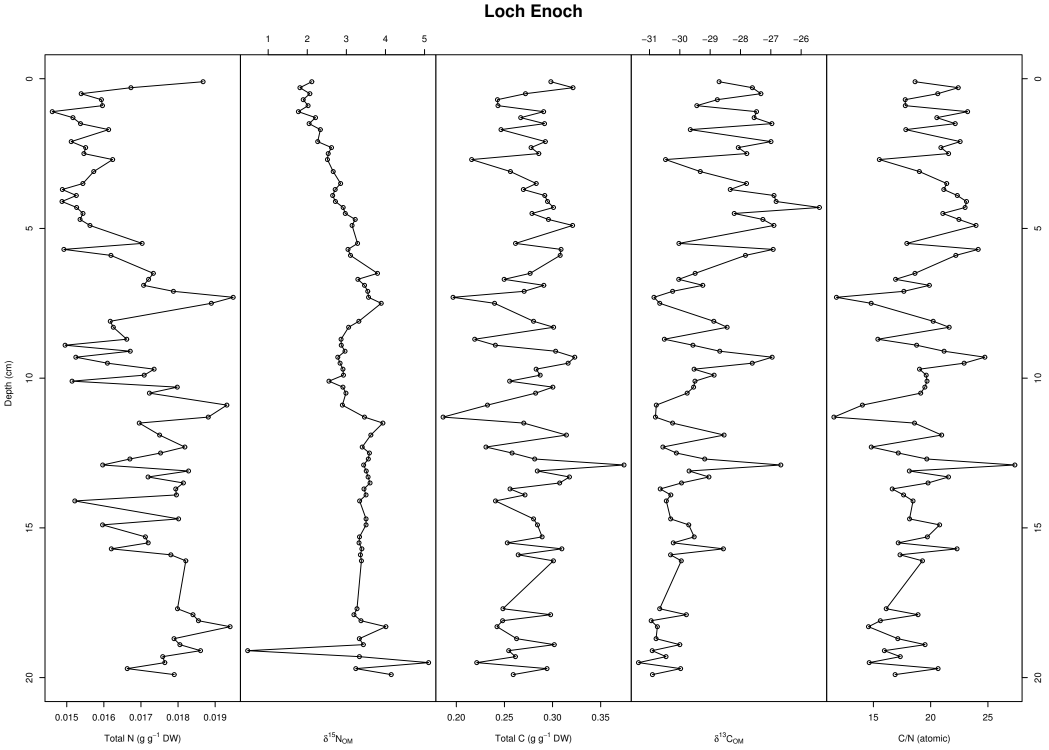


Figure 2.20: Stratigraphic plot of $\delta^{15}N$ and $\delta^{13}C$, total N & C and atomic C/N ratio for Loch Enoch



At the surfaces, $\delta^{15}N$ values of the bulk organic matter are c. -2 to +2‰ with the majority of sites showing values of 0 to +2‰. Where change has taken place, most sites show an approximate decline in $\delta^{15}N$ of 2‰.

The total N (TN) and C (TC) curves are difficult to interpret alone as long term trends in TN and TC could simply reflect progressive degradation of organic matter as it is incorporated in the sediments via diagenetic process occurring in the sediments themselves. The sharp changes in TN and TC apparent in several cores in the uppermost sediment samples are probably the result of early diagenetic process leading to rapid breakdown of the most labile organic compounds as material is incorporated in the sediment.

The C/N ratios are generally low, being less than c. 20 in most sites. In many sites, there is a trend towards lower C/N ratios of c. 8-10, which begins either shortly before or contemporaneously with the shift to lower $\delta^{15}N$ values, suggesting that the two processes are linked, although this is purely correlative. C/N ratios of <10 with $\delta^{13}C$ of c. -25 to -30‰ are often linked to a lacustrine algal source. As such we could interpret the changes in C/N ratios and associated $\delta^{13}C$ values to indicate that the contribution of autochthonous algal material to sediment organic matter has increased, suggesting an increase in algal productivity and biomass.

Sites that do not follow this pattern are Loch nan Eun, Lochnagar, Llyn Nadroedd, Loch Enoch and Loch Coire Mhic Fearchair.

In Loch nan Eun, the trend of increasing C/N ratios is paralleled by a steady increase in $\delta^{15}N$. At about 2.5 cm there is a marked change in the biogeochemistry of this site. With the exception of the uppermost sample, $\delta^{15}N$ values decline rapidly by 2‰, the C/N ratio drops from 16 to c. 11, and the decline in $\delta^{13}C$ values reverses, with a slight enrichment in ^{13}C. This may indicate that this site has reached a threshold in the last few decades that has led to a switch in the biogeochemical cycling in the loch, that is superficially similar to the earlier changes in $\delta^{15}N$ seen in 10 of the studied sites and is consistent with the changes seen in more remote sites in North America and the Arctic.

The following sequence of plots shows isotope cross plots (Talbot, 2001) for each of the studied sites, which draw various aspects of the values shown in the stratigraphic plots above against each other in scatterplots (Figure 2.21-2.32). The points shown in red represent the samples that occur after $\delta^{15}N$ starts to decline.

The isotope crossplots show that in the majority of sites the C and N geochemistry and the isotopic values for C and N for the samples after the change in $\delta^{15}N$ are distinct compared to samples prior to the change. This suggests that the biogeochemical changes are not just restricted to the N cycle in these systems. The most obvious pattern is that the lower $\delta^{15}N$ values are most often associated with low C/N ratios in many sites. Other changes are site specific, but a number exhibit changes in the relationship between the total C of the sediment sample and the C/N ratio for those samples that are associated with the declining trend in $\delta^{15}N$.

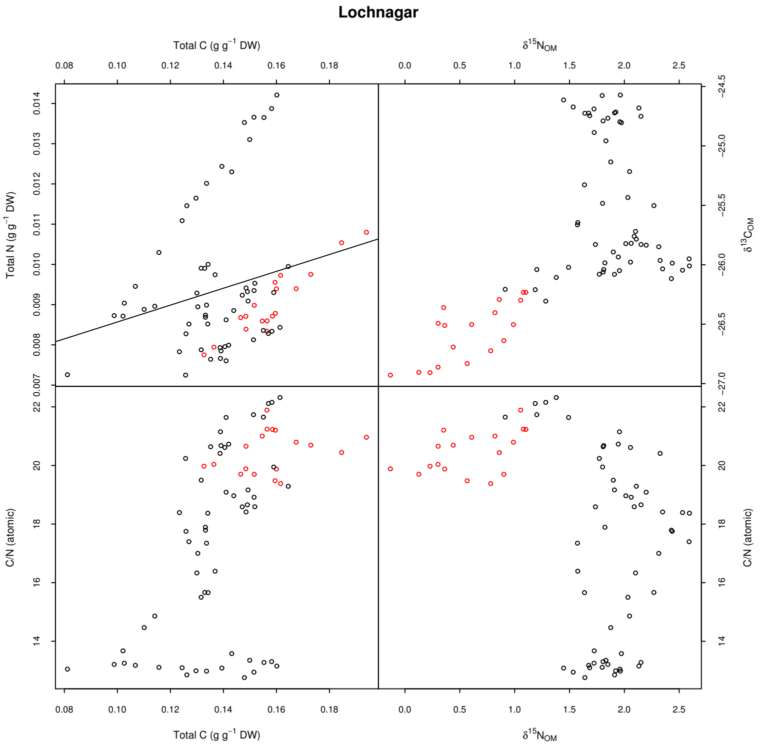


Figure 2.21: Isotope crossplot for Lochnagar

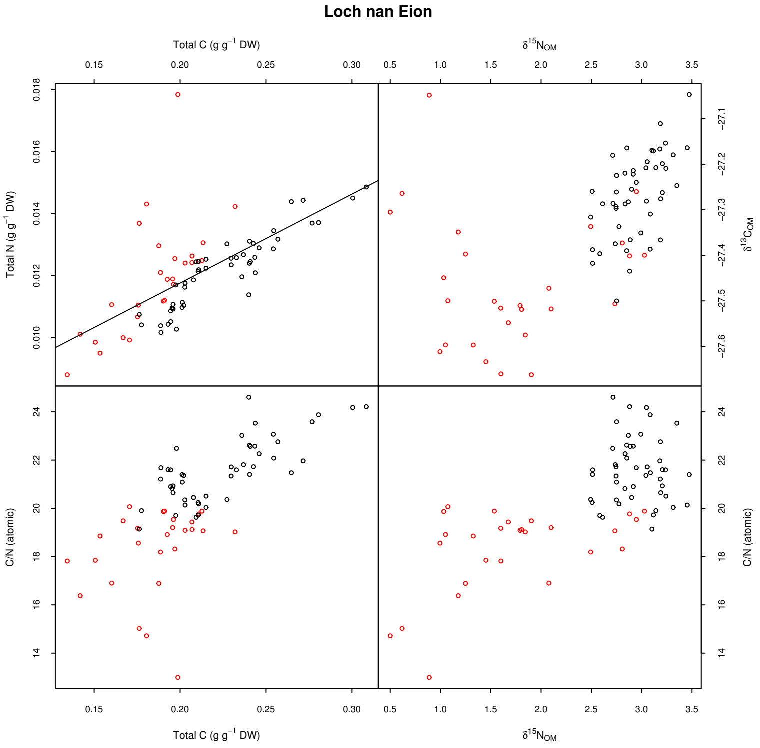


Figure 2.22: Isotope crossplot for Loch nan Eion

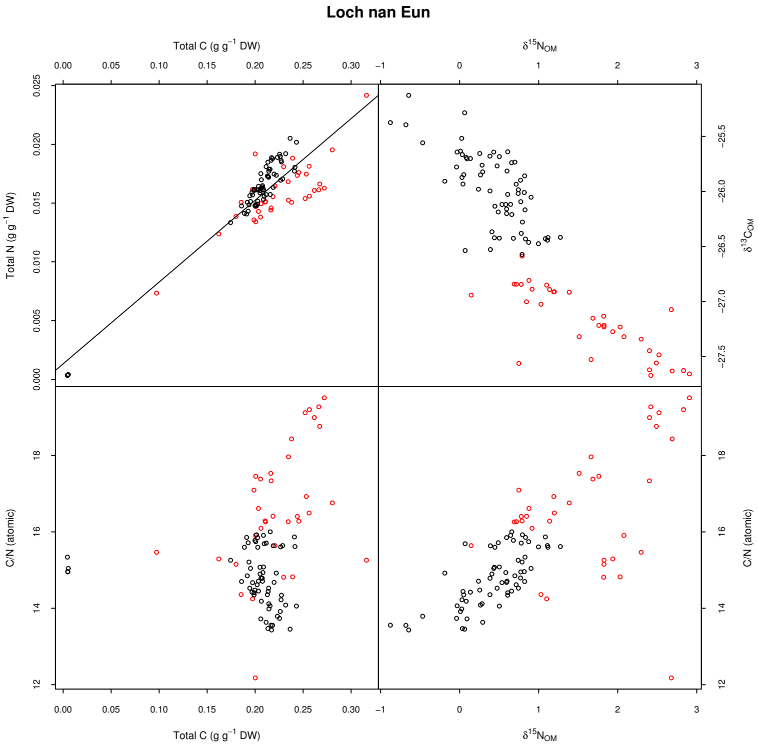


Figure 2.23: Isotope crossplot for Loch nan Eun

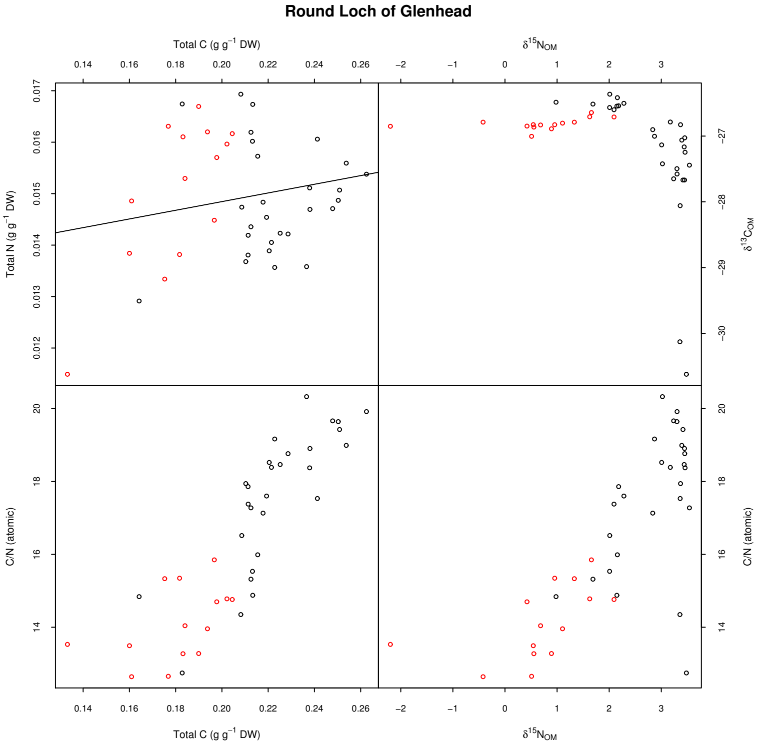


Figure 2.24: Isotope crossplot for Round Loch of Glenhead

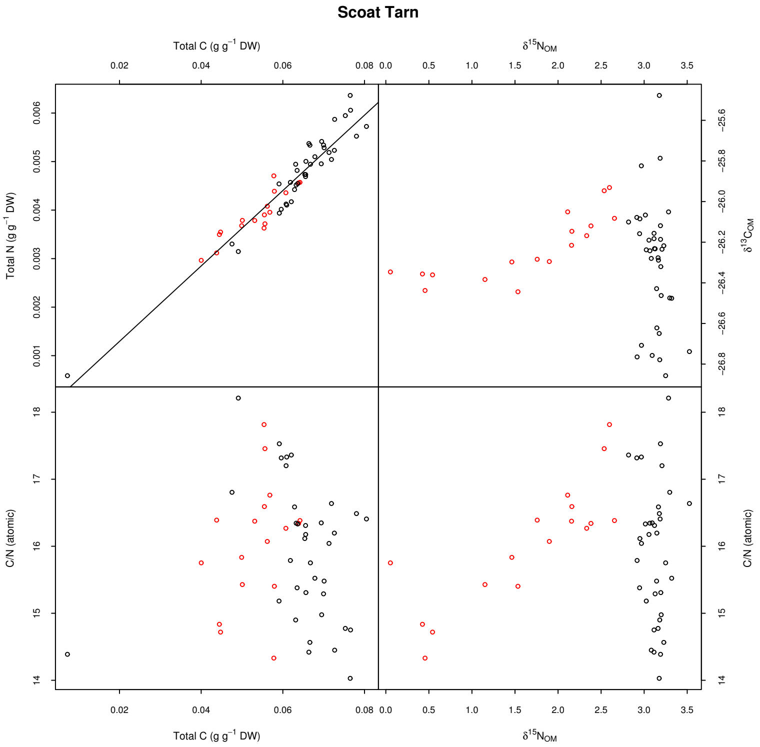


Figure 2.25: Isotope crossplot for Scoat Tarn

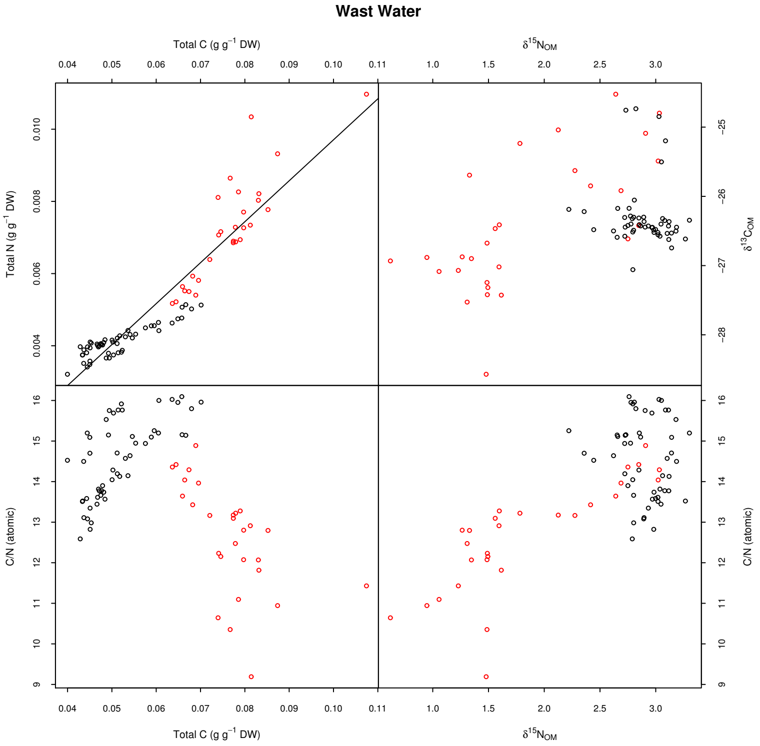


Figure 2.26: Isotope crossplot for Wast Water

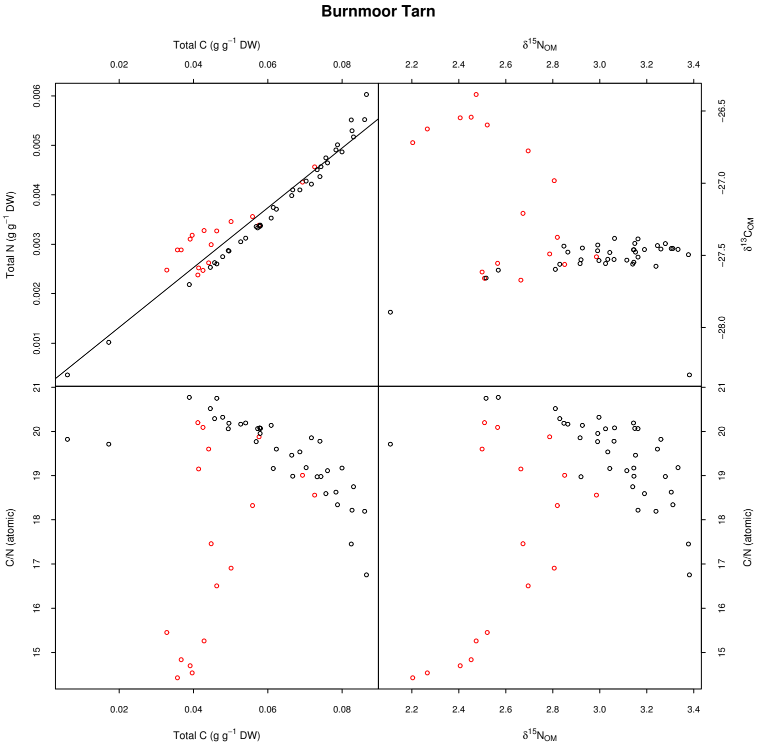


Figure 2.27: Isotope crossplot for Burnmoor Tarn

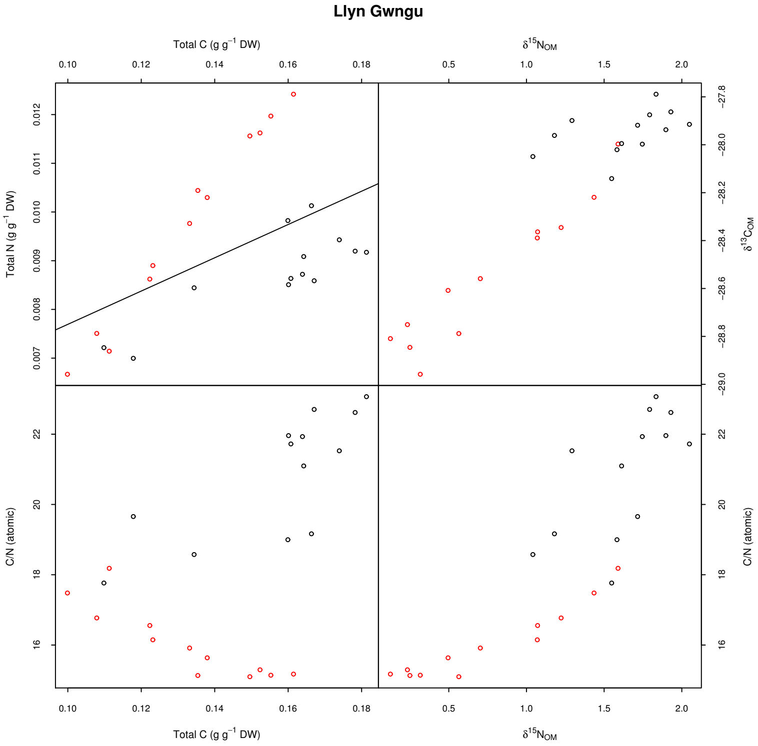


Figure 2.28: Isotope crossplot for Llyn Gwngu

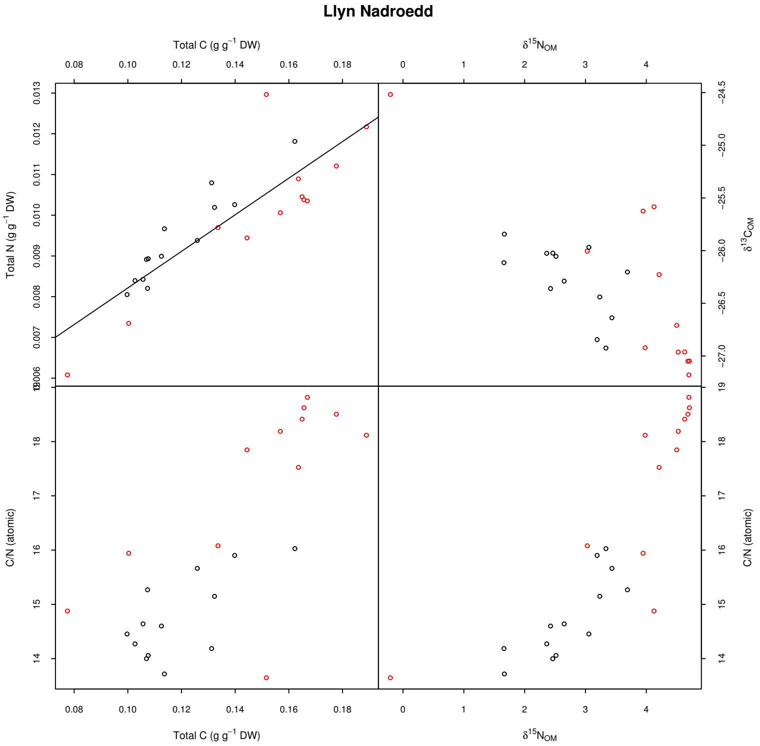


Figure 2.29: Isotope crossplot for Llyn Nadroedd

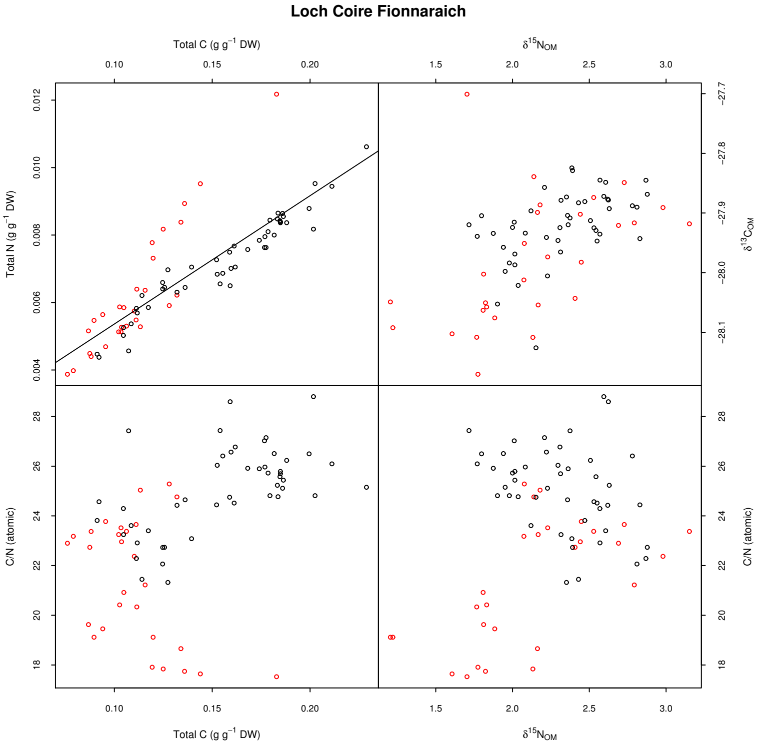


Figure 2.30: Isotope crossplot for Loch Coire Fionnaraich

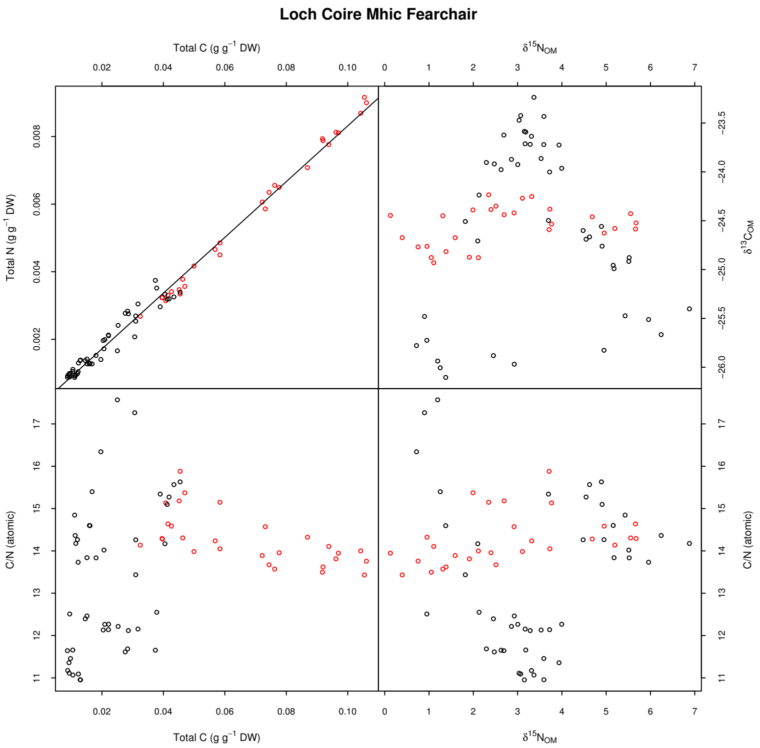


Figure 2.31: Isotope crossplot for Loch Coire Mhic Fhearchair

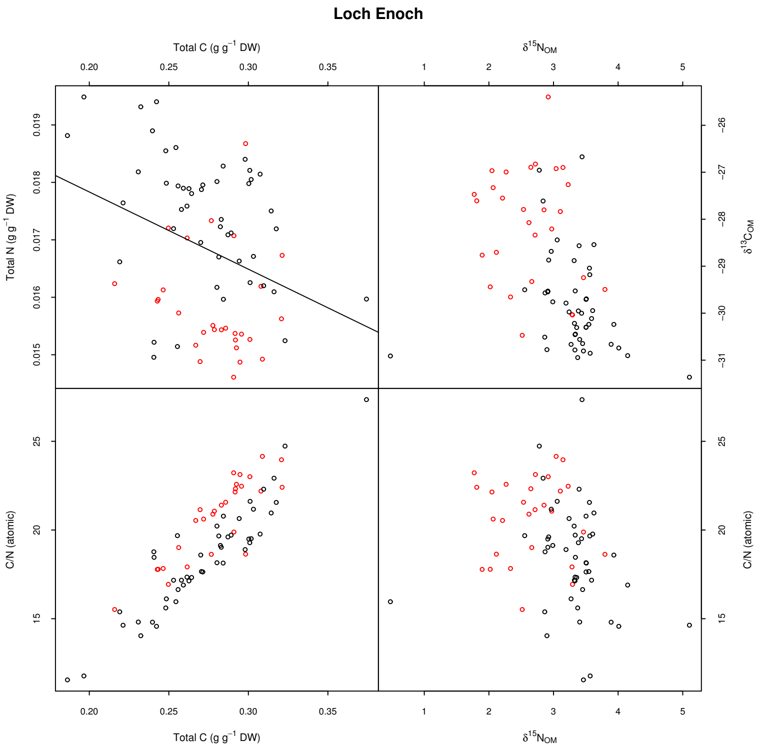


Figure 2.32: Isotope crossplot for Loch Enoch

δ^{15}N in surface sediment and relationship with N deposition

Surface sediments from a total of 83 sites, including those originally analysed by Jones *et al.* (2004), were analysed for δ^{15}N. δ^{15}N values were related to 5x5km deposition data for a period that approximately corresponds to the time period covered by the surface sediments. Table 2.6 shows the range of deposition values for the sites in the data set.

Table 2.6: Summary statistics for NO_x, NH_y and total N deposition across the 83-site data set

Units (kg ha^{-1} yr^{-1})	NO_x	NH_y	Total N
Mean	6.921	11.45	18.37
Min	1.68	2.52	4.76
Max	20.58	28.56	46.90

The distribution of NO_x, NH_y and total N deposition across the data set as well as the δ^{15}N values of the surface sediments is shown in Figure 2.33 below. These data cover a wide range of deposition from high to low, from <5 to >45 kg N per hectare per year total N deposition. The δ^{15}N values are approximately Gaussian, with a mean of c. +2‰.

The results of the regression modelling are shown in Figures 2.34-2.36. There is a strong, statistically significant relationship between sediment δ^{15}N and each of the deposition measures, though the relationship was strongest for NO_x deposition (R^2_{adj} = 0.1015, F = 10.26, p = 0.001945), followed by total N deposition (R^2_{adj} = 0.06514, F = 6.714, p = 0.01134), then NH_y deposition (R^2_{adj} = 0.0493, F = 5.252, p = 0.02451). These results are in agreement with those of Jones *et al.* (2004), although with this much larger data set, there is inevitably more scatter and consequently, the coefficient of variation for the models presented here is lower than those of Jones *et al.* (2004). This high variability and therefore low R^2_{adj}, is indicative there are other important processes that combine to determine surface sediment δ^{15}N values, many of which may be site and site-type specific. Yet superimposed upon this natural variation and noise, is a clear pattern of lower δ^{15}N values in lake sediment organic matter as N deposition (as NO_x, NH_y or total N) increases.

Discussion

The results of the stratigraphic analysis of the 12 sediment cores show that there have been profound changes in the biogeochemistry of many of the studied upland lakes, consistent with results reported elsewhere for more sensitive ecosystems (e.g. Wolfe *et al.*, 2001). 10 of the 12 sites studied showed switches to isotopically lighter bulk organic matter in the upper part of the sediment core, with the possibility that the core from Loch nan Eun has also experienced a similar but more recent change.

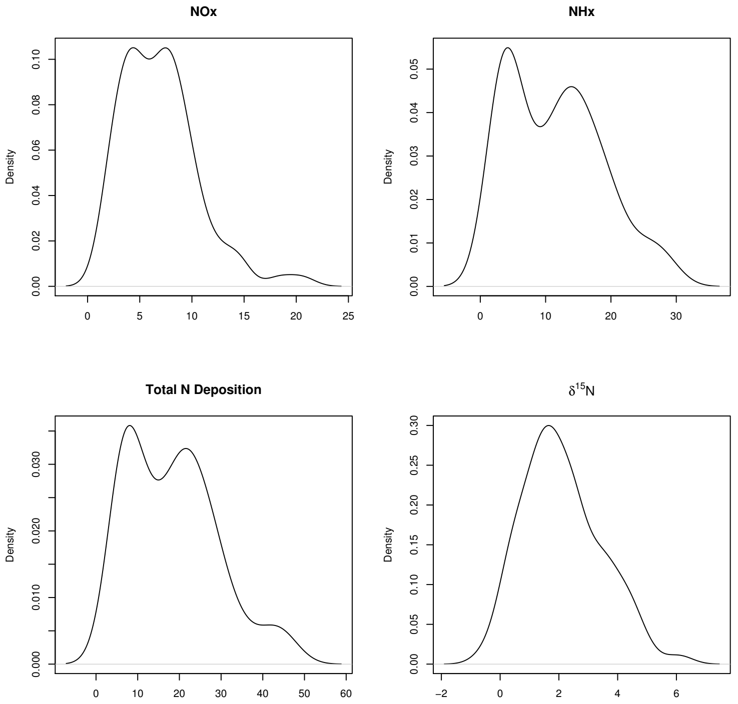


Figure 2.33: Probability density functions illustrate the distribution of NO_x, NH_x, total N deposition and surface sediment δ^{15}N data for the 83-lake data set

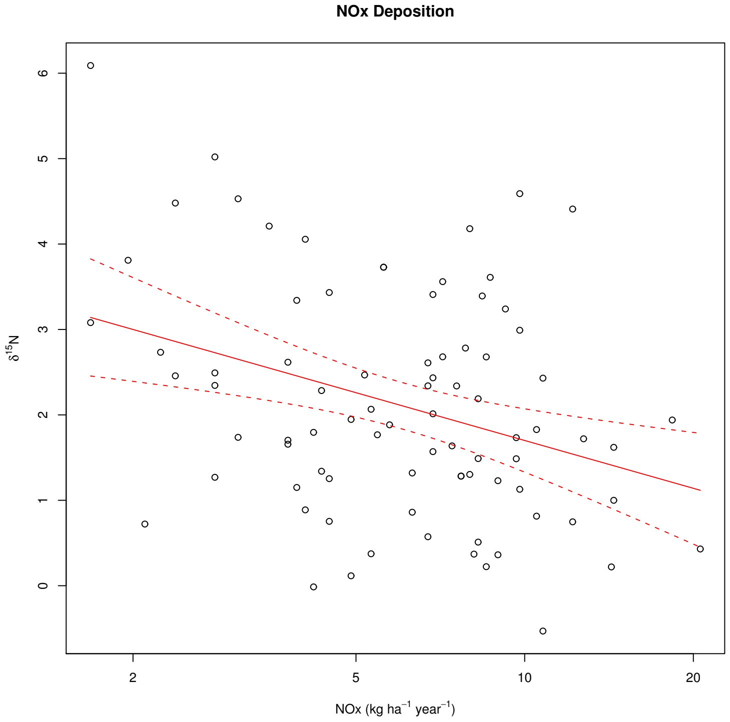


Figure 2.34: Regression relationship between surface sediment δ^{15}N and NO_x deposition

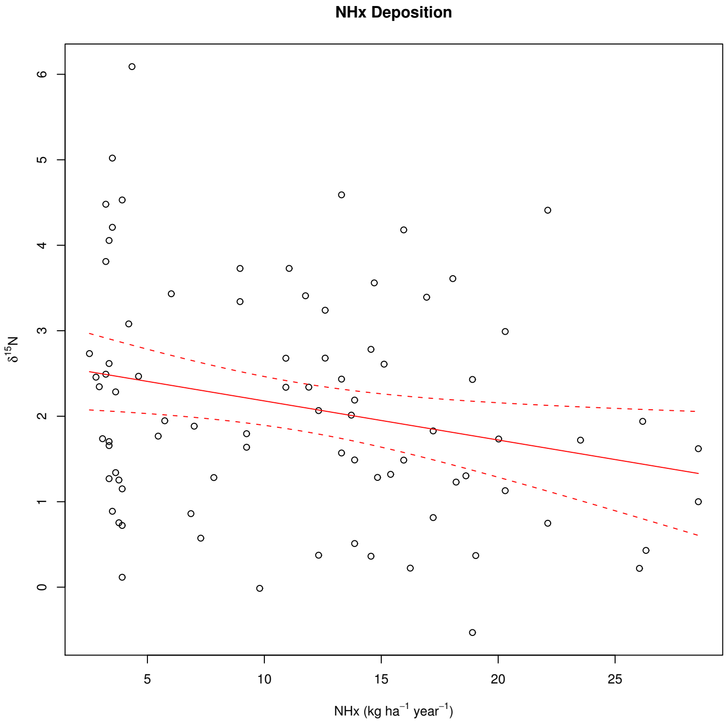


Figure 2.35: Regression relationship between surface sediment $\delta^{15}N$ and NH_y deposition

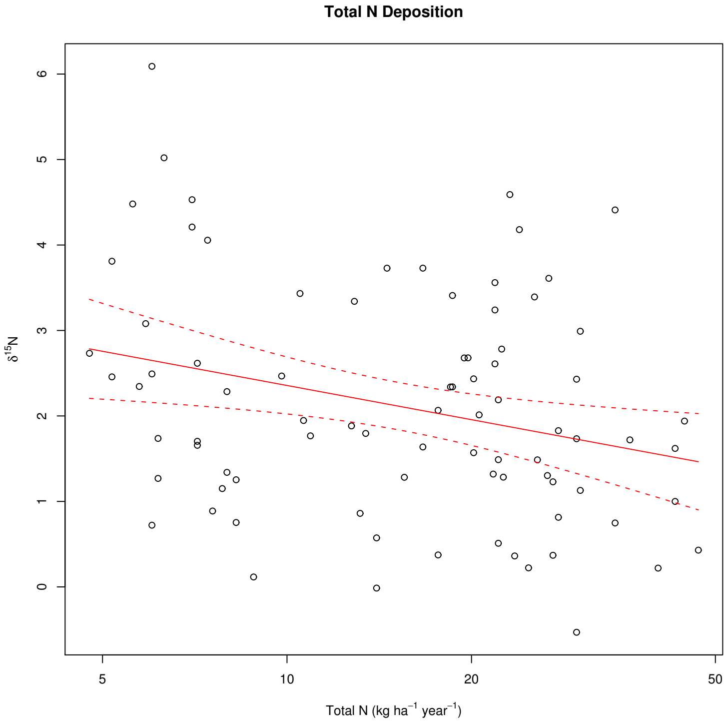


Figure 2.36: Regression relationship between surface sediment $\delta^{15}N$ and total N deposition

Although not all cores were dated, those that were suggest that the changes in $\delta^{15}N$ began in the late 19th and early 20th Centuries, which is again consistent with increased anthropogenic inputs of N from atmospheric deposition since the industrial revolution. This indicates that sites have been experiencing changes in their nitrogen cycle and N and C biogeochemistry for approximately 100 years. This pre-dates the major increases in N emissions from the 1960s onwards and suggests that even moderate amounts of elevated N deposition emitted prior to 1960 were having an influence on the biogeochemistry of upland lakes in the UK.

Wolfe *et al.* (2001) suggest that their observed changes in $\delta^{15}N$ are related to increased inputs of N from fossil fuel and motor vehicular sources, which they suggest is depleted in ^{15}N.

There are few data on the isotopic composition of rainfall in industrialised regions of the world. Existing data are inconclusive as to whether atmospheric N from industrial and vehicular sources is isotopically distinct from natural atmospheric N (e.g. Heaton, 1986). Data from the four sites studied for the dual isotope method in Work Package 3, Tasks 3.2 and 3.3 are the only isotopic measurements of rainfall at upland sites that we are aware of from the UK. The $\delta^{15}N$ of nitrate in rainfall from these four sites lies within the range -6 to +4‰, which is consistent with values reported elsewhere for nitrate in industrial areas. These values vary temporally over the period of data collection and are not consistently depleted in ^{15}N. However, annual mean $\delta^{15}N\text{-}NO_3^-$ values in the four bulk deposition sites monitored are generally depleted; Afon Gwy (mid-Wales) = -0.3‰, River Etherow (South Pennines) = +0.5‰, Scoat Tarn (Lake District) = -1.5‰ and Lochnagar (Grampians) = -1.8‰ (see Tasks 3.2-3.3).

Catchment processes may also act to alter the isotopic values of deposited N, through denitrification, assimilation and mineralisation within soils and vegetation. The dual isotope data for Scoat Tarn and Lochnagar, two of the sites for which sediment cores were analysed, suggest that there is little systematic difference between the $\delta^{15}N\text{-}NO_3^-$ in deposition and that measured in lake inflows, although mean surface water data are slightly enriched in ^{15}N by up to 1‰ relative to deposition (Task 3.3). Surface water $\delta^{15}N\text{-}NO_3^-$ values are still sufficiently depleted relative to lake sediments to drive a depletion in recent sedimenting organic matter. Furthermore there appears to be a very minor fractionation resulting in a depletion in $\delta^{15}N\text{-}NO_3^-$ of 0.1-0.2‰ within the lakes themselves (Task 3.3). Overall these data indicate that catchment processes are not radically altering the isotopic values of N entering the lakes from the catchments, which suggests that the $\delta^{15}N$ measured in lake sediment may be directly influenced by deposited N.

The sediment and deposition $\delta^{15}N$ data demonstrate for the first time that the influence of NO_x deposition alone may be sufficient to explain the observed patterns in lake sediments. Increasingly depleted $\delta^{15}N$ values towards the present day could simply reflect increasing inputs of NO_3^- with a lower $\delta^{15}N$ value than the pre-industrial background level reflected in older lake sediments. The small reversal in sediment $\delta^{15}N$ towards the surface of some sediment cores may reflect the more recent reductions in NO_x deposition over the last 10-20 years. While the evidence is circumstantial, Scoat Tarn and Lochnagar provide the first examples of co-located measurements of bulk deposition NO_3^- and sediment $\delta^{15}N$ that we are aware of and this possible causative relationship demonstrates the exciting potential of the approach for using lake sediment $\delta^{15}N$ as a historical proxy for N deposition.

The results from the surface sediment study reported above provide corroborative evidence that lake surface sediment $\delta^{15}N$ is related to N deposition spatially, which further suggests that changes in $\delta^{15}N$ recorded in sediment cores may reflect historical changes in N deposition. Clearly there is a large degree of scatter in the relationships between N deposition and surface sediment $\delta^{15}N$ attesting to the presence of other processes that influence the $\delta^{15}N$ of lake surface sediments (e.g. deposition of reduced N species), but superimposed upon this variation is a clear signal of lower $\delta^{15}N$ values in lakes experiencing higher N deposition.

In many of the sites, changes in the C/N ratio, which occur at the same time as the decline in $\delta^{15}N$, could be interpreted as a change towards increased algal production, which is again consistent with an increased input of nitrogen to N-limited systems and thence an increase in productivity of the lakes.

Results from the diatom analyses have not been presented here, as there were no clear relationships in species composition that could be related to the changes in $\delta^{15}N$ or C/N ratios. Not all cores were analysed for diatoms, owing to changes in the work programme agreed with DEFRA. Those sites for which diatoms were either analysed here or already existed from previous analyses were generally those sites that had experienced an acidification over the same period as the change in $\delta^{15}N$. It was impossible to separate the acidification response of the diatoms from the response to the change in $\delta^{15}N$, probably because diatoms respond well to changes in pH and most of the studied sites do not have a large planktonic diatom community.

The exception is Loch Coire Fionnaraich, which has not experienced a strong acidification, although at this site it has also proven difficult to identify a change in diatom species composition that can be related to the change in $\delta^{15}N$. However, as part of other NERC funded research at Loch Coire Fionnaraich, the sub-fossil cysts of another algal group, the chrysophtes, were also analysed (S. Pla, in prep). Using a chrysophyte-nitrogen transfer function, lake water N concentrations were reconstructed for Loch Coire Fionnaraich. There is a close match between the reconstructed lake water N concentrations and the $\delta^{15}N$ record at this site. There is also a less close match between cyst composition and $\delta^{15}N$. Whilst further work is required to assess the relationships between the changes in the chrysophytes and $\delta^{15}N$ in Loch Coire Fionnaraich, preliminary results do suggest there is a link between changes in chrysophyte cyst composition and increased N deposition at this site.

Whilst it is disappointing that no clear patterns in the diatom data could be related to the changes observed in the $\delta^{15}N$ records of the lakes analysed, this does not preclude the possibility that the lakes have increased in productivity terms, including in the diatoms. This increase in algal productivity may not show up in the sediment record as a change in diatom species composition, although there is tantalising evidence that other algal groups may be responding to increases in N deposition. Future work should focus on non-acidified, nutrient richer sites, with a well developed diatom planktonic assemblage, as we hypothesise that it is the planktonic taxa that will be the first to respond to increases in N inputs (cf. Wolfe *et al.* 2001, 2006).

Conclusions

The results of the sediment core analysis for $\delta^{15}N$ have shown widespread and marked biogeochemical changes in the majority of the studied sites. This suggests that similar changes may have also taken place over the past 100 years in many other upland and mountain lakes in the UK. The results obtained here are consistent with a cause of this change being increased deposition of anthropogenic N from the atmosphere, resulting from increased emissions of N from burning fossil fuels. However, the available data cannot point conclusively to increased deposition of N as the sole cause of these changes in $\delta^{15}N$. At the two co-locates sites Lochnagar and Scoat Tarn, historically increasing inputs of $\delta^{15}N$ depleted NO_x deposition has been shown to be a possible driver of changes in lake sediment $\delta^{15}N$, but the evidence is circumstantial and the $\delta^{15}N$ of reduced N deposition was not measured.

These results are also in agreement with those observed in more sensitive regions. There is also some evidence to suggest that productivity increases have also taken place in many of the studied lakes, which occurs contemporaneously with the changes in $\delta^{15}N$.

Further work is required to demonstrate conclusively the role of anthropogenic N deposition in the biogeochemical changes observed in these upland lakes. A wider understanding of the isotopic values of the various forms of N in deposition and catchment soils and inflows is required to better describe the inputs of N from the various sources to lake systems. Work is also required to investigate in-lake processes and usage of N, as well as experiments to manipulate in-lake mesocosms with additional N inputs to investigate the in-lake contributions to sedimenting organic matter. Finally, information on the nature of the N bound in organic matter and exactly what is being recorded by $\delta^{15}N$ in lake sediment in these nutrient poor upland lakes is required to confirm that the observed changes in $\delta^{15}N$ are not related to changes in the source of organic matter through time.

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2.3.2: Bioassays for evidence of current biological response to nutrient N deposition independent of any acidification response

Stephen Maberly, Chris Curtis and Gavin Simpson

Using the output from Phase I of Task 2.2 above, predicted % N and P limitation values were used to select 13 sites for direct bioassay assessment of nutrient limitation (Table 2.7). Note that it was decided to reduce the number of bioassay tests at each site to allow work at a greater number of sites on the same budget than the 6 sites from Task 2.3.1 originally specified. This approach should allow more thorough coverage of environmental gradients and greater expansion of the modelling dataset for predicting N limitation. The final list of sites was selected from the Freshwater Umbrella database to cover gradients of %N limitation, %P limitation and regional variations in N deposition.

Table 2.7: Bioassay site selection by region

Sitecode	Site name	%P lim.	%N lim.
Lake District			
SCOATT	Scoat Tarn	36.1	16.7
BURNMT	Burnmoor Tarn	30.5	3.1
VNY4101	Small Water	86.3	18.6
Southern England			
CZTQ32	Hammer Pond	0.8	92.3
North Wales			
EDNO	Llyn Edno	35.0	8.8
MAIR	Llyn Mair	17.4	120.1
GAM	Llyn Gamallt Fawr	21.5	64.9
WSH7301	Llyn Hiraethlyn	7.2	23.0
NW Scotland			
VNG9402	Loch Coire Fionnaraich	*	*
LNEI	Loch Coire nan Eion	*	*
CZNG96	Loch Coire Mhic Fhearchair	16.3	26.3
Cairngorms/Grampians			
NAGA	Lochnagar	17.2	27.9
CZNO16	Loch Beanie	16.6	33.3

* not initially modelled - selected because they were study sites in Task 2.3.1

Water was collected from thirteen lakes in June, July and September 2005 (Table 2.8). A sub-sample was filtered in the field and the water was couriered or driven to CEH Lancaster. The filtered samples were analysed for total dissolved phosphorus, total dissolved nitrogen, nitrate and ammonium. The unfiltered samples were used to measure initial phytoplankton chlorophyll and to perform the bioassays following the procedure in Maberly *et al.* (2002). Briefly this involved measuring the concentration of phytoplankton after fourteen days incubation at constant conditions after no nutrient addition (control), addition of phosphate, ammonium nitrate or both. The experiment was carried out in triplicate. Statistical hierarchical t-tests were used to distinguish between P-limitation (statistically significant greater concentration of chlorophyll compared to control in response to added P), N-limitation (statistically significant greater concentration of chlorophyll compared to control in response to added N) or co-limitation (statistically significant greater concentration of chlorophyll compared to control in response to added P+N if no response to single addition of P or N).

Table 2.8: Sampling dates for the 13 new bioassay sites

Sitecode	Site name	%P lim.	%N lim.	Site Easting	Site Northing	Country	OS Map	Site Alt.	FIRST SAMPLE	SECOND SAMPLE	FINAL SAMPLE
Lake District											
SCOATT	Scoat Tarn	36.1	16.7	315900	510400	ENG	89	602	02-Jun-05	19-Jul-05	21-Sep-05
BURNMT	Burnmoor Tarn	30.5	3.1	318400	504300	ENG	89	252	02-Jun-05	18-Jul-05	21-Sep-05
VNY4101	Small Water	86.3	18.6	345500	510000	ENG	90	450	03-Jun-05	17-Jul-05	22-Sep-05
Southern England											
CZTQ32	Hammer Pond	0.8	92.3	539700	128700	ENG	187	70	06-Jun-05	14-Jul-05	18-Sep-05
North Wales											
EDNO	Llyn Edno	35.0	8.8	266300	349700	WAL	115	500	31-May-05	16-Jul-05	26-Sep-05
MAIR	Llyn Mair	17.4	120.1	265300	341300	WAL	124	80	01-Jun-05	16-Jul-05	27-Sep-05
GAM	Llyn Gamallt Fawr	21.5	64.9	274500	343900	WAL	124	470	01-Jun-05	16-Jul-05	27-Sep-05
WSH7301	Llyn Hiraethlyn	7.2	23.0	274300	337000	WAL	124	310	01-Jun-05	16-Jul-05	27-Sep-05
NW Scotland											
VNG9402	Loch Coire Fionnaraich			194500	849800	SCO	25	230	09-Jun-05	23-Jul-05	24-Sep-05
LNEI	Loch Coire nan Eion			192500	850800	SCO	25	356	09-Jun-05	23-Jul-05	24-Sep-05
CZNG96	Loch Coire Mhic Fhearchair	16.3	26.3	194300	860600	SCO	19	590	10-Jun-05	22-Jul-05	25-Sep-05
Cairngorms/Grampians											
NAGA	Lochnagar	17.2	27.9	325200	785900	SCO	44	790	08-Jun-05	20-Jul-05	23-Sep-05
CZNO16	Loch Beanie	16.6	33.3	316000	768600	SCO	43	410	07-Jun-05	21-Jul-05	22-Sep-05

An example of a bioassay result for the July 2005 samples is shown in Fig. 2.37. Addition of both N and P always produces a statistically significant increase in chlorophyll compared to the control and this represents co-limitation where there is not a significant response to a single addition of P or N as in Llyn Gamallt Fawr for example (Fig. 2.37). In some cases with strong co-limitation, addition of a nutrient causes a reduction in chlorophyll, especially for nitrogen addition. This has been noticed before but the cause is not known but presumably relates to damaging effects of excess nutrient. An example of phosphorus-limitation is seen in Loch Beanie where, unusually, the single P-addition produced as much chlorophyll as the addition of both N and P (Fig. 2.37). In contrast, Loch Fionnaraich is clearly N-limited (Fig. 2.37).

The overall results are shown in Table 2.9. Two lakes, Scoat Tarn and Small Water, had the same nutrient-limitation on the three occasions they were tested. In the ten other cases there was a seasonal variation in nutrient-limitation but at no site was there a switch between N and P limitation. Overall, P-limitation was found in 33% of the cases, N-limitation in 18% of cases and Co-limitation was most frequent, found in 49 % of cases.

This task was completed and fully reported in January 2006. The new data were used to re-run the original models of Maberly *et al.* (2002) for an increased lakes dataset (30 lakes expanded to 43 lakes with N/P limitation information). A key issue was the comparability of new data with the original survey where more bioassay analyses were performed, so subsequent modelling needed to employ common datasets. This work is described under Task 2.2 above.

Figure 2.37: Concentration of phytoplankton chlorophyll a (note log scale) for thirteen lakes in response to no nutrient addition (Control, C), phosphorus addition (P), nitrogen addition (N) and both P and N addition (B). Initial chlorophyll concentration also shown. Error bars = 1SD.

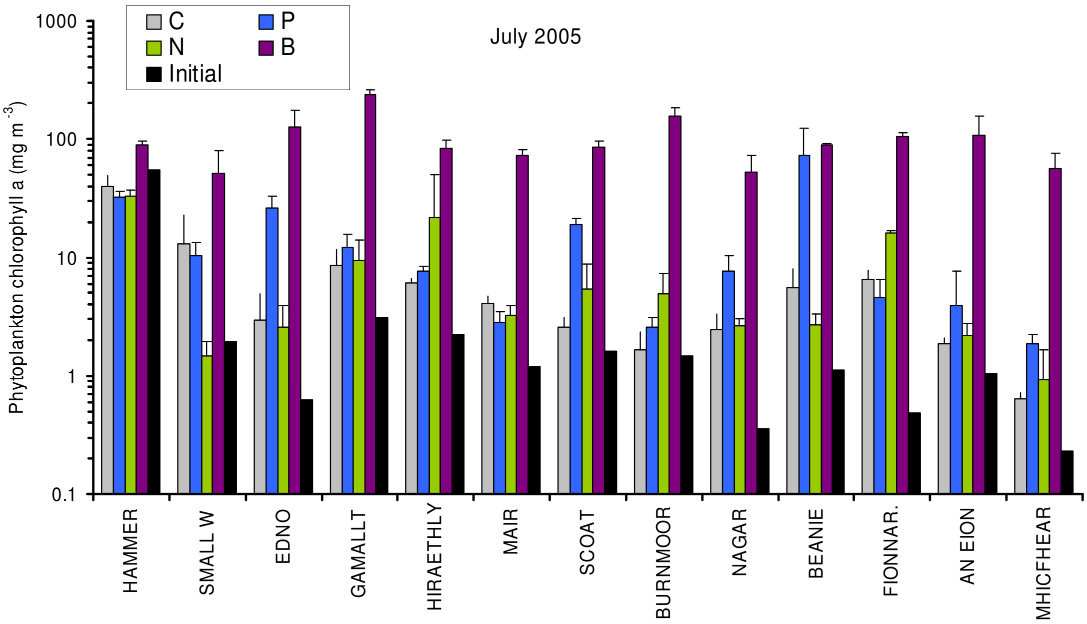


Table 2.9: Summary of nutrient bioassay results.
P = phosphorus-limitation, N = nitrogen-limitation, Co - co-limitation.

Site	June	July	September
Scoat Tarn	P	P	P
Small Water	Co	Co	Co
Burnmoor Tarn	Co	N	Co
Llyn Edno	Co	P	P
Llyn Gamallt Fawr	Co	Co	N
Llyn Hiraethlyn	N	N	Co
Llyn Mair	Co	P	Co
Hammer Pond	N	Co	N
Loch Beanie	Co	P	P
Loch Nagar	Co	P	P
Loch Coire nan Eion	Co	Co	P
Loch Coire Fhionnaraich	Co	N	Co
Loch Coire Mhic Fhearchair	Co	P	P

Task 2.4: Review the case for application of critical loads for nutrient N to UK freshwaters, with preliminary assessment of critical load exceedance

Chris Curtis

Background - nutrient N critical loads

The most widely used definition of a critical load is that of Nilsson and Grennfelt (1988):
"a quantitative estimate of the loading of one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge."

With critical loads for acidity in surface waters, both the specified sensitive element of the ecosystem and the significant harmful effect have been well established in the literature. Empirical studies of brown trout populations in large numbers of Norwegian lakes, with populations defined from historical fish catch records as healthy, reduced or extinct, linked population status to measures of surface water acidity (Lien *et al.*, 1996). Using brown trout as the target organism and the risk of reduced populations as the harmful effect, it was possible to establish a simple chemical criterion on which to calculate a critical load of acid deposition. The relationship between acid neutralizing capacity (ANC) and the probability of damage to brown trout populations was used to select a critical ANC limit of 20 μeq l^{-1}, representing a 10% probability of reduced populations (Lien *et al.*, 1996). This dose-response function was easy to visualise and provided a clearly defined link between a chemical criterion and a harmful effect. Critical loads models such as the Steady-state Water Chemistry (SSWC) model and the First-order Acidity Balance (FAB) model then simply had to determine what deposition load of acidity would result in the critical chemical threshold being exceeded (Henriksen & Posch, 2001).

In order to apply a critical load for nutrient N to freshwaters, both harmful effect and a critical chemical criterion need to be defined. The ICP Mapping and Modelling body co-ordinates the international critical loads activity under the UN-ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) for the Working Group on Effects (WGE). Its Mapping Manual provides details of the approved methods for use under the CLRTAP, and provides some context for the application of nutrient N critical loads (UBA, 2004):

> *"The availability of nutrients is one of the most important abiotic factors, which determine the plant species composition in ecosystems. Nitrogen is the limiting nutrient for plant growth in many natural and semi-natural ecosystems, especially of oligotrophic and mesotrophic habitats. Most of the plant species from such conditions are adapted to nutrient-poor conditions, and can only survive or compete successfully on soils with low nitrogen availability."*

Furthermore, Bobbink *et al.* (1998) stated that most global biodiversity is present in natural or semi-natural habitats which may be negatively impacted by atmospheric N deposition. However, they also stated that with the exception of shallow, soft-water lakes, primary production in all aquatic ecosystems is limited by phosphorus (P) and hence N enrichment has been considered unimportant. This view prevailed amongst European scientists involved in critical loads work until the end of the 1990s, but has subsequently been shown under the Freshwater Umbrella programmes to be a widely-held misconception.

While the Mapping Manual text cited above was written with terrestrial ecosystems in mind, it applies equally to many aquatic habitats in the UK, where the widespread occurrence of N limitation has been demonstrated under the current Freshwater Umbrella programme (see WP2). However, the UK has never previously submitted critical loads for nutrient N to the international mapping and modelling programme at the ICP Mapping and Modelling Co-ordination Centre for Effects (CCE). In the 2005 CCE Status Report which provides details of all national submissions to the programme (Posch *et al.*, 2005), only the Netherlands, Belgium and Switzerland contributed nutrient N critical loads data for freshwaters, even though the Nordic countries and the UK did submit critical loads for freshwater acidity. One of the key reasons is the lack of data and theoretical understanding of what may constitute a harmful effect in terms of nutrients linked to N deposition in sensitive lakes.

For terrestrial ecosystem critical loads, two approaches have been used under the UNECE-CLRTAP, the Simple Mass Balance (SMB) model and empirical critical loads. The mass-balance modelling approach for N, using the same simple mass balance as the FAB model (Posch *et al.*, 1997; Henriksen & Posch, 2001), has been used to determine the total N deposition load that will result in a critical rate of NO_3^- leaching that is associated with a defined harmful effect to soils or vegetation. The application of both of these approaches to freshwaters is considered below.

Mass-balance modelling of critical loads

For acidity critical loads, the FAB model is used to determine the level of N deposition which results in a rate of NO_3^- leaching which, in combination with sulphate leaching, will depress ANC to the selected critical value, which is 20 μeq l^{-1} in the UK. If a criterion based on NO_3^- concentrations in waters could be established for harmful effects in terms of nutrient status, then FAB could in theory be used to set a critical load for nutrient N. For example, if it was determined for a lake that at NO_3^- levels greater than 50 μeq l^{-1} eutrophication resulted, perhaps defined in terms of the appearance of a nuisance organism like an increase in blue-green algae, then FAB could be used to determine what level of N deposition would result in exceedance of a critical NO_3^- threshold of 50 μeq l^{-1}. However, just as acidity critical load models have to take into account between-site differences in sensitivity (buffering capacity), a nutrient based critical load would have to take into account factors limiting growth, productivity and occurrence of sensitive organisms, e.g the N:P ratio.

Empirical critical loads for nutrient N

In North America, critical loads for freshwaters and nutrients have often been applied in a rather different way to the FAB mass-balance employed in Europe (reviewed in Fisher *et al.*, 2007; see also Breiner *et al.*, 2007 for terrestrial critical loads). Several studies have employed an empirical approach based on evidence of impacts from acidification, NO_3^- leaching and/or eutrophication using simple chemical or palaeolimnological measures linked to measured deposition load. Williams and

Tonnessen (2000) proposed a critical load of 4 kgN ha^{-1} yr^{-1} for lakes in the Colorado Front Range of the USA to prevent NO_3^- leaching that could cause acid episodes. Lakes at Baffin Island may have critical loads much lower than the 5-10 kgN ha^{-1} yr^{-1} range proposed for Arctic tundra, since palaeolimnological diatom changes have been attributed to much lower inputs (Wolfe *et al.*, 2006). Williams *et al.* (1996) suggested that the critical load of 10 kgN ha^{-1} yr^{-1} for NO_3^- leaching proposed by Dise and Wright (1995) was far too high for alpine Rocky Mountain lakes since much lower deposition loads resulted in NO_3^- saturation of terrestrial ecosystems and leaching into aquatic ecosystems. In the European sense, this is not strictly a critical load because NO_3^- leaching *per se* is not defined as an adverse effect, but in fact it might be argued for nutrient N that this should be the case.

Empirical critical loads are simply based on observed relationships between levels of deposition and a harmful effect. Until recently, the only lakes considered sensitive to nutrient N inputs from atmospheric deposition in Europe were shallow softwater lakes on sandy soils, with most work done in the Netherlands (summarised in Bobbink *et al.*, 1998). Experimental manipulations with additions of sulphuric acid or ammonium sulphate demonstrated than ammonium inputs adversely affected isoetid macrophyte communities typical of softwater lakes (the *Littorelletea uniflorae*) independently of the acidification effect found with sulphuric acid, i.e. the effect is due to the change in inorganic N supply. Isoetid species are replaced by dense stands of *Juncus bulbosus* or aquatic mosses such as *Sphagnum cuspidatum* and *Drepanocladus fluitans*.

During the Expert Workshop on Empirical Critical Loads for nutrient N held in Berne in November 2002 it was stated under "Gaps in Knowledge" that "*Impacts of nitrogen enrichment in (sensitive) freshwater and shallow marine ecosystems needed further research and were sometimes overlooked*" while the EUNIS classification for surface waters needed clarification and adjustment (Achermann & Bobbink, 2003). The work carried out under the current Freshwater Umbrella programme goes some way towards clarifying the potential issues of nutrient N enrichment in UK upland lakes.

Following the Expert Workshop on nutrient N critical loads, the habitat definition for inland surface waters for which empirical critical loads applied was broadened from shallow soft-water lakes to include all soft-water lakes (Achermann & Bobbink, 2003; Posch *et al.*, 2005). The proposed range of empirical critical loads was set at 5-10 kgN ha^{-1} yr^{-1} with the highest level of confidence used under this system (## = reliable). This broader habitat definition, corresponding to EUNIS class C1.1 (permanent oligotrophic lakes, ponds and pools) is now appropriate for many UK upland waters.

Relevance of nutrient N critical loads in the UK

Soft-water lakes broadly corresponding to the EUNIS class C1.1 are widespread in the uplands of the UK (Fig. 2.38a) and are recognised as being of international conservation importance by the designation of the Special Area of Conservation (SAC) habitat 3130, "Oligotrophic to mesotrophic standing waters with vegetation of the *Littorelletea uniflorae* and/or of the *Isoëto-Nanojuncetea*" (Fig. 2.38b). Many of the lake sites in the national critical loads dataset submitted to the CCE are of this type in the uplands of western Great Britain, although there has not as yet been any attempt to determine a list of such sites.

Figure 2.38a: Distribution of oligotrophic lakes of type 3130 (Oligotrophic to mesotrophic standing waters with vegetation of *Littorelletea uniflorae* and/or *Isoëto-Nanojuncete*) in the UK

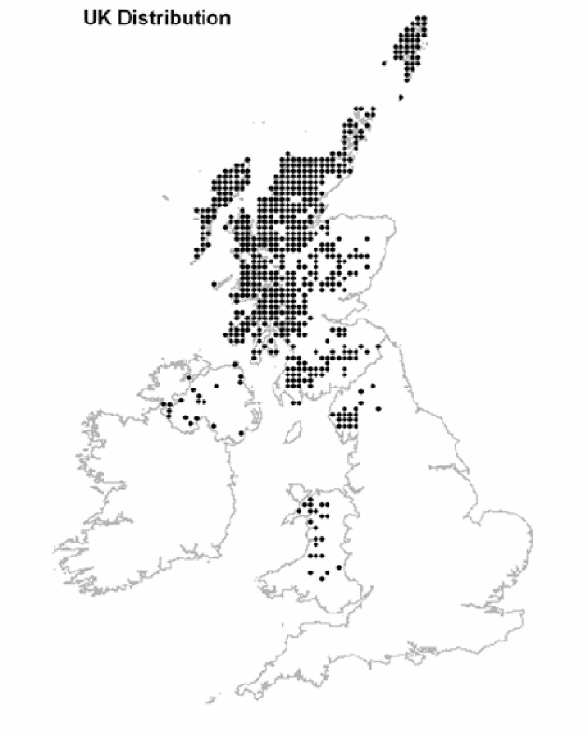
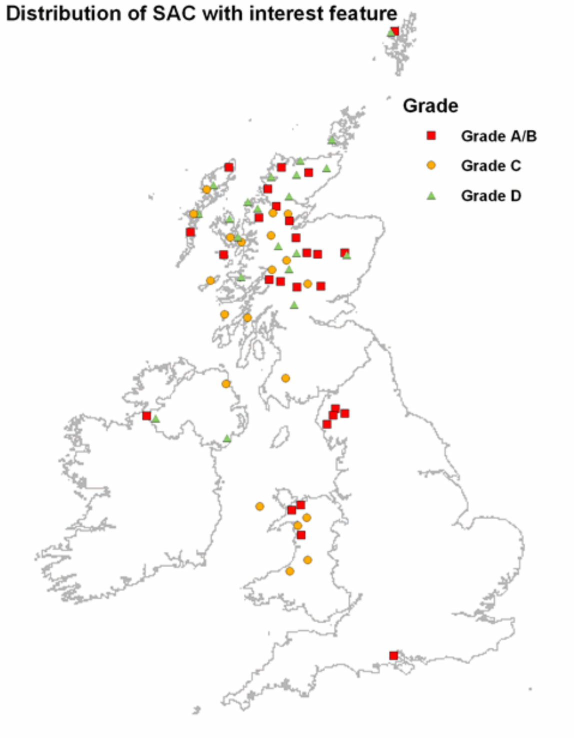


Figure 2.38b: UK distribution of Special Areas of Conservation (SACs) designated for habitat 3130



Source: JNCC
(http://www.jncc.gov.uk/ProtectedSites/SACSelection/habitat.asp?FeatureIntCode=H3130)

The modelled deposition load for the 1595 lake and stream sites in Great Britain's critical loads submission to CCE is plotted in relation to the empirical nutrient N critical loads (5-10 kgN ha^{-1} yr^{-1}) recommended for soft-water lakes in the CCE Mapping Manual (UBA, 2004) in Fig. 2.39. The first map (Fig. 2.39a) shows that very few sites in Great Britain experience total N deposition loads below the lower threshold of 5 kgN ha^{-1} yr^{-1}, with only a small number in the Outer Hebrides and north-west coast of mainland Scotland. Most sites in northern Scotland experience deposition levels in the critical range of 5-10 kgN ha^{-1} yr^{-1} (Fig. 2.39b) so their critical load exceedance under this scheme would depend on whether the upper or lower limit were selected. For most sites in southern Scotland and almost all of England and Wales, deposition levels exceed 10 kgN ha^{-1} yr^{-1} (Fig. 2.39c) which suggests that any softwater lakes in these regions would exceed this empirical critical load for nutrient N.

The distribution of designated SACs of type 3130 covers all three deposition classes but it can be seen by comparison of Figs 1b and 2 that in Scotland, SACs are split between the 5-10 and >10 kgN ha^{-1} yr^{-1} deposition classes while most of the remainder in England and Wales lie in the higher deposition class. The clear implication here is that for a large proportion of designated softwater SACs the empirical critical load for nutrient N is exceeded even at the higher threshold of 10 kgN ha^{-1} yr^{-1}. At the lower threshold of 5 kgN ha^{-1} yr^{-1} almost all SACs exceed nutrient critical loads. The key question is therefore whether these critical loads are appropriate for this ecosystem, given that the empirical values were derived from shallow soft-water lakes in the Netherlands. Ideally, sufficient data would be collated for UK lakes on changes in isoetid plant communities in response to N deposition to derive appropriate regional critical values, but these data are not available at present. However, work under the current Freshwater Umbrella programme has demonstrated that it is not only the macrophyte communities that are affected by N deposition; phytoplankton production is also widely limited by N rather than P in many sites (Fig. 2.40).

The nutrient limitation bioassays carried out under the Freshwater Umbrella (Task 2.3.2) and the previous GANE work show that N limitation is almost as common as P limitation in upland lakes, while co-limitation by N and P is the most common outcome of the bioassays. Predominant N limitation is found in some lakes in central Scotland, Galloway, the Lake District, North Wales and one site in southern England (Fig. 2.40a). Predominant P limitation is found in north-west Scotland, the Grampians of eastern Scotland, some sites in the Lake District and one site in North Wales. Relatively few sites showed only N- or P- limitation in all samples; most varied between N- and co-limitation or P- and co-limitation (Fig. 2.40b).

While N deposition to N-limited sites will result in increased phytoplankton production, effects on species assemblages or other aspects of the ecosystem are unknown. It is therefore not possible at this stage to define a "harmful effect" for use in critical load calculations beyond the prediction of increased phytoplankton production in what would otherwise be considered low-productivity upland lakes - but this in itself may be an important change in designated SACs in terms of the good ecological status required by the Water Framework Directive.

Figure 2.39: Total modelled N deposition at Freshwater Umbrella critical loads mapping sites (CEH 1999-2001 annual mean data) for a) <5 kgN ha^{-1} yr^{-1}, b) 5-10 kgN ha^{-1} yr^{-1} and c) >10 kgN ha^{-1} yr^{-1}

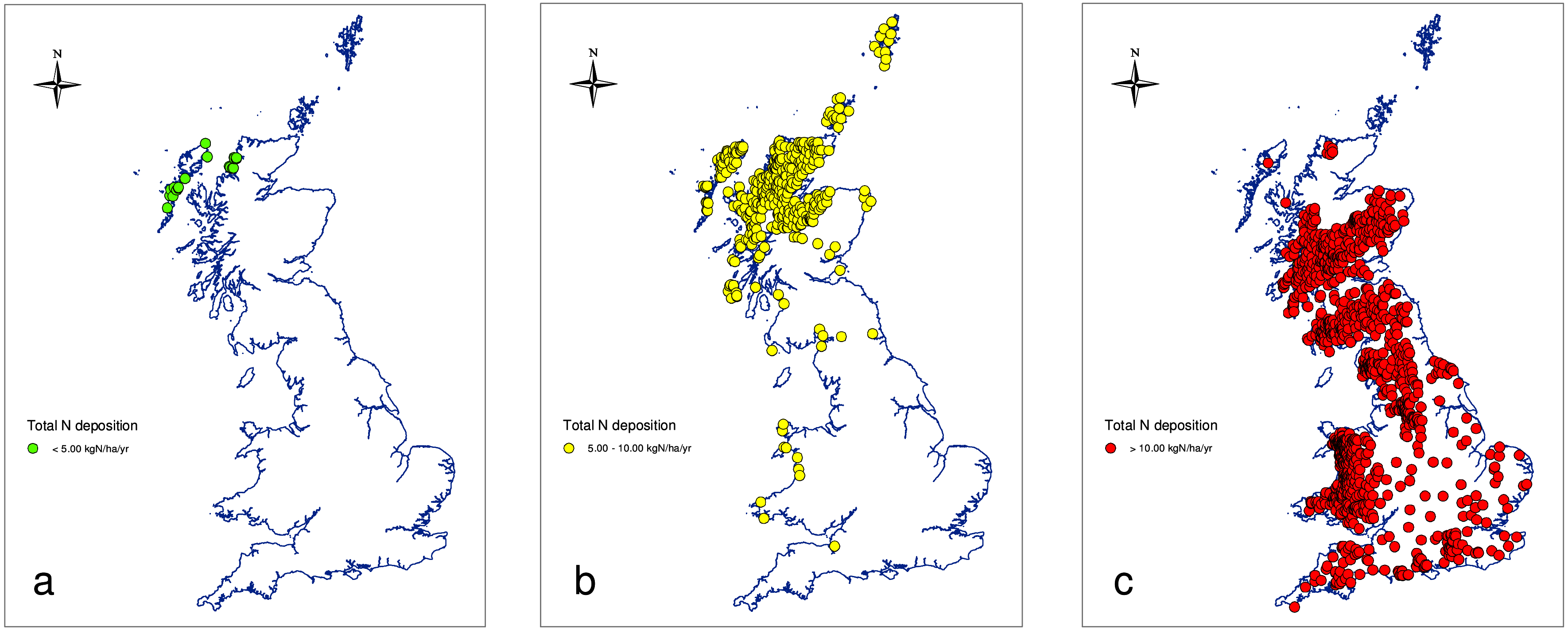


Figure 2.40a: Dominant limitation class for 3 replicated phytoplankton bioassays

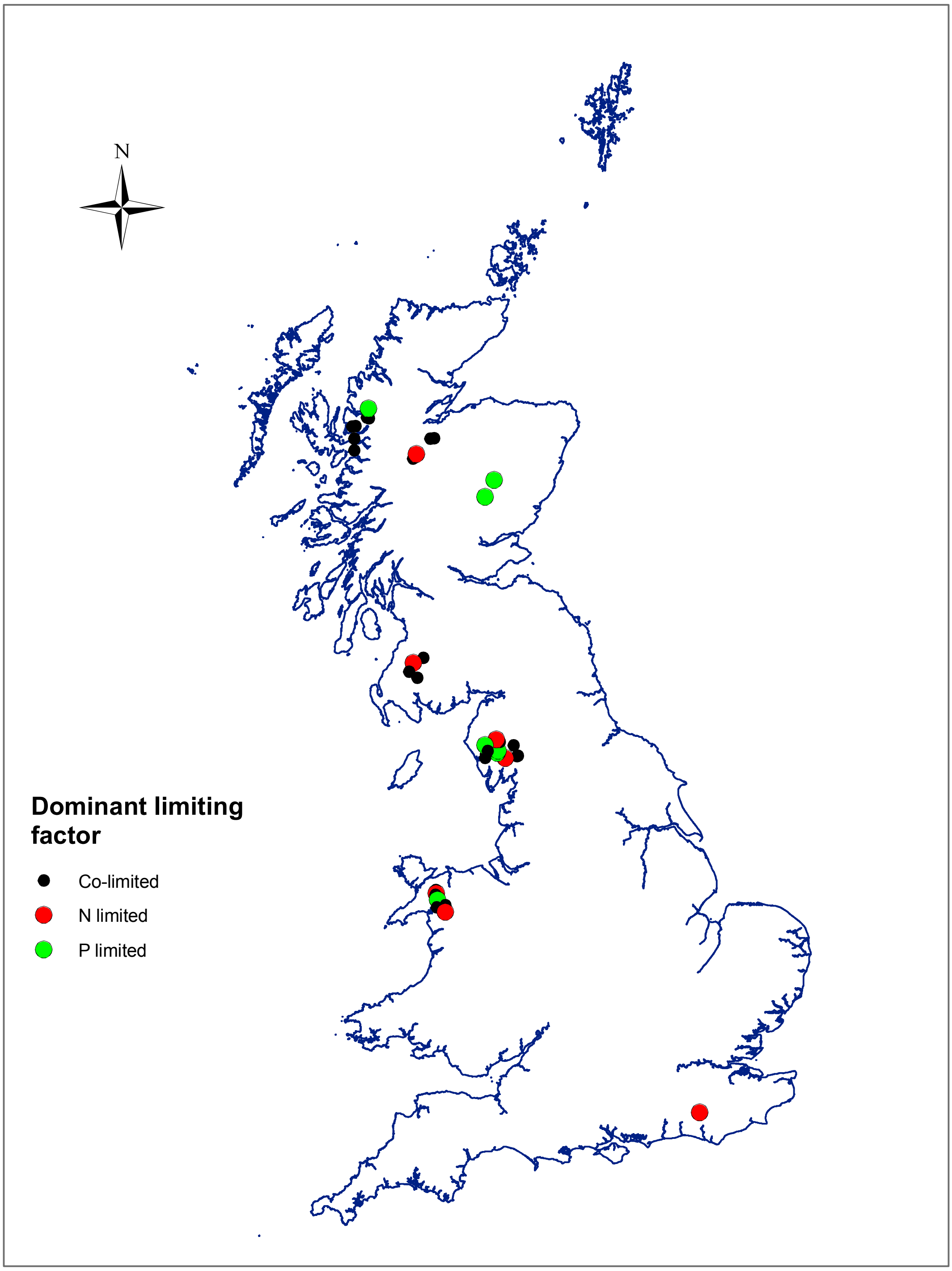
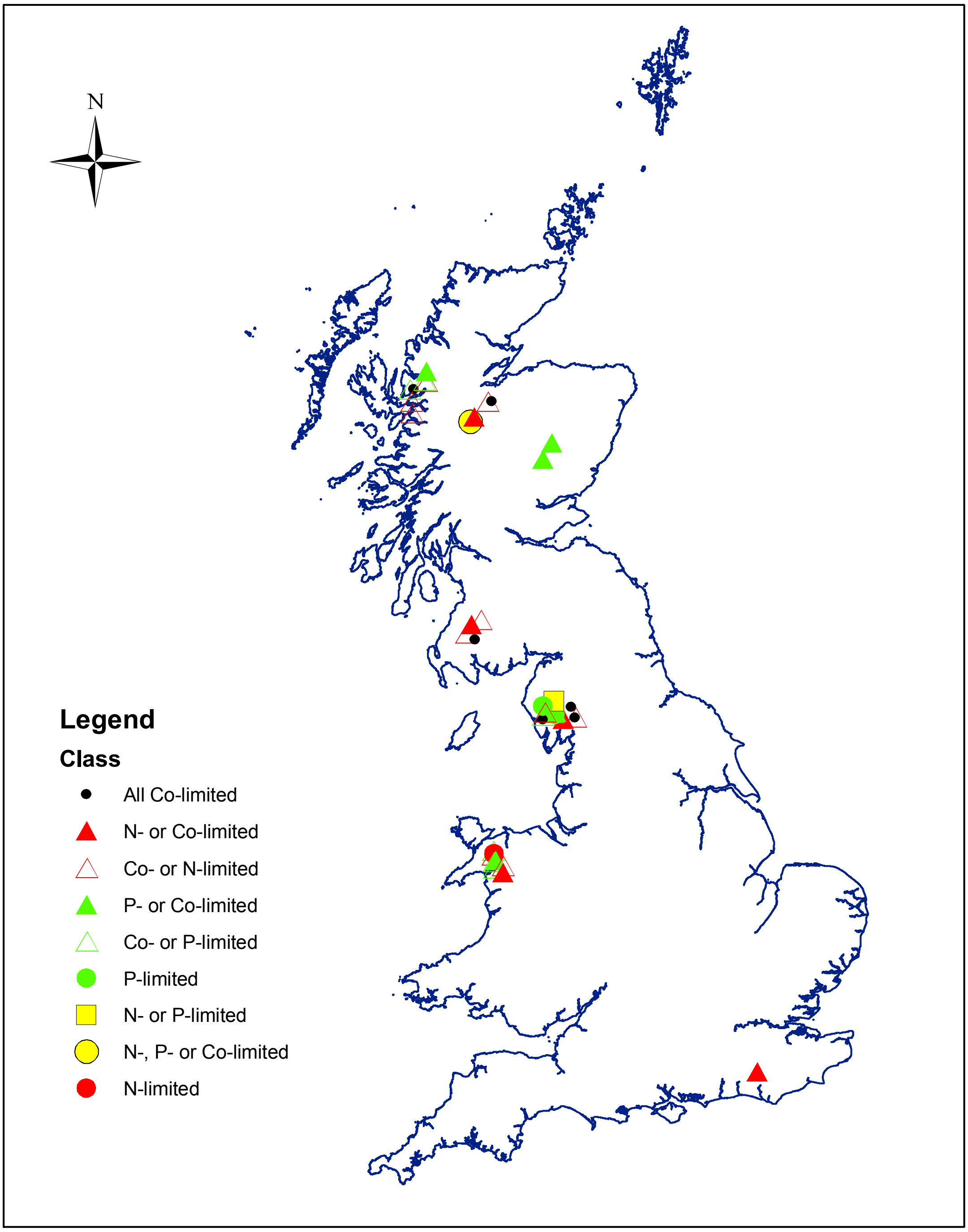


Figure 2.40b: N, P or Co-limitation status for 3 replicated phytoplankton bioassays



While modelling efforts under this programme and planned for the future will aim to characterise and map the lake-catchment types that are susceptible to N limitation and therefore to N deposition impacts, more ecological and bioassay work is required to define harmful effects. Furthermore, even a solely P-limited site may have been impacted by nutrient N deposition if it was originally N limited; there is evidence from North America, Sweden and Finland that anthropogenic N deposition has switched many lakes from natural N to P limitation by increasing inorganic N supply (see literature review, Task 2.1). According to Hessen *et al.* (1997), N saturation may just be "P limitation in disguise". Wolfe *et al.* (2003) claimed that alpine lakes in the Rocky Mountain National Park in Colorado, USA were probably N limited before anthropogenic N deposition induced P limitation. Indeed, Fenn *et al.* (2003) described N saturation as the removal of N limitation on biotic activity with a corresponding decrease in N retention capacity.

Conclusions

Despite the uncertainties attached to the definition of "harmful effects" for deriving critical loads of nutrient N deposition in the UK, there are several reasons to conclude that nutrient N critical loads should be further developed in this country:

1. the softwater lake ecosystem for which nutrient N critical loads are recommended in the CCE Mapping Manual is not only widespread in the UK uplands, but it is a designated habitat under EU legislation (Habitats Directive) for SACs and Natura 2000 sites (SAC type 3130);
2. most softwater lakes in Wales and England and many in Scotland receive total N deposition loads above the CCE recommended upper threshold of 10 kgN ha^{-1} yr^{-1} and in some important conservation and amenity regions where these lakes are numerous, such as the Lake District and Snowdonia National Parks, N deposition loads are among the highest in the country;
3. there is a paucity of empirical data for the UK linking N deposition to adverse ecological effects beyond acidification, but;
4. work under the current Freshwater Umbrella programme has built on previous GANE studies to demonstrate that N limitation of phytoplankton production is common so N deposition must be leading to increased production in some lakes, with inevitable effects across aquatic food webs which may impact on biodiversity in these highly adapted and relatively species-poor systems;
5. palaeolimnological analysis of lake sediments cores under the current programme have found changes in sediment $\delta^{15}N$ consistent with N deposition enrichment at 10 out of 12 sites, including the important SAC Wast Water;
6. the definition of good ecological status required under the Water Framework Directive needs clarification in this regard, but N enrichment of ecosystems adapted to low N availability is likely to result in a deviation from this status; and
7. water bodies other than softwater upland lakes may be impacted by atmospheric N deposition and the relative importance of atmospheric sources of N may be grossly underestimated in UK approaches to implementation of the EU Water Framework Directive in streams, rivers and lowland lakes.

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Work package 3: Nitrate leaching

Task 3.1: Tracer ^{15}N studies at the Afon Gwy to determine short-term pathways for transport of N into surface waters

Chris Evans, David Norris, Edwin Rowe, Nick Ostle, Helen Grant, Chris Curtis

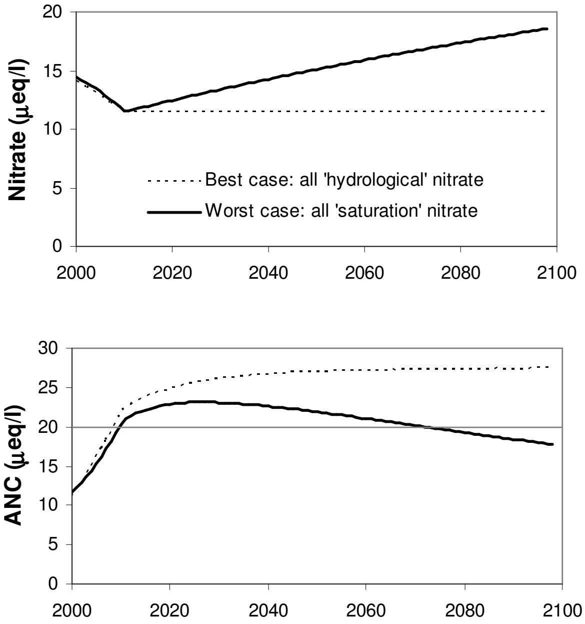
Summary

An ^{15}N isotope experiment was undertaken on a podzolic hillslope at Plynlimon, a component of the upland landscape typically responsible for much of the NO_3^- leaching to surface waters. The experiment was designed to test whether NO_3^- leaching occurred because the soil and vegetation were already receiving N deposition in excess of biological demand (i.e. 'N saturated'), or because N inputs during rain events simply overwhelmed soil assimilation capacity or bypassed the soil completely via 'macropores' such as soil cracks (so called 'hydrological' NO_3^-). Additions of ^{15}N-labelled NO_3^- and a conservative bromide (Br) tracer were applied during simulated rain to 12 replicate plots, and Br and $^{15}NO_3^-$ measured in lateral throughflow out of the soil. Results showed very rapid transport of Br tracer, suggesting that water infiltrates rapidly through soil cracks, and hence that a mechanism exists for fast transit of hydrological NO_3^- through the soil to the stream. However, despite this rapid water transfer, 80% of the $^{15}NO_3^-$ in this water was on average retained as it passed through the vegetation and soils. This suggests that soil microbes, perhaps located on the surfaces of soil cracks, are highly efficient at assimilating incoming N in infiltrating water. In support of the dual-isotope work (Task 3.2), this study suggests that some hydrological NO_3^- transport *does* occur, but that it can only account for a small part of observed stream NO_3^- most of which must therefore result from terrestrial N saturation. Within the hillslope, N retention was found to be highly heterogeneous, with locally N enriched areas that leached more of the added NO_3^-. Conceptually, this suggests that N saturation develops within the landscape through the formation and expansion of nutrient rich 'hotspots', for example where soils are thinner or where water flowpaths converge and concentrate nutrients. These hotspots are likely to be responsible for much of the observed NO_3^- leaching to surface waters, and may also be most susceptible to eutrophication responses in terrestrial vegetation.

Policy relevance

An understanding of the processes controlling N retention versus N leaching in soils is vital in order to correctly predict how N deposition will impact on aquatic and terrestrial ecosystems in the future, and what levels of emission control are required to protect them. The different possible mechanisms to explain current levels of NO_3^- in surface waters have very different future consequences: if it is 'hydrological' NO_3^-, this indicates that the terrestrial ecosystems are not yet N saturated, and may be able to continue assimilating large amounts of deposited N into the future. It also suggests that reductions in N deposition should translate directly into reductions in surface water NO_3^- concentrations. Effectively, this is the 'best case' scenario shown in Figure 3.1. If, on the other hand, the NO_3^- we currently observe in surface waters is 'saturation' N, then this indicates that terrestrial ecosystems are already N saturated, are likely to leach an increasing amount of NO_3^- in future, and that reductions in N deposition may have only limited benefits for surface waters. This is the 'worst case' scenario in Figure 3.1. Constraining future model predictions within these extreme cases will greatly reduce uncertainty in model predictions.

Figure 3.1: Illustration of the effect that the two different mechanisms to explain current stream NO_3^- have on the future modelled NO_3^- and ANC at the Afon Gwy.



In the best case (hydrological nitrate) scenario, a 20% reduction in N deposition leads directly to a reduction in stream NO_3^-, and ANC recovers above the critical ANC threshold of 20 µeq l^{-1} by 2010. In the worst case (saturation nitrate) scenario, worsening N saturation reverses the effect of the N deposition reduction by 2040, re-acidifying the stream below the critical ANC by 2070.

Methods and results

This task was undertaken at the Afon Gwy in mid-Wales, a long term CEH and AWMN monitoring catchment with a history of process work on N cycling (e.g. NERC GANE programme, DEFRA Terrestrial and Freshwater Umbrellas). The catchment is largely sheep-grazed acid grassland on organo-mineral soils, with areas of deep peat on hilltops and in valley basins. The land-use and soils in the Gwy catchment are broadly representative of grazed UK upland grasslands generally, and previous work suggests that catchment NO_3^- leaching characteristics are typical of those observed in Welsh moorland areas, and other areas of moderately high N deposition (Evans *et al.*, 2006). A detailed stream survey within the catchment (Evans *et al.*, 2004) showed locally high levels of NO_3^- leaching associated with areas of steeper, thinner soils, termed 'nitrate leaching zones'. However Curtis *et al.* (2005) found very little NO_3^- in soil organic soil solution, and near-complete retention of ^{15}N labelled NH_4NO_3 added in small doses over a year. It was therefore hypothesised that NO_3^- leaching to the stream might only be occurring under very wet conditions, where water containing wet-deposited N was able to pass rapidly through cracks and other large pores into the mineral horizon (where N retention is less effective), and from there to the stream network (i.e. 'hydrological' NO_3^-, as described above).

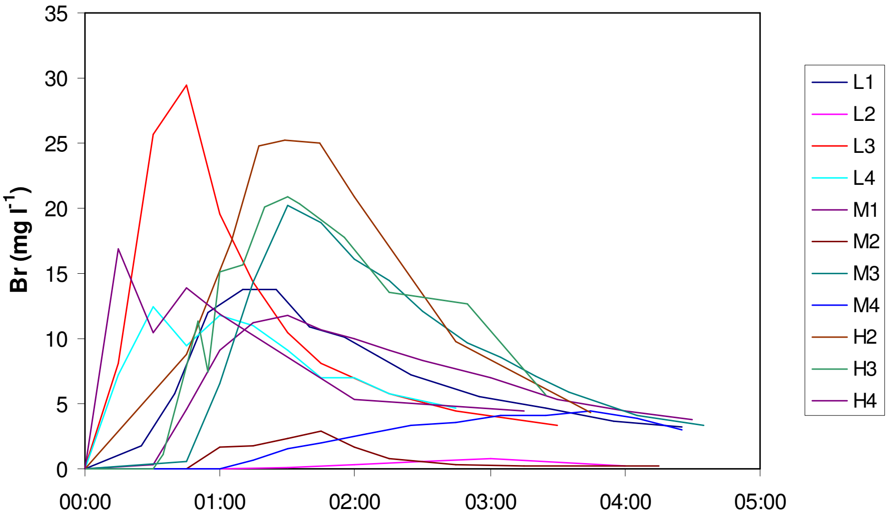
The ^{15}N addition experiment was designed to test this hypothesis. Twelve replicate 1m^2 plots were constructed along the edge of an exposed podzol soil face, with water draining from the plots collected via guttering from both the organic (O) horizon, and from the mineral soil, in which most water drained out above an impermeable ironpan at around 0.5 to 1m depth. Plots were grouped in three blocks along the exposed face, termed Lower, L; Middle, M and Higher, H. In each plot, a rainfall event was simulated by watering the plots at a steady rate of 20 l/hr, equivalent to a heavy rain event and enough to initiate throughflow in all plots. For the first hour, unlabelled water was applied. Then, 1 g of Br tracer (as NaBr) and 1.85 mg of 99 atom% $^{15}NO_3^-$ (as $NaNO_3$) were added in 10 l of water over a 30 minute period, after which unlabelled water was again added at a rate of 20 l/hr for the remainder of the experiment. Of the 12 replicate plots, tracer additions were undertaken at six during November 2005, and at the remaining six in March 2006. Hydrological and meteorological conditions were very similar on each occasion, with experiments carried out in cold, dry conditions following moderately wet weather. Because the hydrological and chemical response of the plots was not found to differ between the two periods, results from all 12 plots are analysed together. Samples of water draining each plot were collected regularly through the experiment at each plot, and water flow rates were measured simultaneously. Chemical analysis was undertaken at CEH Bangor, and isotopic analysis at the Stable Isotope Facility, CEH Lancaster.

Hydrological response

All plots showed a rapid hydrological response to tracer addition. In all but one of the plots, most water was leached as throughflow from the mineral horizon (above the ironpan). Br tracer (indicating the presence of 'new' tracer-labelled water) was measured in most plots within 30 minutes of the start of tracer addition, and Br concentrations peaked within 90 minutes in 75% of plots (Figure 3.2). This speed of hydrological response can *only* be explained by very rapid hydrological transfer of water through the upper soil, which could not have occurred if water were passing evenly through the soil matrix. Dye tracer studies at the same site (R. Bartlett, U. Leeds unpublished data) clearly demonstrate that most water passes through the clayey E horizon via cracks, probably aligned with cracks in the overlying O horizon. Based on Br tracer recovery, the total percentage of tracer-labelled new water collected in samplers over the course of the experiment ranged from 2% at L2 to 58% at H1; recovery was greater than 18% at 10 out of 12 plots, and averaged 31% (Table 3.1, Figure 3.3a). The two plots with tracer recovery < 10% (L2 and M4) were also those with by far the longest delays between tracer addition and the Br peak, suggesting that there were fewer macropores in these plots transferring water from the surface to the mineral soil, and that the tracer which was recovered was transported via smaller pores within the soil matrix.

Only half of the experimental plots showed any significant lateral flow directly out of the O horizon. In all but one case (H1) the volume of water collected via this pathway was relatively small, but in general it was more Br-enriched than flow from the mineral horizon. It therefore accounted for a substantial proportion of overall Br-labelled new water recovery in these six plots, and in three of them (M2, H1 and M4) for more than half of the total (Figure 3.3a). Flow of tracer-labelled water into O horizon samplers typically occurred soon after tracer addition, and tailed off relatively rapidly.

Figure 3.2: Mineral horizon Br tracer concentrations for the 11 plots where significant throughflow took place. Large peaks soon after the tracer application at time zero demonstrate rapid hydrological transfer of water through the organic soil into the deeper mineral horizon



Overall, however, mineral throughflow accounted for most (59%) of the Br tracer recovered, and in general the hydrological response of most plots indicates that large amounts of rain water can infiltrate rapidly through the biologically active upper horizons, via cracks and large pores, into the mineral horizon, through which it can be transported to the stream. This provides a clear physical pathway by which NO_3^- deposited on well-drained hillslope soils may be transferred to the stream as 'hydrological' NO_3^-.

Nitrate leaching response

The results of adding a conservative tracer indicate that physical water transport within the soil is such that rapid hydrological NO_3^- leaching could occur at the Gwy. The $^{15}NO_3^-$ tracer data provide an indication of the extent to which it does occur. In general, the temporal characteristics of $^{15}NO_3^-$ leaching from the mineral soil were similar to those for Br (Figure 3.4), with ^{15}N-enriched NO_3^- observed in mineral horizon leachate within 30 minutes of tracer addition at most plots, and peak ^{15}N-enrichment within 75 minutes at all plots other than the slow-responding L2 and M4. Although the sampling resolution does not permit a detailed comparison of Br and $^{15}NO_3^-$ tracer peak times, it is noteworthy that the $^{15}NO_3^-$ peak apparently preceded the Br peak in 7 out of 12 plots, and was only lagged behind it in the slowest-responding M4 plot. The apparent precedence of the $^{15}NO_3^-$ peak is evident in a number of the example tracer curves shown, and may be explained by a gradually increasing efficiency of NO_3^- retention as water transit times increase (i.e. the water reaching the samples has travelled through increasingly small soil pores). Despite the generally similar timing of ^{15}N and Br recovery, however, measured total recovery of ^{15}N from mineral soil throughflow was much lower than that of Br from the same horizon (average 4.2% versus 18%). This indicates that significant NO_3^- retention must have taken place, despite the rapid physical transfer for water to depth.

Figure 3.3a: Cumulative recovery of Br and $^{15}NO_3^-$ tracers from organic horizon and mineral horizon throughflow in each plot as a percentage of the amount of each tracer added.

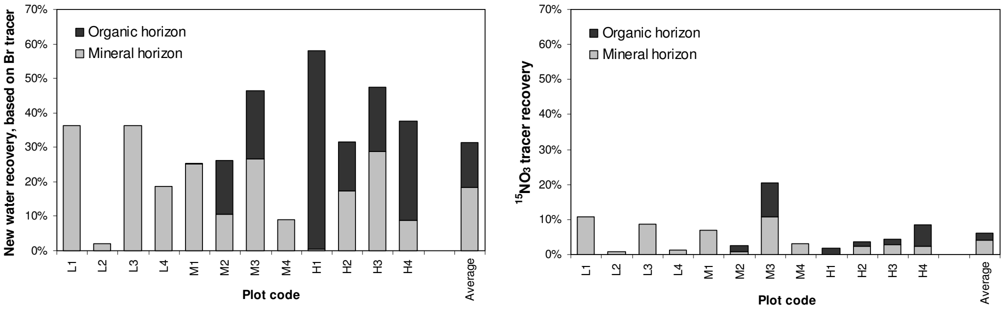
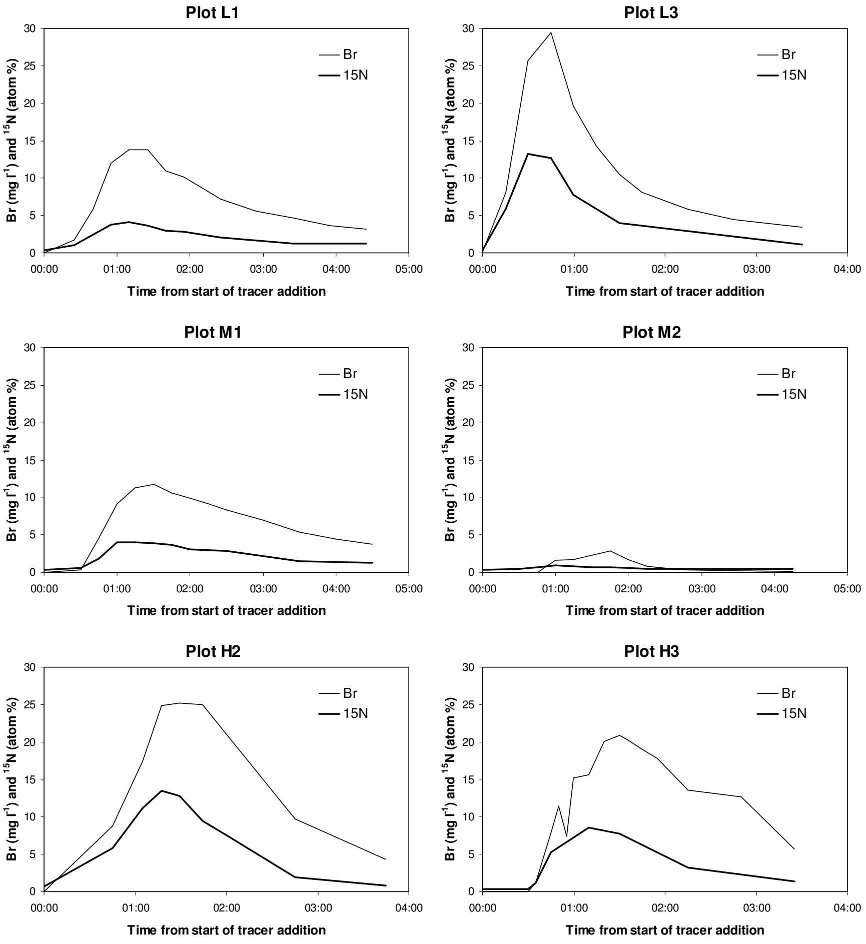


Figure 3.3b: Examples of Br and $^{15}NO_3^-$ tracer concentrations measured in mineral soil throughflow during the course of the experiment.



As noted above, significant O horizon throughflow only occurred in six plots, but in some plots where it occurred, a substantial proportion of $^{15}NO_3^-$ was recovered via this pathway (more than via the mineral horizon in three plots; Table 3.1, Fig. 3.3b). Nevertheless, ratios of $^{15}NO_3^-$/Br recovery were on average lower in water draining the O horizon than in water draining the mineral horizon, even though the latter must have passed through the O horizon first. Plot H1, where almost all water was collected from O horizon throughflow, had the lowest overall ratio of ^{15}N to Br recovery of any plot. Again, these observations suggest that water draining the mineral horizon was rapidly transported through the O horizon via macropores, bypassing the more effective NO_3^- retention thought to occur within the organic soil matrix.

Table 3.1: Recovery of Br and $^{15}NO_3^-$ tracers added to each plot during the experiment.

	Organic horizon leachate			Mineral horizon leachate			Combined horizon leachate		
Plot	Br recovered	^{15}N recovered	^{15}N/Br	Br recovered	^{15}N recovered	^{15}N/Br	Br recovered	^{15}N recovered	^{15}N/Br
L1				36.2%	10.7%	29.7%	36.2%	10.7%	29.7%
L2				2.0%	0.7%	34.2%	2.0%	0.7%	34.2%
L3				36.4%	8.7%	24.0%	36.4%	8.7%	24.0%
L4				18.8%	1.3%	6.7%	18.8%	1.3%	6.7%
M1	0.3%	0.0%	16.6%	25.2%	6.8%	27.1%	25.5%	6.9%	27.0%
M2	15.8%	1.8%	11.4%	10.5%	0.8%	7.2%	26.3%	2.6%	9.7%
M3	19.8%	9.5%	48.0%	26.6%	10.8%	40.5%	46.4%	20.3%	43.7%
M4				9.1%	3.0%	32.6%	9.1%	3.0%	32.6%
H1	57.7%	1.8%	3.1%	0.4%	0.0%	1.5%	58.1%	1.8%	3.0%
H2	14.3%	1.3%	9.1%	17.4%	2.2%	12.6%	31.7%	3.5%	11.0%
H3	18.6%	1.5%	8.0%	28.9%	2.8%	9.7%	47.4%	4.3%	9.1%
H4	28.9%	6.2%	21.3%	8.7%	2.3%	26.5%	37.6%	8.5%	22.5%
Average	**12.9%**	**1.8%**	**16.8%**	**18.3%**	**4.2%**	**21.0%**	**31.3%**	**6.0%**	**21.1%**

Combining data from both soil horizons, average recovery of $^{15}NO_3^-$ tracer was 6% (range 0.7 to 20%), much lower than the 31% average recovery of Br. Comparing total recovery of the conservative Br tracer with the reactive $^{15}NO_3^-$ tracer indicates that on average 79% (range 56 to 97%) of the labelled NO_3^- originally contained within the tracer-labelled water recovered had been retained during transit (Table 3.1). Despite the rapidity of hydrological transfer, therefore (and the timing of the experiments during early and late winter), it appears that biological N retention in the Gwy soils is remarkably efficient.

Because of the low $^{15}NO_3^-$ dosage applied (in order to maintain realistically low total NO_3^- concentrations during the experiment), changes in soil and vegetation ^{15}N due to this N retention were very difficult to detect. However, samples analysed from the first (November 2005) experiments show slightly higher ^{15}N enrichment in above-ground biomass, relative to N in the O horizon (including below-ground biomass). Taking into account the greater mass of O horizon versus above-ground biomass, it is estimated that approximately equal amounts of N were retained in above-ground plant material, and in the organic soil (Figure 3.4).

Spatial controls on nitrate leaching

The 12 'replicate' plots showed huge spatial variation in their capacity to retain deposited NO_3^-. Additionally, ambient throughflow NO_3^- concentrations (which did not change appreciably during the experiment, due to the low dose) varied from 1.5 to 22.5 meq l^{-1}, indicating similar heterogeneity in the natural 'leakiness' of each plot. In fact, there is a negative correlation between ^{15}N retention and ambient NO_3^- concentration (Figure 3.5a), i.e. plots already enriched with NO_3^- are less able to retain additional NO_3^-. This is highly consistent with N saturation theory, but suggests that N saturation develops very variably across the landscape, even within areas (such as that studied) of relatively uniform vegetation and soil type. Surprisingly, plot ^{15}N retention was not well related to the C/N ratio of the organic horizon (Figure 3.5b), but a much stronger relationship was observed with the average C/N ratio of the whole soil profile above the ironpan (Figure 3.5c).

Figure 3.4: Average percentage of ^{15}N-labelled nitrate leached from plots, and approximate percentages retained in above-ground vegetation and the organic soil (note soil and vegetation ^{15}N data are from the first set of experiments only).

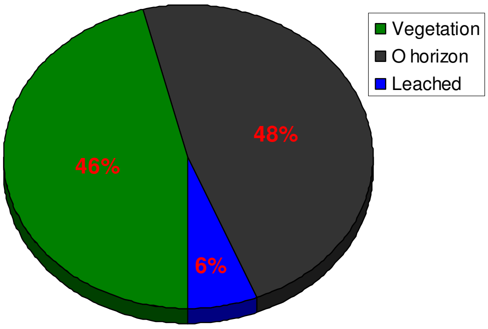
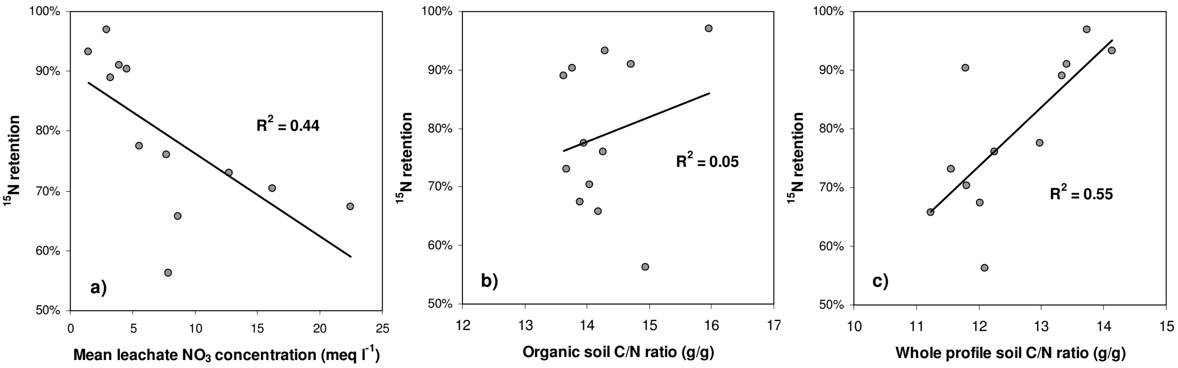


Figure 3.5: Relationship between the amount of NO_3^- retained in each plot and a) mean NO_3^- concentration in throughflow (volume-weighted mean of organic and mineral horizon throughflow), b) organic horizon C/N ratio, and c) whole profile mean C/N ratio.



Discussion and implications

The ^{15}N experiment undertaken at Plynlimon demonstrates that, in a typical upland podzol (a soil type covering a major part of the UK upland area), much of the rainfall hitting the soil surface can pass rapidly into deeper mineral soils, without passing through the (strongly N-retaining) organic soil matrix. This would seem to suggest that hydrological NO_3^- might contribute a major part of the N leaching from the site. However, the ^{15}N data suggest that, even in water passing through the soil within a few hours, around 80% of all the labelled NO_3^- added was retained. The implication is that large populations of soil microbes, able to rapidly and efficiently immobilise NO_3^-, must exist within the relatively nutrient-rich 'microhabitats' provided preferential flowpaths such as soil cracks (Hagedorn *et al.*, 1999). This micro-scale heterogeneity in soil N retention may explain why catchment-scale studies (at Plynlimon and elsewhere) usually show NO_3^- leaching to surface waters, whereas detailed studies of the soil matrix (e.g. soil solution measurements taken with suction samplers) often suggest near-total N retention.

One objective of this study was to provide a quantitative estimate of the proportion of hydrological NO_3^- in runoff for use in dynamic models. On average, 18% of tracer-labelled 'rainfall' was recovered from the mineral soil during the experiments, and this could be taken as a crude estimate of the amount of matrix-bypass flow occurring. However, this was only sufficient to transport 4.2% of ^{15}N-labelled NO_3^- to the mineral soil ($^{15}NO_3^-$ leached from the O horizon is likely to be retained downslope, and was therefore excluded from this calculation). Even if all rainfall entering the plots were (over a longer period) to be transported to the mineral soil, this would transport a maximum of 23% of deposited NO_3^- based on these figures. There are several reasons why these figures may overestimate overall hydrological NO_3^- leaching: 1) Only around 25% of the catchment comprises hillslope soils connected to the stream network (i.e. 'nitrate leaching zones'), with hydrological NO_3^- transport unlikely in other areas where water passes through strongly N-retaining peats (Evans *et al.*, 2004); 2) NO_3^- concentrations in the stream are near-zero between May and October, so hydrological NO_3^- leaching can only realistically occur during the remaining 6 months of the year; and 3) only 48% of total N deposition occurs as NO_3^- ; that occurring as NH_4^+ is abiotically immobilised via cation exchange (and subject to biological utilisation thereafter), and will not therefore be hydrologically leached. Combining these figures gives a best estimate of hydrological NO_3^- leaching at the Gwy as 0.25% of N deposition, with an upper limit of perhaps 2%. Actual NO_3^- leaching is closer to 7% of N deposition (Curtis *et al.*, 2004), which cannot therefore be explained by hydrological NO_3^-. These results agree well with dual isotope data for the Afon Gwy (Task 3.2), indicating that the majority of NO_3^- leached from the catchment has been biologically cycled before being exported, and therefore does represent 'saturation' NO_3^-, and is closer to the 'worst case' scenario for future leaching represented in Figure 3.1.

Finally, results show a remarkable degree of variability in the susceptibility of different areas of (apparently homogenous) hillslope to N saturation: some of the study plots retained almost all added N, others retained only around half of the $^{15}NO_3^-$ in the tracer-labelled water recovered. It therefore appears that N saturation develops unevenly within the landscape, for example in areas where nutrients are flushed in from upslope, or where soils are thinner. This has implications for surface water NO_3^- modelling, as it would imply an earlier and more gradual onset of N saturation than the current approach of aggregating soils across the whole catchment and assuming homogenous N enrichment of this aggregated pool. It is also relevant to the prediction of N eutrophication effects on terrestrial ecosystems, since it suggests that 'hotspots' of N enrichment develop, likely to be the areas most susceptible to detrimental species change. A good example of this is small riparian wetlands, which are typically enriched by large nutrient inputs from upslope. It is emphasised that these issues of local heterogeneity are important to consider at the national (not just site) scale, as they will affect the development and impacts of N enrichment across the whole landscape.

Future work

Ideally, these experiments would be repeated elsewhere, to obtain representative data for a wider range of UK N-sensitive areas. However, given time and financial constraints it is considered more important to extend the dual-isotope survey work in Task 3.2 to a larger area, since this provides a simpler means of quantifying the role of hydrological NO_3^- at a larger scale. This experiment has provided fundamental insights into the mechanisms controlling N retention versus leaching within the hillslope, which aid the interpretation of dual-isotope data at larger scales.

The evidence from this study of heterogeneous development of N saturation suggests that further development of current models is required to take account of this. A GIS-based modelling approach in which lateral water and nutrient transfers are simulated would permit this spatial variability to be modelled. Such an approach would be particularly valuable for predicting the development of eutrophication hotspots within particular locations of conservation importance, but could in principle (using large-scale soils, land-cover and topographic data) be scaled up to larger scales.

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Task 3.2: Dual isotope studies at the Afon Gwy: "new" atmospheric versus "old" microbial N in surface water nitrate (Pilot Scheme)

Chris Curtis, Gavin Simpson, Tim Heaton, Simon Turner, James Shilland and Chris Evans

Introduction

The importance of NO_3^- leaching in contributing to acidification and critical load exceedance has been demonstrated through several DEFRA funded research programmes over the last 10 years. An early application of the FAB model (Posch *et al.*, 1997) revealed that nitrogen mass balance calculations predicted far higher NO_3^- concentrations than were currently observed in UK waters (Curtis *et al.*, 1998). The wide spatial contribution of N to critical load exceedance resulting from these predicted concentrations was shown in national maps (Curtis *et al.*, 1999, 2000). The need to understand the key controls on NO_3^- leaching and to determine the feasibility of these dire predictions of increased NO_3^- concentrations led to the setting up of plot based experiments under the DEFRA funded Critical Loads of Acidity and Metals (CLAM) programme.

Much of the work focussed on four intensively studied sites from the Acid Waters Monitoring Network across gradients of N deposition and leaching. The Allt a'Mharcaidh was selected as the low deposition / low N leaching site while the River Etherow represented a very high N deposition / leaching catchment. The Afon Gwy and Scoat Tarn catchments were chosen as intermediate deposition and leaching sites. Biogeochemical studies at these catchments entailed measurement of bulk deposition inputs, leaching outputs, trace gas fluxes (denitrification) and ^{15}N-labelled N additions (NH_4NO_3). While denitrification was shown to be a very minor pathway for removal of deposited N (Curtis *et al.*, 2006), a possible microbial control on NO_3^- leaching linked to soil C:N ratios was suggested, but the data were inconclusive (Curtis *et al.*, 2004). In the shorter term, rapid uptake and retention of deposited N by bryophytes and lichens was also found to be important (Curtis *et al.*, 2005a).

Recent trend analysis from the UK Acid Water Monitoring Network suggested that nitrate will be the major acid anion in many acidified systems within 5-10 years as excess sulphate continues to decline and nitrate leaching remains relatively constant (Curtis *et al.*, 2005b). Hence measures to reduce S emissions alone will be insufficient to allow recovery of acidified sites to achieve "good ecological status".

One of the four intensively studied CLAM sites, the Afon Gwy, was also the subject of research carried out under the NERC thematic programme GANE which was attempting to determine the impacts of N deposition on semi-natural ecosystems (Evans *et al.*, 2004). In order to investigate the importance of physical catchment characteristics such as soil type and slope on NO_3^- leaching, water sampling was carried out at a number of subcatchments at the site (Fig. 3.6). The spatial variation in NO_3^- leaching from subcatchments was attributed to the proportion of "NO_3^- leaching zones" in which steeper mineral soil hillslopes drained directly into streams (Fig. 3.7).

Figure 3.6: Afon Gwy subcatchments studied in the GANE project (Evans *et al.*, 2004), with current sampling subcatchments.

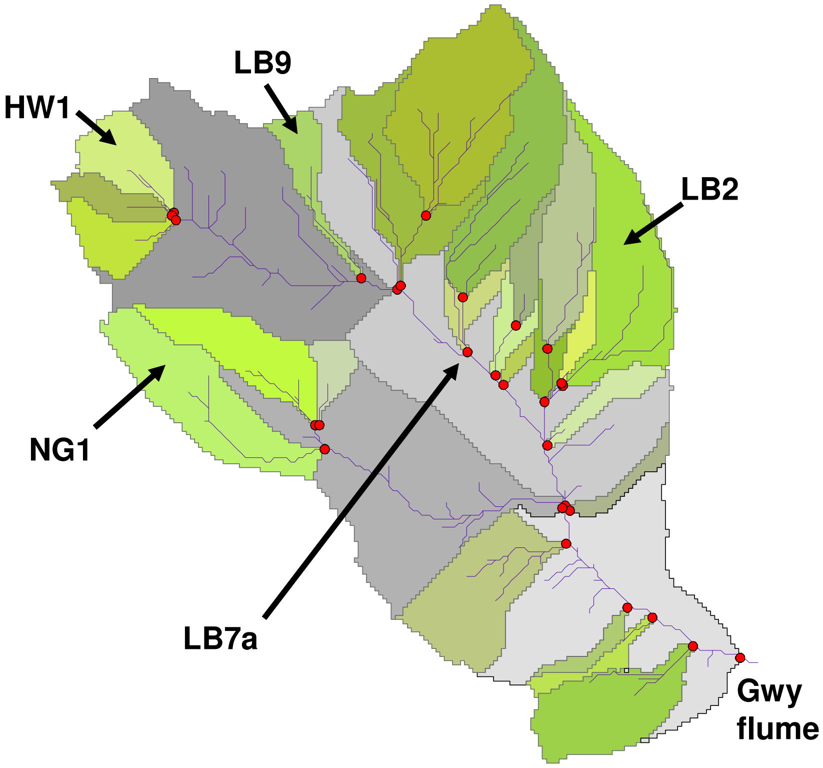
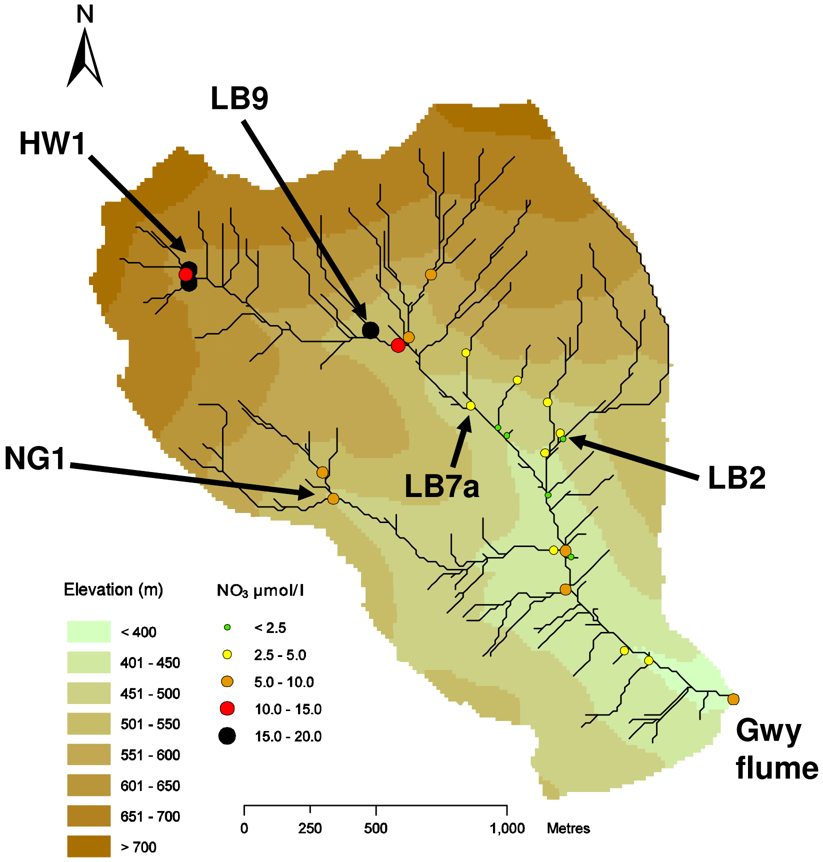


Figure 3.7: GANE NO_3^- concentrations in current Afon Gwy subcatchments (Evans *et al.*, 2004)



The CLAM and GANE studies demonstrated the importance of both physical catchment characteristics and the process of N saturation in determining NO_3^- leaching. However, a key uncertainty remained to be addressed in quantifying the relative roles of these physical (hydrological) and biological processes in controlling the short- and longer-term release of inorganic N from terrestrial systems. The timescale over which N saturation and leaching may occur and the magnitude of increase from present levels is determined by the balance between three key processes (Fig. 3.8):

1) "hydrological" nitrate which bypasses biological retention mechanisms in the soil/vegetation system via saturation overland flow and/or pipe/macropore flow (plus direct deposition to the surface of lakes);
2) "saturation" nitrate which is present in excess of biological demand and leaches through the soil profile unchanged; and
3) nitrate produced within the soil profile by microbial nitrification, which may or may not have derived originally from anthropogenic N deposition taken up by vegetation and/or immobilised by soil microbes, and may be determined by changes in soil C:N ratio in response to elevated N deposition

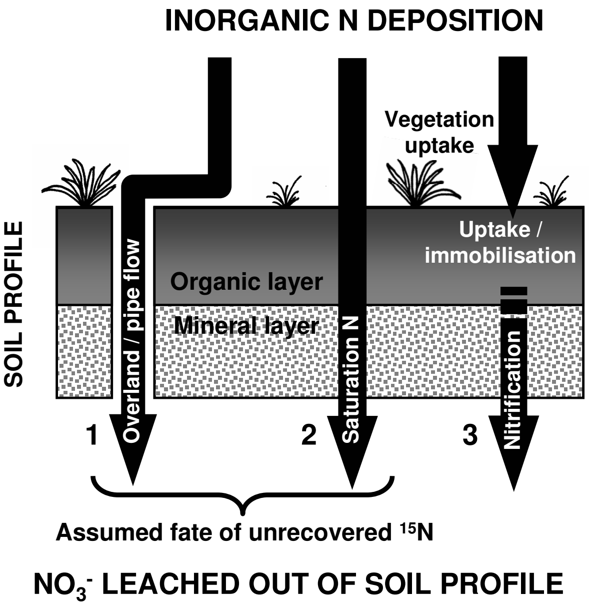
The previous CLAM ^{15}N tracer work showed that the sum of pathways 1) and 2) may reach one third of deposition inputs, with the rest tightly retained in the soil-plant system (Curtis *et al.*, 2005a). This proportion is sufficient to explain observed nitrate leaching at some sites. However, possible links with C:N ratio (Curtis *et al.*, 2004) and high nitrification potentials in some upland soils suggest there may also be a component of microbial nitrate in leaching to surface waters (pathway 3).

The split between the three possible pathways is critical for modelling the potential future leaching of nitrate. If current surface water nitrate already contains a "saturation N" component (pathway 2) or a microbial component (pathway 3), then the function of terrestrial ecosystems as N sinks may have already changed in response to elevated N inputs, and timescales to attain the worst leaching predictions of the FAB model could be just years to decades. Furthermore, large pools of stored "anthropogenic" N in the soil-plant system could potentially sustain nitrification and leaching even with reduced deposition inputs.

On the other hand, if surface water nitrate is purely hydrological (pathway 1) then terrestrial systems have not shown a saturation response (either through reduced immobilisation or increased nitrification) to many decades of high N deposition with elevated leaching, suggesting that their capacity to retain N is very large. In the latter case there may be no measurable N saturation effects and no increase in pathways 2) and 3) for many decades to come. Responses to changes in total N deposition should therefore be very rapid. Effectively, the routing of N through the soils determines the extent to which N impacts on terrestrial systems (i.e. soil and vegetation N enrichment) versus freshwaters (i.e. NO_3^- leaching).

Given the previous work done under GANE and CLAM at the Afon Gwy, it was decided to use this site for a pilot study employing the dual isotope technique (see Burns & Kendall, 2002; Campbell *et al.*, 2002; Durka *et al.*, 1994; Spoelstra *et al.*, 2001; Williard *et al.*, 2001) to determine the relative contributions of deposited and microbial nitrate to observed concentrations in surface waters. This work provides the split between pathway 3) and the sum of pathways 1) plus 2) in Figure 3.8.

Figure 3.8: Schematic diagram of 3 potential nitrate leaching pathways (Source: Curtis *et al.*, 2005a)



Methods

The pilot scheme for dual isotope analysis of NO_3^- at the Afon Gwy commenced on 1st September 2004 with the installation of a large volume bulk precipitation collector with small collecting roof adjacent to the main AWMN sampling point at the Gwy flume and three tray lysimeters in an exposed roadside cutting further up the catchment (Fig. 3.9a-b). Five of the GANE subcatchments covering gradients of NO_3^- concentration and "NO_3^- leaching zones" were selected to determine whether there was spatial variation in the dominant NO_3^- leaching flowpaths within the wider Gwy catchment (Fig. 3.6). The first batch of streamwater, bulk precipitation and soil water samples was collected on the subsequent visit to the site on 29th September 2004. Thereafter, 10 monthly samples were collected over a 12 month period with additional wider stream surveys of the five GANE tributary subcatchments (Fig. 3.6) carried out in December 2004, April and June 2005 (Table 3.2). Despite attempted visits to the site in February and March 2005, access was not possible (first because of iced roads and on the second occasion access was denied by the landowner) so samples could not collected for these months.

Water chemistry analyses were performed in the field using a portable spectrophotometer (Hach DR/2400) for NO_3^- (low-range cadmium reduction method, detection limit 0.01 mgl^{-1} or 0.7 μeql^{-1}), sulphate (SulfaVer 4 Method, detection limit 1 mgl^{-1} or 20.8 μeql^{-1}) and chloride (mercuric thiocyanate method, detection limit 0.1 mgl^{-1} or 2.8 μeql^{-1}). Streamwater and bulk deposition NO_3^- samples were then filtered and pre-treated through cation exchange resins (AG50W-X8) prior to collection on anion exchange resins (AG2-X8) according to the method of Chang *et al.* (1999).

A volume of water sufficient to provide at least 100 µeq of NO_3^- was passed through the exchange columns if possible, but in some cases logistical considerations meant that only 50 µeq or less was collected. Care had to be taken not to exceed the exchange capacity of the anion resins (6000 µeq) to avoid possible fractionation of the collected NO_3^- sample, so the loading of acid anions had to be calculated (sum of acid anions SAA=NO_3^-+chloride+sulphate). If the calculated loading of acid anions to provide the minimum quantity of NO_3^- for dual isotope analysis was greater than 6000 μeq the sample was split and loaded onto two anion columns.

Low NO_3^- concentrations in the streamwaters compared with previous years meant that large volumes of sample had to be collected to provide the required quantity of NO_3^-, 45L on the first visit. These large sample volumes presented a great logistical challenge in sample collection and transport, while processing times (filtration and column loading) were very long. The anion resins were refrigerated for up to several weeks prior to being transported to NIGL, Keyworth, where $\delta^{15}N$ and $\delta^{18}O$ were analysed according to the method of Silva *et al.* (2000).

Table 3.2: Samples obtained in the Afon Gwy Pilot Study

Sampling month	Gwy flume	Deposition	Soilwaters	Subcatchment streams
September 2004	Y	Y	3	
October 2004	Y	Y	3	
November 2004	Y	Y	3	
December 2004	Y	Y	3	5 sampled & loaded
January 2005	Y	Y	3	
February 2005	N	N	0	
March 2005	N	N	0	
April 2005	Y	Y	3	5 sampled & loaded + 4 soilwaters
May 2005	Y	Y	1	
June 2005	Y	Y	1	5 sampled; 3 loaded
July 2005	Y	Y	2	
August 2005	Y	Y	1	

Given that low soilwater NO_3^- concentrations had been observed during the CLAM project (Curtis *et al.*, 2004) and that streamwater concentrations had been relatively low, it was not considered feasible to collect sufficient soilwater NO_3^- for dual isotope analysis. Instead, 100ml soilwater samples were analysed only for $\delta^{18}O$-H_2O, from which a theoretical microbial $\delta^{18}O$-NO_3^- could be calculated. The calculation is based on the assumption that during autotrophic microbial NO_3^- production, the oxygen is derived one part from atmospheric oxygen (of known $\delta^{18}O$ = +23‰) and two parts from soilwater oxygen, which is measured directly:

$$\delta^{18}\text{O-NO}_3^- = (2/3\ \delta^{18}\text{O-H}_2\text{O soilwater}) + (1/3\ \delta^{18}\text{O atmospheric oxygen})$$

This theoretical calculation of the $\delta^{18}O$-NO_3^- value for soil microbial nitrate makes a number of assumptions which may be valid for many, but not all environments (Kendall, 1998; Mayer *et al.*, 2001). Thus, from experimental results Mayer *et al.* (2001) suggested that there may be some circumstances under which heterotrophic nitrification might yield nitrate oxygen derived from two parts atmospheric oxygen and only one part soilwater oxygen. In this report we calculate the soil microbial nitrate end-member for using two models: Model 1, the commonly used equation above, assuming ratio of atmospheric-O to water-O = 1 to 2; and Model 2 assuming ratio of atmospheric-O to water-O = 2 to 1.

The analysis of oxygen and nitrogen isotopes at NIGL was performed in batches every 3-6 months. Given the novel application of this method in the UK, the ability of the sampling and analytical methods to provide sufficient uncontaminated NO_3^- was not known, and assessment of methods formed a key part of this pilot phase.

Figure 3.9a: High volume bulk deposition collector at Afon Gwy flume

Figure 3.9b: Tray lysimeters at Afon Gwy showing different horizons sampled

Results

<u>Water chemistry data</u>

Analysis of the bulk deposition and soilwater samples for NO_3^- concentration using the portable Hach kit indicated that relatively low concentrations of NO_3^- were found throughout the sampling period at the Afon Gwy (Fig. 3.10). Streamwater concentrations at the Gwy flume reached a maximum of only 4 μeq l^{-1} while bulk deposition concentrations varied from 1-9 μeq l^{-1}. These low concentrations combined with relatively high concentrations of other acid anions (sulphate and chloride), particularly in streamwater samples, meant that it was not always possible to collect sufficient NO_3^- for dual isotope analysis (Table 3.3).

Figure 3.10: Measured NO_3^- concentrations in rain (bulk deposition) and streamwater (flume)

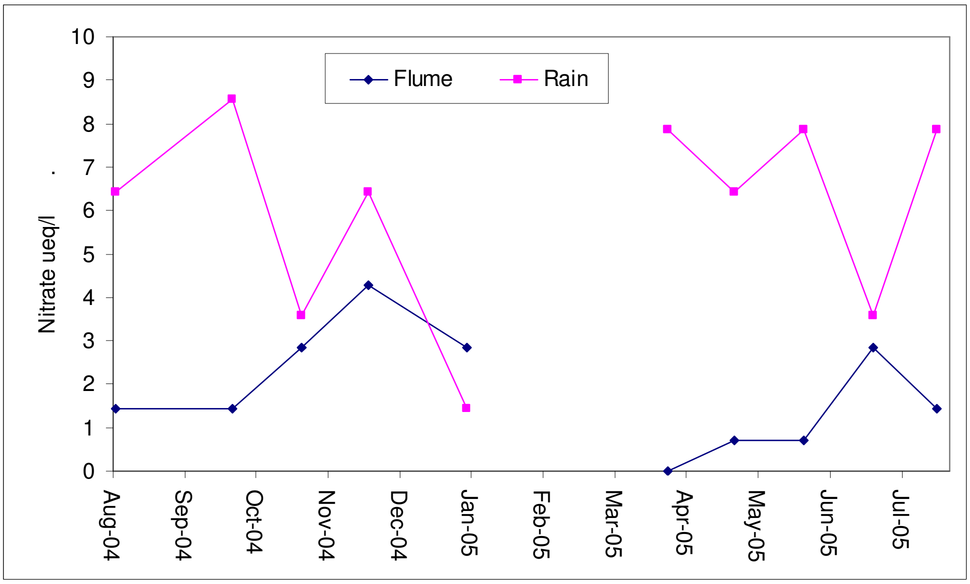


Table 3.3: Water chemistry data, sum of acid anions (SAA) and required volume loadings for collection of 100 µeq or a minimum of 50 µeq NO_3^- on anion exchange resins

	Sampling	Concentration µeq l^{-1}				Volume	Min vol.	Volume	Nitrate	
Site	Date	Nitrate	Sulphate	Chloride	SAA	required	required	loaded	loaded	Notes
Rain	20-Sep-04	6.4	0.0	87.3	93.8	16	8			Loading not recorded
Rain	20-Oct-04	8.6	0.0	33.8	42.4	12	6	20	171.4	
Rain	18-Nov-04	3.6	20.8	135.2	159.6	28	14	20	71.4	
Rain	16-Dec-04	6.4	41.7	81.7	129.8	16	8	20	128.6	
Rain	26-Jan-05	1.4	0.0	183.1	184.5	70	35	21	30.0	x2 columns
Rain	28-Feb-05									No sample
Rain	19-Mar-05									No sample
Rain	20-Apr-05	7.9	0.0	50.7	58.6	13	6	20	157.1	
Rain	18-May-05	6.4	0.0	14.1	20.5	16	8	15.5	99.6	
Rain	16-Jun-05	7.9	0.0	47.9	55.7	13	6	13	102.1	
Rain	15-Jul-05	3.6		0.0		28	14	10	35.7	
Rain	11-Aug-05	7.9	0.0	169.0	176.9	13	6	15	117.9	
Flume	01-Sep-04	1.4	0.0	129.6	131.0	70	35			Loading not recorded
Flume	20-Oct-04	1.4	20.8	169.0	191.3	70	35	80	114.3	
Flume	18-Nov-04	2.9	0.0	157.8	160.6	35	17	80	228.6	
Flume	16-Dec-04	4.3	41.7	233.8	279.8	23	12	30	128.6	
Flume	26-Jan-05	2.9	20.8	191.6	215.2	35	17	21	60.0	
Flume	28-Feb-05									No sample
Flume	19-Mar-05									No sample
Flume	20-Apr-05	0.0	20.8	115.5	136.3					TOO LOW - NOT LOADED
Flume	18-May-05	0.7	0.0	95.8	96.5	140	70	35	25.0	x2 columns
Flume	16-Jun-05	0.7	0.0	123.9	124.7	140	70	20	14.3	x2 columns
Flume	15-Jul-05	2.9		0.0		35	17	18	51.4	
Flume	11-Aug-05	1.4	20.8	22.5	44.8	70	35	27	38.6	
HW1	17-Dec-04	4.3	0.0	171.8	176.1	23	12	20	85.7	
HW1	20-Apr-05	1.4	0.0	146.5	147.9	70	35	25	35.7	
HW1	16-Jun-05	0.0								TOO LOW - NOT LOADED
LB2	17-Dec-04	2.9	0.0	163.4	166.2	35	17	30	85.7	
LB2	20-Apr-05	0.7	0.0	101.4	102.1	140	70	30	21.4	
LB2	16-Jun-05	0.7	0.0	154.9	155.6	140	70	20	14.3	x2 columns
LB7a	17-Dec-04	2.1	0.0	202.8	205.0	47	23	16	34.3	x2 columns
LB7a	20-Apr-05	1.4	0.0	138.0	139.5	70	35	34	48.6	
LB7a	16-Jun-05	2.1	0.0	121.1	123.3	47	23	25	53.6	
LB9	17-Dec-04	7.9	0.0	149.3	157.2	13	6	30	235.7	
LB9	20-Apr-05	6.4	0.0	109.9	116.3	16	8	25	160.7	
LB9	16-Jun-05	0.7	0.0	146.5	147.2	140	70	35	25.0	x2 columns
NG1	17-Dec-04	0.7	0.0	200.0	200.7	140	70	30	21.4	
NG1	20-Apr-05	1.4	0.0	118.3	119.7	70	35	34	48.6	
NG1	16-Jun-05	0.0								TOO LOW - NOT LOADED

Soilwaters and microbial nitrate

Soilwater $\delta^{18}O-H_2O$ data and the corresponding theoretical microbial NO_3^- values, assuming different nitrification models, are presented in Table 3.4a-b. Missing data indicate no soilwater retained from the tray lysimeter except for February and March 2005 when the catchment was inaccessible.

Table 3.4a: Soilwater $\delta^{18}O-H_2O$ and mean theoretical $\delta^{18}O-NO_3^-$ at the Afon Gwy (‰)

Date	Soil 1	Soil 2	Soil 3	Mean	Microbial nitrate, model 1*	Microbial nitrate, model 2*
Sep-04	-5.1	-4.2	-5.1	-4.8	4.5	13.7
Oct-04	-7.3	-7.5	-8.2	-7.7	2.6	12.8
Nov-04	-6.5	-6.2	-4.7	-5.8	3.8	13.4
Dec-04	-5.9	-5.5	-8.3	-6.6	3.3	13.1
Jan-05	-5.5	-6.7	-5.3	-5.8	3.8	13.4
Feb-05						
Mar-05						
Apr-05	-5.8	-6.7	-6.8	-6.4	3.4	13.2
May-05	-7.0			-7.0	3.0	13.0
Jun-05		-5.1		-5.1	4.3	13.6
Jul-05		-4.7	-1.5	-3.1	5.6	14.3
Aug-05		-6.7		-6.7	3.2	13.1
Mean:	**-6.2**	**-5.9**	**-5.7**	**-5.9**	**3.7**	**13.4**

* Microbial nitrate. Model 1 assumes ratio of atmospheric-O to water-O = 1 to 2; Model 2 assumes ratios of atmospheric-O to water-O = 2 to 1.

Table 3.4b: Soilwater $\delta^{18}O-H_2O$ and mean theoretical microbial $\delta^{18}O-NO_3^-$ from Afon Gwy subcatchments sampled on 19th April 2005 (‰)

Gwy subcatchment	Soil water	Microbial nitrate, model 1*	Microbial nitrate, model 2*
HW1	-6.9	3.0	13.0
LB2	-6.8	3.1	13.1
LB7a	-6.7	3.2	13.1
NG1	-7.2	2.9	12.9

* See Table 3.4a

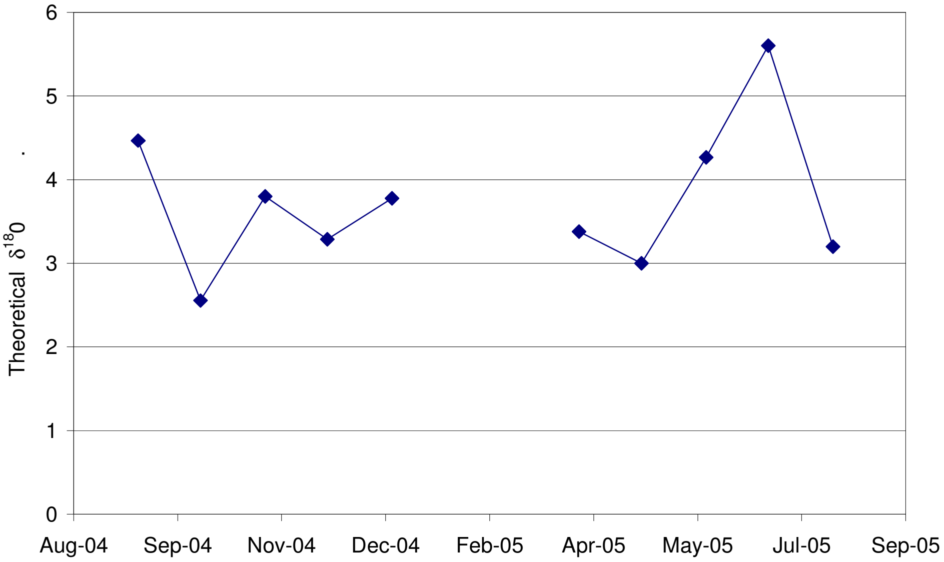
The theoretical $\delta^{18}O-NO_3^-$ under the assumptions of Model 1, based on measured soilwater $\delta^{18}O-H_2O$, varies between 2.6‰ and 5.6‰ with a maximum value in July 2005 (Fig. 3.11). The overall mean value of 3.7‰ (Table 3.4a) is assumed to be the expected value for streamwaters if 100% of collected NO_3^- is microbially produced. Values based on soilwaters from subcatchments sampled in April 2005 are all slightly lower than this figure with a mean of 3.05‰ (Table 3.4b).

Dual isotope analysis of bulk deposition and streamwater

For the bulk deposition and streamwater NO_3^- dual isotope analysis, the first batch of results indicated that the methods were working well:

1) the 'quality' of the silver nitrate prepared from the anion resins was generally quite good, with little evidence of organic contaminants (except in the first two samples), and
2) the amount of NO_3^- collected on the resins was perfectly adequate for dual isotope analysis even at the very low concentrations encountered at the Gwy.

Figure 3.11: Theoretical soilwater $\delta^{18}O\text{-}NO_3^-$ of microbial NO_3^- at the Afon Gwy (Model 1 assumption)



The first two samples, collected with the newly-installed equipment in September 2004, showed evidence of contamination, and their data are not considered further. Subsequent rain and stream samples form into two quite well-constrained groups which have very similar $\delta^{15}N$, but very different $\delta^{18}O$ (Figure 3.12). The $\delta^{15}N$ values in the -2 to +2 per mille range are quite typical for rainwater NO_3^-, but are equally quite typical for NO_3^- in nutrient-poor, uncultivated, upland soils. Studies in other ecosystems outside the UK have also commonly found poor separation between the $\delta^{15}N$ values of rainwater and soil nitrates.

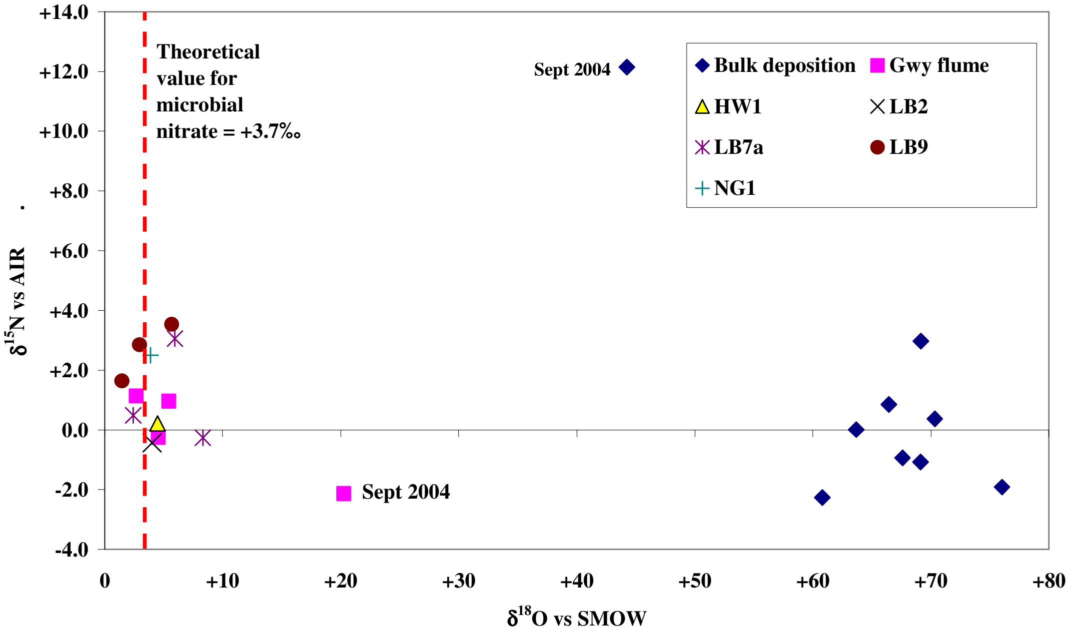
The $\delta^{18}O\text{-}NO_3^-$ values for the rainwater samples at the Gwy are the first reported for the UK. Their range, +60 to +80 per mille, is comparable with the limited published data for atmospheric nitrate in other parts of the globe (Heaton *et al.*, 2004).

With the exception of the contaminated September samples, all of the stream $\delta^{18}O\text{-}NO_3^-$ measurements lie close to the theoretical value for microbial $\delta^{18}O\text{-}NO_3^-$ of +3.7‰, calculated assuming the Model 1 assumptions (Fig. 3.12). The proportion of the NO_3^- collected from streamwater that comprises untransformed rainwater NO_3^-

may be estimated by interpolation between the mean values for bulk deposition (overall mean = +68‰: Table 4) and for microbial NO_3^-. For microbial nitrate formed using Model 1 assumptions (+3.7‰) the calculated proportions of atmospheric NO_3^- lie between -3.5 and +7.2%. For Model 2 assumptions (microbial nitrate $\delta^{18}O\text{-}NO_3^-$ = +13.4‰) the proportions of atmospheric NO_3^- would all be negative.

The proportion of atmospheric or "hydrological" NO_3^- in streamwater may also be estimated from the calculated soilwater microbial and bulk deposition data for the corresponding month (Table 3.5), giving very similar results to the mean-based values. Ideally, if hydrological residence times of soilwaters were known, the time lag between precipitation and discharge at the sample point would be taken into account, i.e. for a given streamwater sample, the deposition sample for the date of the rainfall source of the streamwater would be used. This factor could be important if there was major temporal variation in the proportion of atmospheric NO_3^- calculated for streamwaters, but this is not the case at the Afon Gwy. However, possible temporal mismatch between rainwater and streamwater samples may account at least partly for the calculation of small negative (or positive) values for the proportion of atmospheric NO_3^- in some cases. The estimation error associated with this problem is not known but is of little importance at the Afon Gwy where only a very small proportion of leached NO_3^- is atmospheric.

Figure 3.12: Isotopic separation of streamwater and bulk precipitation NO_3^-. The theoretical $\delta^{18}O$ of microbial NO_3^- is from the Model 1 calculations of Table 3.4a



Unfortunately, only three good streamwater NO_3^- samples were collected from the Afon Gwy flume; the very first sample appears to be contaminated, two months of sampling were missed because of lack of access to the site during the period when highest NO_3^- concentrations might be expected, and summer NO_3^- concentrations were too low at the flume to obtain enough NO_3^- for dual isotope analysis. However, additional streamwater data were obtained for some of the GANE subcatchments sampled on three occasions during the study (Table 3.6).

Table 3.5: Results of dual isotope analysis & estimated proportion of atmospheric NO_3^- at Gwy flume based on mean & corresponding monthly microbial & bulk deposition $\delta^{18}O$ values

Date	Microbial	Bulk deposition		Gwy flume		% atmospheric	
	$\delta^{18}O\text{-}NO_3^-$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	(mean)	(monthly)
Sep-04	4.5	+44	+12.1	+20	-2.1	25.8	39.7
Oct-04	2.6	+70	+0.4	+5	+1.0	2.7	4.2
Nov-04	3.8	+69	+3.0				
Dec-04	3.3	+76	-1.9	+5	-0.3	1.3	1.7
Jan-05	3.8	+68	-0.9	+2.7	+1.1	-1.6	-1.7
Feb-05							
Mar-05							
Apr-05	3.4	+69	-1.1				
May-05	3.0	+66	+0.9				
Jun-05	4.3	+64	+0.0				
Jul-05	5.6	+61	-2.3				
Aug-05	3.2		-0.7				
Mean:	**3.7**	**+68**	**-0.3**	**+4.2**	**+0.6**	**+0.8**	**+1.4**

Table 3.6: Results of dual isotope analysis & estimated proportion of atmospheric NO_3^- in GANE subcatchment streamwaters based on mean & corresponding monthly microbial & bulk deposition $\delta^{18}O$ values from Gwy flume (* based on measurement in subcatchment)

Sub-catchment	Date	Soilwater	Bulk deposition		Streamwater		% atmospheric	
		$\delta^{18}O\text{-}NO_3^-$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	Mean	Monthly
HW1	Dec-04	3.3	+76	-1.9	4.5	0.2	1.2	1.6
LB2	Dec-04	3.3	+76	-1.9	4.0	-0.4	0.5	1.0
LB7a	Dec-04	3.3	+76	-1.9	2.4	0.5	-2.0	-1.2
LB9	Dec-04	3.3	+76	-1.9	1.5	1.6	-3.5	-2.5
LB7a	Apr-05	*3.2**	+69	-1.1	6.0	3.1	3.5	4.2
LB9	Apr-05	3.4	+69	-1.1	5.7	3.5	3.1	3.5
NG1	Apr-05	2.9	+69	-1.1	3.9	2.5	0.3	1.5
LB7a	Jun-05	4.3	+64	+0.0	8.3	-0.3	7.2	6.8
LB9	Jun-05	4.3	+64	+0.0	3.0	2.8	-1.1	-2.2

Nine samples were successfully analysed for both $\delta^{18}O$ and $\delta^{15}N$ in streamwater NO_3^- and all showed a similar pattern to the Gwy flume samples, i.e. very little evidence for the significant presence of atmospheric NO_3^- in streamwaters. The highest value of around 7% atmospheric NO_3^- was recorded for subcatchment LB7a in June 2005. Hence these data support the conclusion from the limited Gwy flume data that in this catchment, more than 90% of the streamwater NO_3^- collected appears to have been microbially produced, with only a very small proportion (possibly less than the detection limit of the method) transported directly from rainfall.

Conclusions

The very high proportion of microbially produced NO_3^- in the Gwy streamwaters (both at the flume and in the sampled subcatchments) suggests that NO_3^- leaching is primarily biologically mediated in this catchment. The atmospheric proportion of streamwater NO_3^- is negligible, although atmospheric deposition must contribute to the pool of cycled N from which NO_3^- is released by nitrification.

The successful application of the method at the Afon Gwy, even with the very low NO_3^- concentrations found there during sampling, provided the justification for expansion of the work to new sites with higher expected NO_3^- concentrations under the second phase of the study (Task 3.3). Higher N deposition and leaching at these sites might be expected to reveal a higher proportion of NO_3^- derived directly from deposition sources.

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Task 3.3: Expansion of dual isotope work to other sites

Chris Curtis, Gavin Simpson, Tim Heaton, Simon Turner and James Shilland

With the success of the pilot study at the Afon Gwy under Task 3.2 above, the next phase entailed the expansion of the study to three new sites. Given the logistical challenges that were presented by the low NO_3^- concentrations at the Gwy and the apparent dominant microbial source of streamwater NO_3^-, it was decided to include sites with higher input (deposition) and higher NO_3^- output in the next phase. It was hoped that these sites would be more likely to show a greater proportion of precipitation NO_3^- in surface waters, perhaps on a seasonally varying basis.

Site selection and descriptions

The three sites selected for the new work were chosen on the basis of existing data from previous DEFRA funded work (CLAM and AWMN):

1) River Etherow, South Pennines,
2) Scoat Tarn, Lake District, and
3) Lochnagar, Grampian Mountains.

These sites were instrumented in the first sampling trip of Year 2 during July 2005 and sampling commenced immediately. For the first sampling runs, comprehensive sampling of inflows and springs was carried out to determine the most appropriate and useful sample points (Fig. 3.13a-d; Table 3.7). These points were chosen on the basis of existing data from previous studies in these catchments.

Table 3.7: Dual isotope sampling locations on initial sample runs

LOCHNAGAR	**Location**
Loch outflow	NO 25317 86268
Bulk deposition	NO 25376 86098
Soilwater1	NO 25380 86096
Soilwater2	Furthest from outflow
Spring (main inflow)	NO 25279 85770
SCOAT TARN	**Location**
Scoat outflow	NY 15819 10344
Bulk deposition	NY 15797 10061
Soilwater1	"
Soilwater2	"
Spring	NY 15713 11105
Scoat Fell stream (inflow1)	NY 15866 10423
Red Pike stream (Inflow2)	NY 15935 10503
RIVER ETHEROW	**Location**
Etherow weir	main channel
Bulk deposition	SK 12408 98885
Soilwater1	Closest to bulk collector
Soilwater2	Farthest from bulk collector
Rose Clough tributary	SK 12181 99532
Swan Clough tributary	SK 11909 99453

Figure 3.13a: Dual isotope sampling points in the Lochnagar catchment.
Lys = soilwater lysimeter.

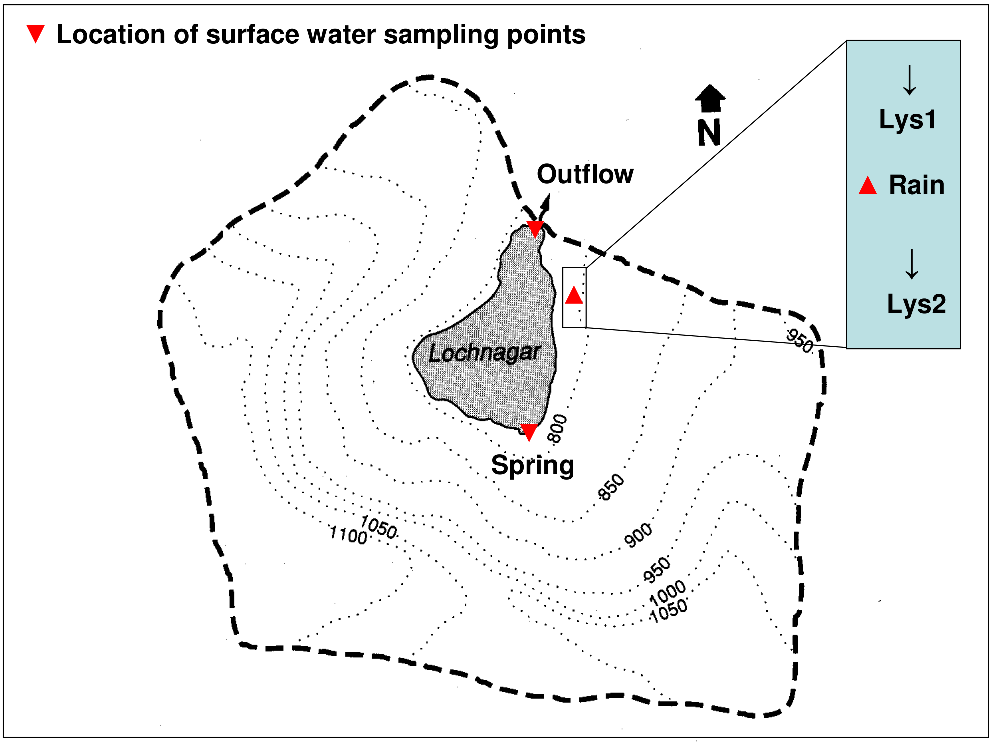


Figure 3.13b: Dual isotope sampling points in the Scoat Tarn catchment.
Lys = soilwater lysimeter.

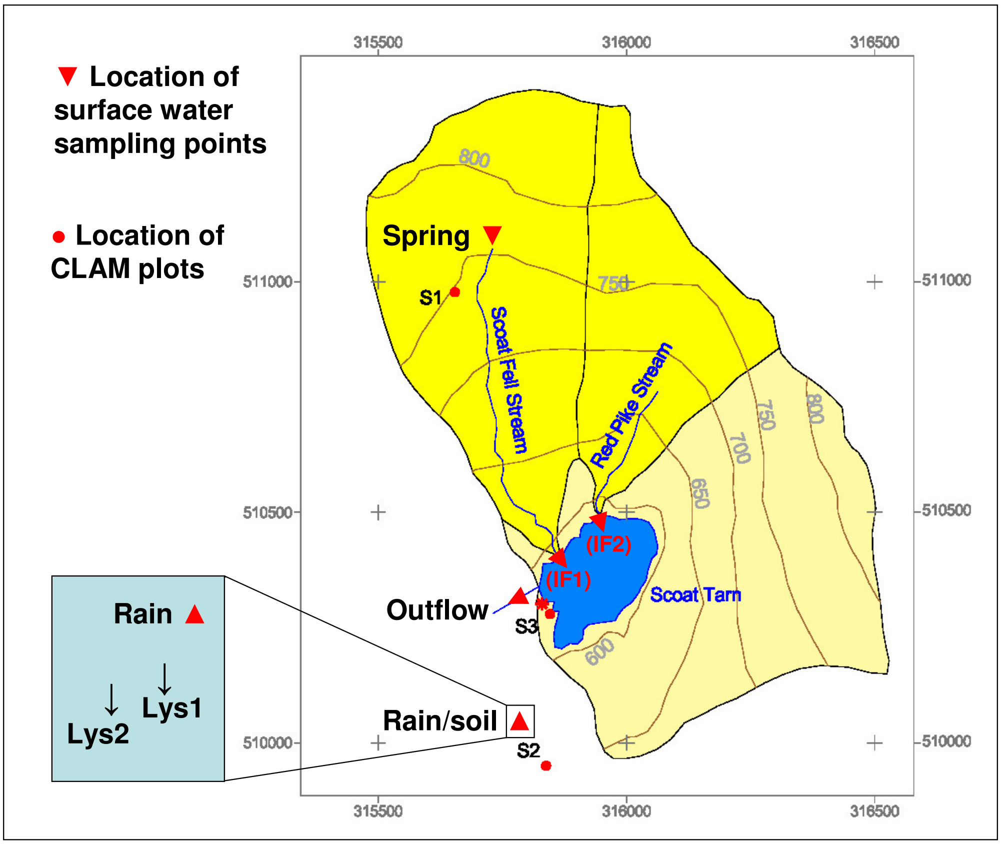
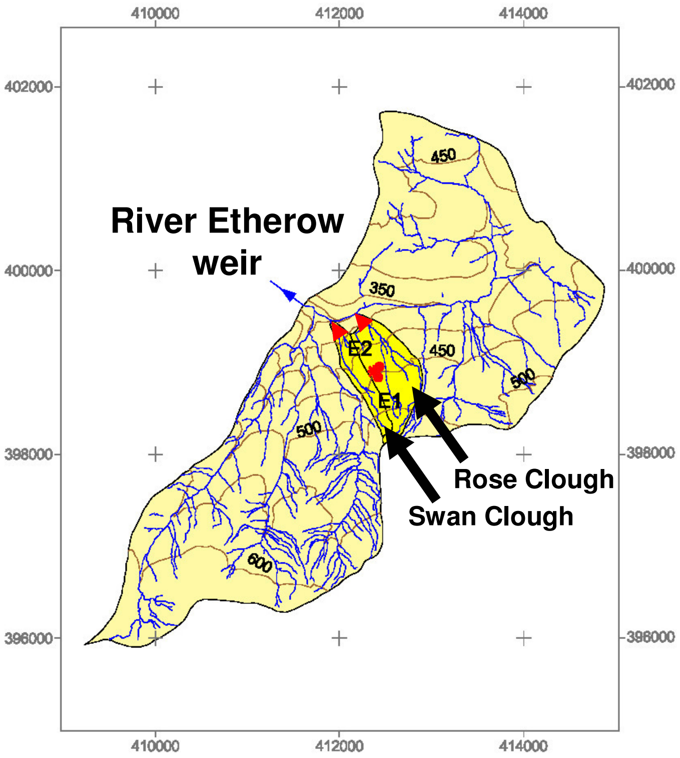


Figure 3.13c: Dual isotope sampling points in the River Etherow catchment, showing Rose Clough and Swan Clough subcatchments.

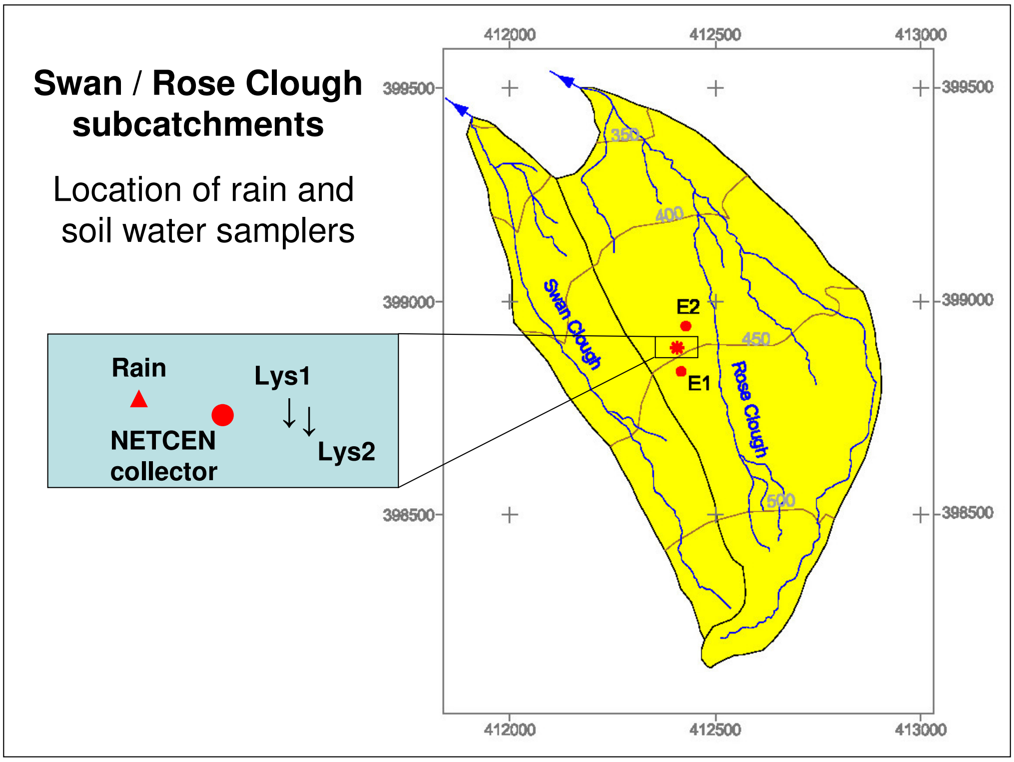


Etherow catchment from weir sampling point.

Stream samples from weir, Rose Clough confluence and Swan Clough confluence

Rain and soil samplers in Rose Clough subcatchment

Figure 3.13d: Dual isotope sampling points in Rose Clough subcatchment of the River Etherow. Lys = soilwater lysimeter.



With the absence of a major inflow stream at Lochnagar, a small spring-fed inflow stream at the southern end of the loch was selected for sampling (Fig. 3.13a). Two soilwater lysimeters were located adjacent to the bulk deposition collector on the eastern side of the loch.

At Scoat Tarn, two inflow streams plus a groundwater spring were initially sampled, although the spring was not included in routine sampling (Fig. 3.13b). Because of the risk of disturbance to field instruments based on previous experience at the site (a popular hiking and camping spot) the bulk deposition collector and lysimeters were located just to the south of the lake outflow, well away from popular paths. While this site is outside the catchment, the soils are very typical of the area and there is no reason to suspect that the deposition or soil biogeochemical regime will differ from much of the lake catchment.

The River Etherow catchment includes an area of improved grassland in the northern half and a major road (the A628 Sheffield-Manchester Woodhead Pass) passing along the northern banks of the river. Therefore we selected the same study sites as in previous CLAM work, on level ground to the south of the main river between the Rose Clough and Swan Clough tributaries (Fig. 3.13c-d). These streams were sampled along with the main Etherow weir which is the UK AWMN sample site.

The final sampling run under this Task was undertaken in July 2006, providing 13 sets of monthly samples over a 12 month period.

Results

In line with the pilot study at the Afon Gwy (Task 3.2) most of the samples continued to yield relatively pure (i.e. not organically-contaminated) silver nitrate, as witnessed by reasonably high N/O ratios. Hence there were no evident analytical problems at the new catchments.

Results of the NO_3^- dual isotope analyses, the theoretical microbial value for $\delta^{18}O$-NO_3^- based on soilwater $\delta^{18}O$-H_2O and the percentage of atmospheric or "hydrological" NO_3^- calculated by interpolation between bulk deposition and microbial values are presented for each catchment in Tables 3.8a-c. Mean values for a full sampling year from August 2005 to July 2006 (n=12) are presented, i.e. the first samples from July 2005 are excluded. These initial samples are to most likely to have been contaminated during catchment instrumentation, although isotopic values show little evidence that this was a problem.

Patterns in $\delta^{15}N$

For the two lake sites, there is little separation between $\delta^{15}N$-NO_3^- in surface waters and bulk deposition, with most surface water values falling within the range covered by bulk deposition samples (Fig. 3.14a-b). Values range from -1.7 to +1.1‰ in the Lochnagar spring and -1.5 to + 1.1‰ in the loch itself, compared with -5.7 to +1.0‰ in bulk deposition (Table 3.8a). At Scoat Tarn, values of $\delta^{15}N$-NO_3^- range from -1.4 to +0.3‰ in Inflow 1, -1.5 to +0.8‰ in Inflow 2 and -1.7 to +0.6‰ in the lake outflow, compared with -4.3 to +1.0‰ in bulk deposition (Table 3.8b).

Table 3.8a: Dual isotope results from Lochnagar sites (initial July 2005 samples excluded from mean)

Sample	Spring inflow		Loch outflow		Bulk deposition		Soilwater (H_2O)		Inflow	Outflow
Date	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{18}O$	Theor. Microbial	% atmospheric	
Jul-05	*+0.3*	*+7.2*	*-0.2*	*+17.2*					*6.6*	*21.4*
Aug-05	-0.0	+3.2	+0.4	+15.2	-5.7	+57.5			0.8	22.7
Sep-05	+1.1	+2.2	+1.1	+13.0	-2.4	+70.5	-5.6	+3.9	-2.6	13.6
Oct-05	+0.5	+7.9	+0.1	+16.7	-2.2	+82.1	-0.5	+7.3	5.8	17.0
Nov-05	+1.0	+4.2	+0.6	+13.9	+1.0	+74.6	-7.5	+2.7	2.1	15.5
Dec-05	-0.6	+11.9	-1.3	+15.9	+0.9	+80.2	+0.8	+8.2	12.2	17.4
Jan-06	-0.2	+15.6	-0.8	+16.9	-0.4	+76.3	-8.3	+2.1	18.1	19.9
Feb-06	+0.1	+9.5	-0.9	+16.3	-1.1	+70.9	-7.1	+3.0	9.6	19.6
Mar-06										
Apr-06	-1.7	+20.2	-1.3	+22.4	-2.9	+64.4	-0.3	+7.5	28.5	31.9
May-06	-1.6	+16.4	-1.5	+16.1	+0.3	+48.3	-7.2	+2.9	29.7	29.1
Jun-06	-0.8	+13.0	-1.1	+18.7	-3.7	+71.2	-0.5	+7.3	15.2	23.4
Jul-06	-1.0	+16.4	-1.4	+19.2	-3.9	+69.2	+1.3	+8.5	20.9	25.2
Mean:	**-0.3**	**+10.9**	**-0.5**	**+16.7**	**-1.8**	**+69.6**	**-3.5**	**+5.3**	**12.8**	**21.4**

Table 3.8b: Dual isotope results from Scoat Tarn sites (initial July 2005 samples excluded from mean)

Sample	Inflow 1		Inflow 2		Lake outflow		Bulk deposition		Soilwater (H_2O)		Inflow 1	Inflow 2	Outflow
Date	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{18}O$	Theor. Microbial	% atmospheric		
Jul-05	*-0.7*	*+11.2*	*-0.2*	*+9.7*	*+0.3*	*+15.7*				*+3.4*	*12.2*	*9.9*	*19.3*
Aug-05	+0.2	+7.2	-1.5	+9.7	-0.3	+11.6	-1.2	+63.2	-5.8	+3.8	5.8	9.9	13.0
Sep-05	+0.2	+11.5	+0.5	+3.9	+0.6	+11.4	-2.1	+68.9		+3.4	12.4	0.8	12.2
Oct-05	+0.3	+7.5	+0.8	+7.1	+0.4	+14.8	-0.8	+73.9	-5.4	+4.0	4.9	4.4	15.4
Nov-05	-0.9	+6.4	-0.8	+5.2	-1.0	+8.6	+1.0	+65.5	-6.9	+3.0	5.3	3.4	8.8
Dec-05	-0.5	+7.3	-0.3	+7.3	-0.2	+10.6	-0.8	+74.5	-5.8	+3.8	5.0	5.0	9.6
Jan-06	-0.8	+18.1	-1.4	+18.8	-0.7	+13.7				+3.4	23.1	24.3	16.1
Feb-06	-0.2	+10.6	-0.5	+8.6	-0.4	+13.8	-0.2	+72.2	-5.9	+3.7	10.1	7.1	14.7
Mar-06	-1.0	+9.9	-0.6	+7.8	-1.1	+14.0	-0.5	+66.4	-7.0	+3.0	10.9	7.6	17.3
Apr-06	-1.4	+9.3	-0.8	+10.5	-1.3	+12.1	-1.4	+60.6	-7.5	+2.7	11.5	13.5	16.2
May-06	-0.5	+10.6	-0.2	+9.6	-1.2	+13.1	-1.8	+51.2	-7.1	+2.9	15.9	13.9	21.1
Jun-06	-0.3	+12.0	-1.3	+10.6	-1.7	+14.3	-3.9	+70.2	-6.9	+3.1	13.2	11.2	16.7
Jul-06	-	+13.5	-0.4	+8.6	-0.7	+14.1	-4.3	+67.1	-5.6	+3.9	15.1	7.4	16.1
Mean:	**-0.5**	**+10.3**	**-0.5**	**+9.0**	**-0.6**	**+12.6**	**-1.5**	**+66.7**	**-6.4**	**+3.4**	**11.1**	**9.0**	**14.8**

Table 3.8c: Dual isotope results from River Etherow sites (initial July 2005 samples excluded from mean)

Sample	River Etherow		Rose Clough		Swan Clough		Bulk deposition		Soilwater (H_2O)		Etherow	Rose	Swan
Date	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{18}O$	Theor. Microbial	% atmospheric		
Jul-05			*+4.8*	*+6.0*	*+4.8*	*+5.5*				*+3.7*		*3.6*	*2.8*
Aug-05	+3.2	+6.7	+6.7	+5.0	+6.3	+4.1	-0.5	+66.0	-6.0	+3.7	4.9	2.1	0.6
Sep-05	+4.3	+5.9	+7.3	+4.4	+6.9	+2.4	-0.5	+71.6	-4.9	+4.4	2.2	0.0	-3.0
Oct-05	+4.1	+6.0	+6.8	+4.5	+6.3	+3.7	+2.8	+66.8	-4.9	+4.4	2.6	0.2	-1.1
Nov-05	+2.5	+5.8	+4.5	+4.4	+5.1	+4.8	-2.7	+61.3	-6.5	+3.3	4.3	1.9	2.5
Dec-05	+3.6	+6.9	+3.7	+4.0	+4.8	+5.1	+3.1	+67.0	-7.2	+2.9	6.2	1.7	3.5
Jan-06	+2.7	+8.9	+4.2	+5.4	+5.3	+5.3	+2.3	+69.3		+3.7	7.9	2.5	2.5
Feb-06	+2.5	+8.5	+4.6	+4.9	+5.4	+5.6	+1.4	+67.4	-7.4	+2.7	8.9	3.4	4.5
Mar-06	+3.0	+6.9	+4.3	+4.5	+5.4	+4.9	+0.9	+70.7		+3.7	4.7	1.1	1.7
Apr-06	+0.6	+6.0	-0.3	+7.6	+2.6	+5.3	+1.4	+62.0		+3.7	4.0	6.7	2.8
May-06	+2.5	+8.9	+4.7	+5.9	+5.1	+6.5	+2.0	+60.4		+3.7	9.1	3.9	5.0
Jun-06	+2.6	+8.5	+4.4	+5.6	+4.9	+5.8	-0.2	+66.5	-6.9	+3.1	8.5	4.0	4.2
Jul-06	+2.8	+8.4	+4.0	+7.2	+4.3	+7.3	-4.5	+69.2	-4.1	+4.9	5.5	3.5	3.8
Mean:	**+2.9**	**+7.3**	**+4.6**	**+5.3**	**+5.2**	**+5.1**	**+0.5**	**+66.5**	**-6.0**	**+3.7**	**5.7**	**2.6**	**2.2**

Variation in δ^{15}N-NO_3^- is therefore much greater in bulk deposition than surface waters in both lake catchments. However, annual mean δ^{15}N-NO_3^- values are slightly enriched by 1.0-1.5‰ in surface waters relative to bulk deposition in both sites. There also appears to be a very minor fractionation occurring within the lakes, since outflow δ^{15}N-NO_3^- is slightly depleted relative to inflows by -0.2‰ at Lochnagar and -0.1% at Scoat Tarn. Alternatively, this difference may be due to the direct deposition of NO_3^- to lake surfaces, since bulk deposition NO_3^- has a lower value of δ^{15}N-NO_3^- (see below).

Data from the River Etherow catchment streams show a rather different pattern, with an obvious discrimination between surface water and bulk deposition δ^{15}N-NO_3^- (Fig. 3.14c). Variation in δ^{15}N-NO_3^- is much greater in the surface waters here compared with the lake catchments and values are much more enriched. Values range from +0.6 to +4.3‰ in the River Etherow, -0.3 to +7.3‰ in Rose Clough and +2.6 to +6.9 in Swan Clough, compared with -4.5 to +3.1 in bulk deposition. δ^{15}N-NO_3^- values show much greater discrimination between surface waters and deposition, with annual mean values enriched by +2.4 to +4.7‰ in the streams.

Patterns in δ^{18}O

While δ^{15}N separation between surface waters and deposition is relatively minor, reaching a maximum of +4.7‰ at Swan Clough, there is a very large discrimination in δ^{18}O (Table 3.8; Figs. 3.14a-c). δ^{18}O-NO_3^- is also clearly higher in lake outflows than in inflow streams.

At Lochnagar, bulk deposition δ^{18}O-NO_3^- varies from +48.3 to +82.1‰ (mean +69.6‰) while values range from +3.2 to +20.2‰ in the spring and +13.0 to +22.4‰ in the loch outflow (Table 3.8a; Fig. 3.14a). Using Model 1 to determine the theoretical value of δ^{18}O-NO_3^- for microbially produced NO_3^- (see Task 3.2), the proportion of atmospheric NO_3^- varies from -2.6 to 29.7% in the inflow and 13.6 to 31.9% in the loch. The mean proportions of atmospheric NO_3^- are 12.8% in the spring inflow and 21.4% in the loch outflow. The loch:catchment ratio at Lochnagar is 0.1, indicating that 10% of catchment N deposition lands directly on the loch surface. If it is assumed that there is negligible uptake of deposited NO_3^- within the loch and the spring inflow is representative of all catchment inputs to the loch, then direct deposition alone could account for the difference in atmospheric N of c. 9% between loch inflow and outflow.

At the other lake site Scoat Tarn, bulk deposition δ^{18}O-NO_3^- varies from +51.2 to +74.5‰ (mean +66.7‰) while values range from +6.4 to +18.1‰ in Inflow 1, +3.9 to +18.8‰ in Inflow 2 and +8.6 to +14.8‰ in the lake outflow (Table 3.8b; Fig. 3.14b). These figures correspond to proportions of atmospheric NO_3^- varying from 4.9-23.1% in Inflow 1, 0.8-24.3% in Inflow 2 and 8.8-21.1% in the lake outflow. As at Lochnagar the mean proportion of atmospheric NO_3^- is greater in the lake outflow than the inflow streams. The annual mean values are 11.1% in Inflow 1, 9.0% in Inflow 2 and 14.8% in the lake outflow. Making the same assumptions about direct deposition to the lake surface as at Lochnagar, the lake:catchment area ratio of 0.05 for Scoat Tarn would suggest a 5% increase in the proportion of atmospheric NO_3^- from lake inflow to outflow, which is remarkably close to the observed isotopic data (mean for two inflows = 10.1% cf. outflow value of 14.8%).

The greatest discrimination between bulk deposition and surface water $\delta^{18}O-NO_3^-$ is found at the River Etherow. Values range from +5.8 to +8.9‰ in the Etherow, +4.0 to +7.6‰ in Rose Clough and +2.6 to +7.3‰ in Swan Clough, compared with +60.4 to +71.6‰ in bulk deposition. These values correspond to 2.2-9.1% (Etherow), 0.0-6.7% (Rose Clough) and -3.0 to 5.0% (Swan Clough) atmospheric NO_3^-.

Figure 3.14a: Final NO_3^- dual isotope data for Lochnagar

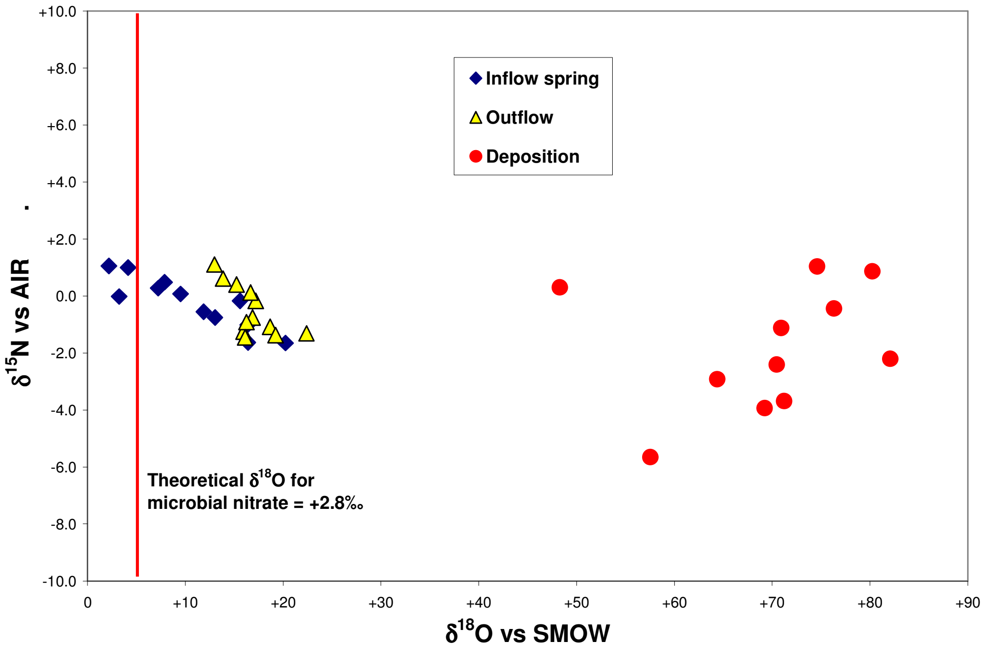


Figure 3.14b: Final NO_3^- dual isotope data for Scoat Tarn

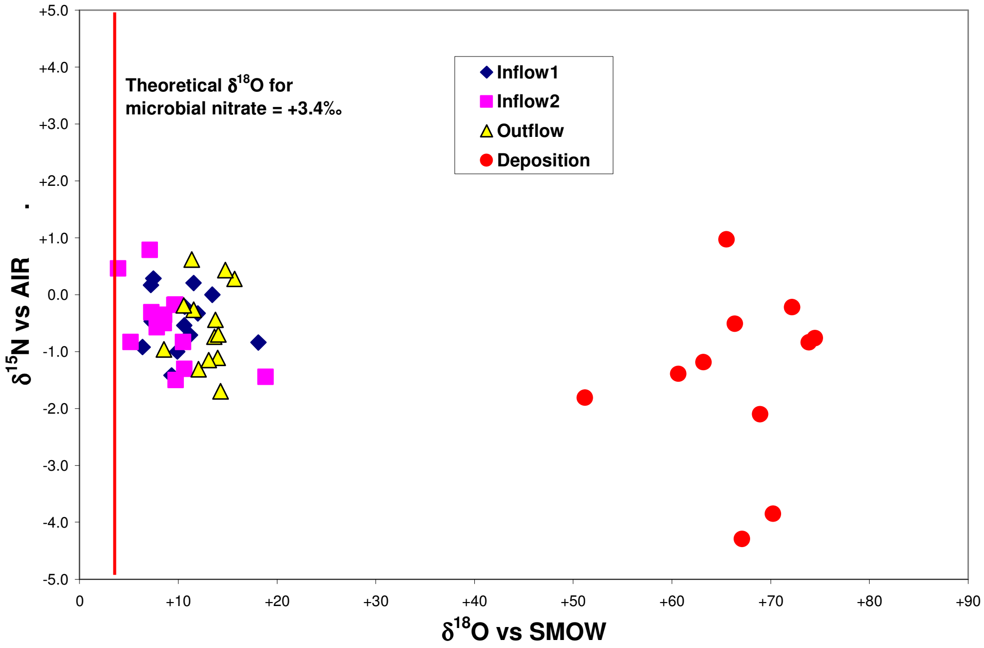
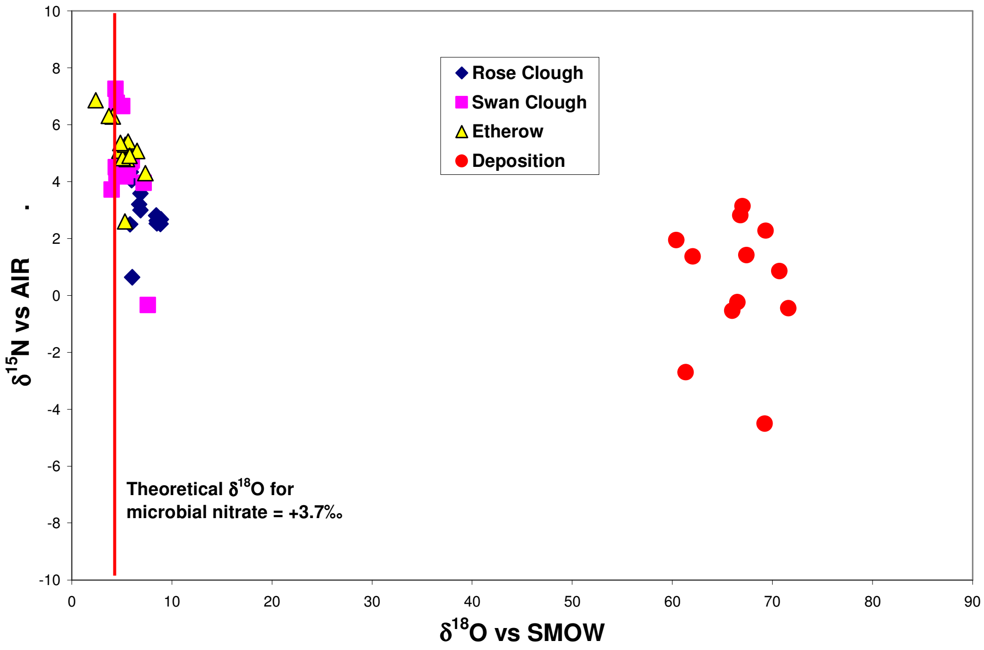


Figure 3.14c: Final NO_3^- dual isotope data for River Etherow



Discussion

The $\delta^{18}O$ data indicate that over 20% of leached NO_3^- in Lochnagar and 15% in Scoat Tarn is of direct atmospheric origin, but a smaller proportion (10-13%) in lake inflows and only 2-6% at the River Etherow sites, contrary to expectations. Therefore most of the leached NO_3^- has been biologically cycled and microbially produced, especially in stream sites, with important implications for modelling N leaching.

An important observation that only become apparent with the full dataset is that there is a strong seasonal pattern in the proportion of leached NO_3^- that derives directly from deposition (Figs 3.15a-c). Hence a bare minimum of quarterly sampling would be required to detect these changes in any new sites where this work may be upscaled under the next phase of the Umbrella. These seasonal patterns will reflect not only a changing influence of direct leaching due to precipitation events, but also a changing relative importance of groundwater inputs which have greater opportunity for microbial cycling due to their much longer residence times. The seasonality is more pronounced in the stream sites than the lakes, reflecting the smoothing effects of lake retention times on seasonal patterns.

Another observation that only became apparent with the full dataset is that some surface water samples show an inverse relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ that is not found in bulk deposition samples, i.e. as the proportion of atmospheric NO_3^- increases (increasing $\delta^{18}O\text{-}NO_3^-$), $\delta^{15}N\text{-}NO_3^-$ decreases. This pattern is strongest in the Lochnagar spring (Fig. 3.16; r^2 =0.79) but $\delta^{18}O\text{-}NO_3^-$ is also a reasonable predictor of $\delta^{15}N\text{-}NO_3^-$ in the Lochnagar ouflow (r^2=0.50), Swan Clough (r^2=0.42), Rose Clough (r^2=0.40) and Inflow 2 at Scoat Tarn (r^2=0.37). There is no relationship between $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ in the River Etherow, Scoat Tarn or Inflow 1 at Scoat Tarn.

Figure 3.15a: Seasonal variation in the proportion of atmospheric (hydrological) NO_3^- at Lochnagar

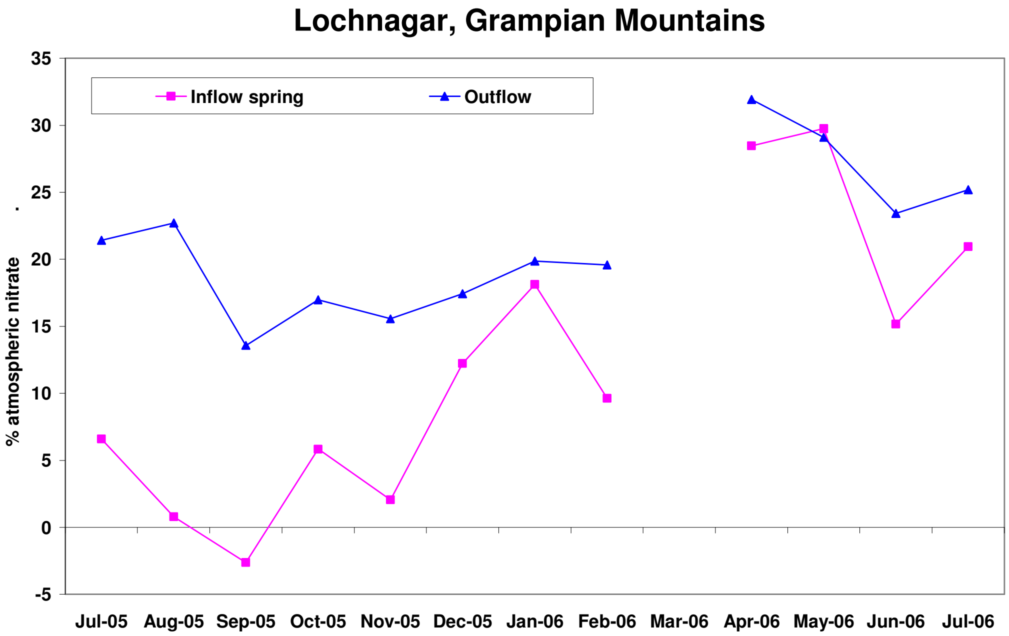


Figure 3.15b: Seasonal variation in the proportion of atmospheric (hydrological) NO_3^- at Scoat Tarn

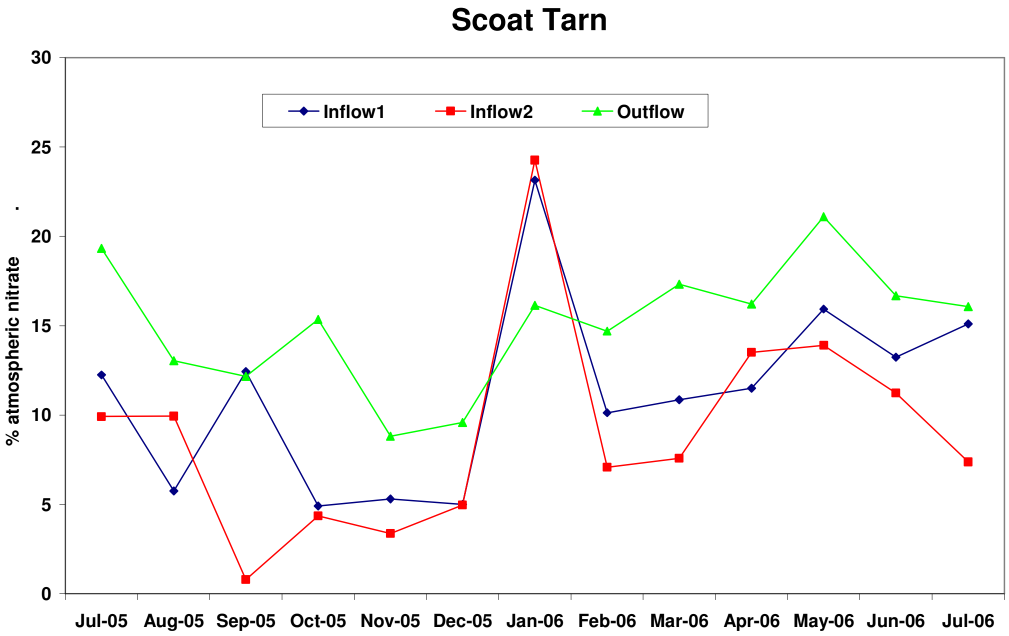


Figure 3.15c: Seasonal variation in the proportion of atmospheric (hydrological) NO_3^- at the River Etherow

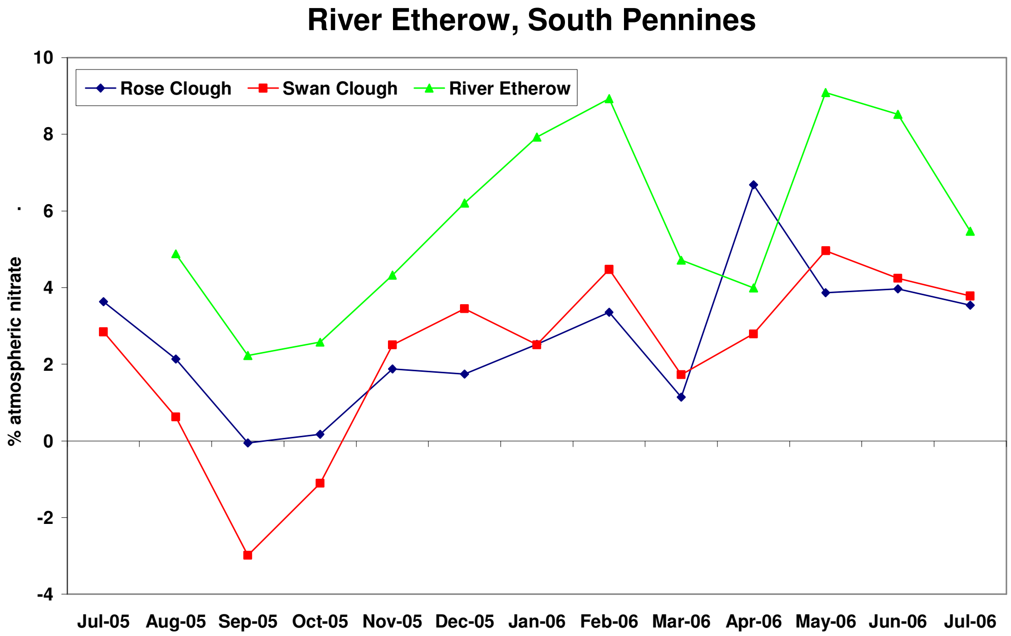
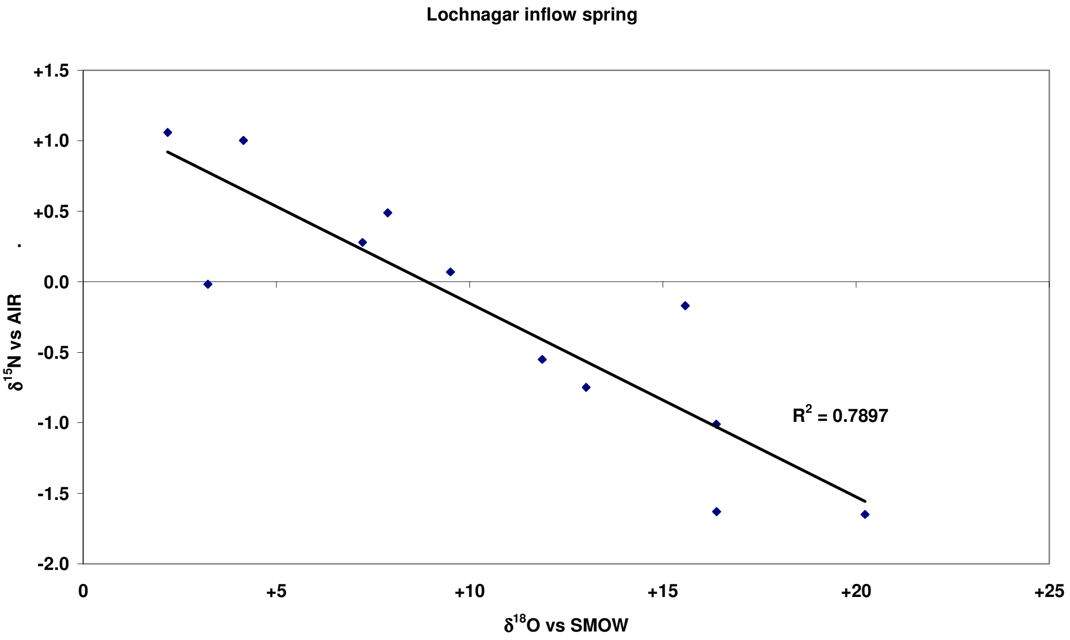


Figure 3.16: Relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in Lochnagar inflow spring



Where this inverse relationship is found it could indicate that the sources of N used in the production of microbial NO_3^- are more enriched in ^{15}N than bulk deposition NO_3^-, so that an increasing proportion of atmospheric NO_3^- reduces the overall $\delta^{15}N\text{-}NO_3^-$ of the surface water sample. However, it is unclear why the same relationship is not found for the adjacent inflow streams at Scoat Tarn, for example, where the proportions of atmospheric NO_3^- are not very different and yet only one shows a clear relationship between $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ (Fig. 3.15b). Further exploration of other data sources (e.g. CLAM soil $\delta^{15}N$ measurements) from the site is required to address this issue.

Overall, this study demonstrates the over-riding importance of rapid uptake and microbial processing of deposited inorganic N in the terrestrial part of catchments, with microbially produced NO_3^- contributing 68-100% of leached NO_3^- on a seasonal basis and 79-97% on an annual mean basis. These results are consistent with the tracer experiment work carried out at the Afon Gwy under Task 3.1. The figures are based on concentrations, which are the most biologically relevant measures, but are likely to be smaller if converted into fluxes, since the greatest proportion of hydrological NO_3^- occurs during the period of higher flows in late winter and spring.

Microbially produced NO_3^- may be considered to reflect "saturation" NO_3^- whereby total N deposition reduces C:N ratios and increases N availability for mineralization and nitrification (see Task 3.5). Hence N deposition is already overwhelming biological demand and leading to N saturation in terrestrial ecosystems (see also N literature review in WP4). This means that for a large proportion of NO_3^- leaching, soil processes are mediating catchment responses to N deposition so that emissions reductions may not result in rapid reductions in the production of microbial NO_3^-. Anthropogenic N that has already accumulated in catchment soils may cause a time lag in responses to changing N deposition. Furthermore, the deposition source of biologically cycled N may be either NO_x or reduced N compounds.

However, a proportion of leached NO_3^- is hydrological, i.e. rapidly leached, unchanged, from wet deposition, reaching 21% of total leaching at Lochnagar. On a seasonal basis this proportion increases to almost a third at Lochnagar and a quarter in the Scoat Tarn Inflow 2. This proportion of NO_3^- may be attributed directly to NO_x deposition, so that emissions reductions should lead to an immediate response in this component of leached NO_3^-. Given that both concentrations and fluxes of NO_3^- are greatest at the time when the direct atmospheric contribution is greatest in late winter and spring, peak values of both would be reduced in proportion to any reductions in NO_x deposition during the period of greatest potential impact on aquatic ecosystems.

This work has demonstrated that for individual catchments it is possible using the dual isotope approach to apportion NO_3^- leaching to microbial sources that may respond very slowly to changes in N deposition and hydrological sources that will respond very rapidly to changes in input. This finding is of major importance for dynamic modelling of future catchment responses to changes in N deposition (see Task 3.1). Models using catchment C pools and soil C:N ratios are required for the greater part of NO_3^- leaching responses but the remainder should respond proportionately to changes in NO_x deposition. Expansion of this approach to other sites would facilitate upscaling and modelling at a national scale in the UK.

Task 3.4: Moss survey of AWMN sites and Task 3.5: C:N survey of AWMN sites

Chris Curtis, Gavin Simpson and James Shilland

Introduction

A recently published paper by Curtis *et al.* (2005) demonstrated a close correspondence between increasing nitrate leaching and declining biomass of moss+lichen with increasing N deposition. While the data were restricted to just four Acid Waters Monitoring Network sites (Allt a'Mharcaidh, Afon Gwy, Scoat Tarn, River Etherow) they strongly suggested a decline in mosses in response to elevated N (and S) deposition. Since mosses and lichens are the most efficient biological compartment for retaining deposited N and converting it into recalcitrant organic N, there could be a causative link between a decline in mosses and increase in nitrate leaching. The aim of Task 3.4 was to test this hypothetical link for sites with existing nitrate leaching data across the UK Acid Waters Monitoring Network by measurements of moss biomass at up to 20 randomly selected points in each catchment.

The same study showed that at least two thirds of N inputs enter the terrestrial N cycle (Curtis *et al.*, 2005) and contribute to increased N content and reduced C:N ratio of soils and vegetation. Soil surface organic matter C:N ratio has been shown to have potential for the prediction of microbial nitrate leaching (i.e. nitrate produced by mineralisation of organic N and subsequent nitrification) via pathway 3 (see Fig. 3.8) in previous DEFRA (Curtis *et al.*, 2004) and NERC (Evans *et al.*, 2006) funded studies. Hence the aim of Task 3.5 was to test the relationships between NO_3^- leaching measures and the C:N ratio of the upper organic soil horizon at the same plots analysed for mosses in Task 3.4.

Methods

Given the major impacts of forestry management practices on NO_3^- leaching over cropping or rotation cycles, there are problems in determining shorter term mass balances for N. Furthermore, the primary purpose of the present study is to determine the major controls on NO_3^- leaching from semi-natural catchments. Hence it was decided to focus resources in these Tasks on the 16 unafforested AWMN catchments (Table 3.9). The AWMN provided long-term NO_3^- concentrations over the period of monitoring (1988-2005) and contemporary with the most recent available CEH Edinburgh modelled deposition data (2002-2005). Runoff data derived from the 30 year mean MORECS 1km dataset were used with concentration data to estimate mean annual leaching flux for 2005 from each of the study catchments (Table 3.9).

Random plot locations for sampling mosses, lichens and soils were generated using digital catchment outlines within ArcMap GIS software (Fig. 3.17). While the intention was to collect 20 random samples, it was recognised from the outset that points identified on maps may turn out to be inaccessible or otherwise impossible to sample in the field, so additional plots were added to the field maps up to a total of 30 locations (40 in catchments with very steep areas). The GIS software provided precise locations to ±1m which were programmed into a portable GPS for use in the field. Plots were located to within just a few metres of the randomly generated grid references (determined by the accuracy of the GPS) using the GPS and a 0.25m^2 quadrat thrown backwards on arrival at the pre-programmed plot location to minimise operator bias. If a plot was found to be inaccessible or inappropriate for sampling (e.g. on disturbed ground) in the field, the next plot in the numerical sequence was used until the requisite number of at least 20 plots had been visited. In such cases the sampling was not truly random, but may be considered random for the accessible parts of the study catchments.

Table 3.9: AWMN study sites with NO_3^- concentrations (μeql^{-1}), leaching and total N deposition fluxes (keq ha^{-1} yr^{-1})

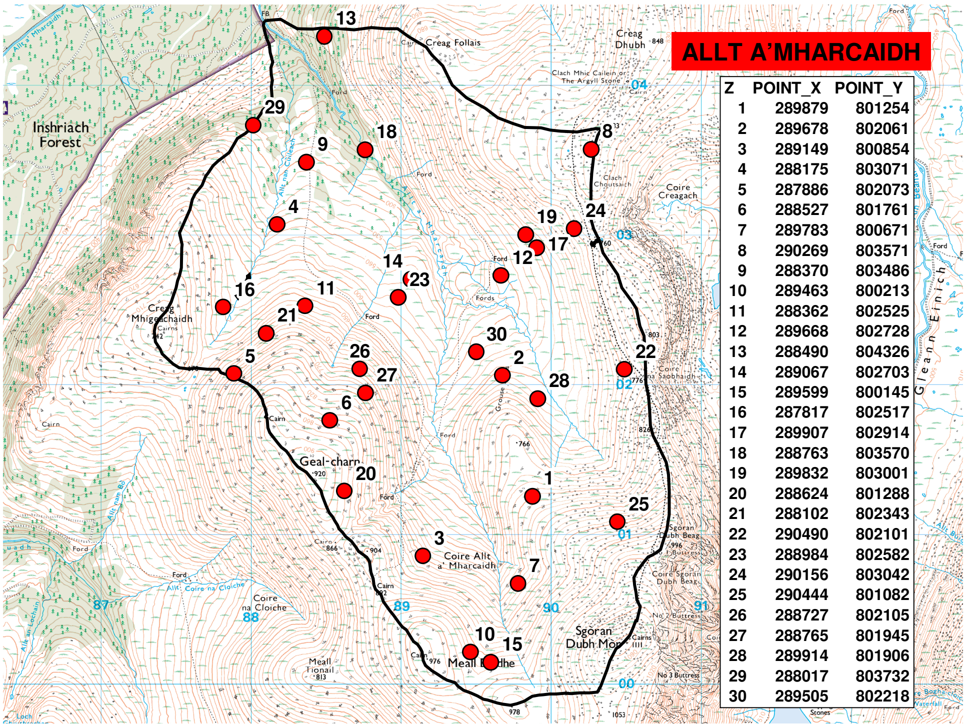
AWMN No.	Site Code	Site Name	Long-term mean		2005 mean values			
			NO_3^-	Q (mm)	Ndep flux	NO_3^-	Leach flux	% leach
1	ARR	Loch Coire nan Arr	2.5	2590	0.48	1.9	0.05	10.1
2	MHAR	Allt a' Mharcaidh	1.4	1062	0.67	1.5	0.02	2.3
4	NAGA	Lochnagar	16.8	1368	1.33	14.8	0.20	15.2
6	TINK	Loch Tinker	3.0	1864	1.58	1.7	0.03	2.0
7	RLGH	Round Loch of Glenhead	7.5	1828	1.57	9.8	0.18	11.4
9	DARG	Dargall Lane	11.4	1724	1.27	17.5	0.30	23.9
10	SCOATT	Scoat Tarn	18.5	2581	1.60	14.4	0.37	23.3
11	BURNMT	Burnmoor Tarn	5.5	2021	1.32	5.2	0.11	8.0
12	ETHR	River Etherow	45.2	1140	2.21	34.6	0.39	17.8
13	LODG	Old Lodge Stream	8.2	403	1.14	7.0	0.03	2.5
15	LAG	Llyn Llagi	7.7	2854	1.26	4.3	0.12	9.7
19	BEAH	Beaghs Burn	3.0	1222	1.17	5.1	0.06	5.3
20	BENC	Bencrom River	30.8	1344	1.63	42.1	0.57	34.6
21	BLU	Blue Lough	25.5	1238	1.66	24.4	0.30	18.3
24	GWY	Afon Gwy	8.4	2039	1.54	6.1	0.13	8.1
26	VNG9402	Loch Coire Fionnaraich	1.8	2572	0.56	2.1	0.05	9.7

Sampling was carried out during late July/early August 2006. All identifiable bryophytes and lichens within the quadrat were collected, bagged and labelled in the field, using shears and scissors to remove other surface vegetation if necessary. In a few cases (Afon Gwy, Llyn Llagi) the quadrat was subsampled due to time constraints. For mosses, a zero value is a valid data point so sampling points within areas of bare rock or scree were included. The only exclusions were areas of standing water or disturbed ground (e.g. eroded paths).

Soil augers were used to obtain O horizon samples to a maximum of 10cm depth and the total depth of the O horizon was determined by augering. While moss data were to be used for deriving a catchment mean biomass value requiring the inclusion of zero values where found, the intention of the soil survey was to determine the mean C:N value for the soils present in the catchment. Therefore where quadrats fell on bare rock, the nearest available soil profile was sampled to maximise the number of samples for analysis.

All samples were dried at 40°C in the laboratory. Dried bryophyte samples were weighed to give total moss biomass per quadrat (0.25m^2). Dried soil samples were sent to NRM Laboratories, Bracknell for analysis of total N and C content (% w/w) from which C:N ratios were calculated. If no O horizon was present for a plot, the surface organic (turf) layer was analysed instead. In some cases where catchments contained large areas of bare rock or scree without soil cover it was not possible to obtain soil or turf samples from all points on the random plot list so the actual number of samples obtained varied from 15 (Coire nan Arr) to 20 (Table 3.10).

Figure 3.17: Example of random plot maps generated in ArcMap GIS and used in the field to locate random quadrats. X (easting) and Y (northing) given in metres.



Z	POINT_X	POINT_Y
1	289879	801254
2	289678	802061
3	289149	800854
4	288175	803071
5	287886	802073
6	288527	801761
7	289783	800671
8	290269	803571
9	288370	803486
10	289463	800213
11	288362	802525
12	289668	802728
13	288490	804326
14	289067	802703
15	289599	800145
16	287817	802517
17	289907	802914
18	288763	803570
19	289832	803001
20	288624	801288
21	288102	802343
22	290490	802101
23	288984	802582
24	290156	803042
25	290444	801082
26	288727	802105
27	288765	801945
28	289914	801906
29	288017	803732
30	289505	802218

Results - Task 3.5: C:N survey of AWMN sites

Summary data for soil %N, %C and C:N ratio are presented in Tables 3.10-3.12. Mean C:N ratio varies from a minimum of 12.15 at Dargall Lane to a maximum of 30.09 at the River Etherow, which is contrary to expectations given the hypothetical inverse relationship between C:N ratio and the NO_3^- leaching data (Table 3.9).

There is a weak, positive relationship between soil %N and total N deposition (Fig. 3.18). However, there is no apparent relationship between C:N ratio and N deposition (data not shown), but a weak inverse relationship between C:N ratio and long-term mean annual runoff from the catchment (Fig. 3.19).

The hypothesised relationship between soil C:N ratio and NO_3^- leaching is not supported by the mean data for all catchments which show no significant relationship (Fig. 3.20). There is also no relationship between C:N ratio and the proportion of N deposition that is leached (Fig. 3.21).

Table 3.10: Soil O horizon %N for 16 AWMN catchments (n_{tot}=296)

Sitecode	Count	Mean	Min	Max	SD
ARR	15	0.82	0.15	2.19	0.66
BEAH	20	1.69	1.20	2.44	0.33
BENC	18	1.77	0.44	2.42	0.60
BLU	17	1.38	0.58	2.51	0.57
BURNMT	19	2.09	1.31	3.13	0.57
DARG	19	1.56	0.10	2.88	0.82
ETHR	20	1.73	0.50	3.36	0.69
GWY	20	1.45	0.32	2.74	0.74
LAG	18	1.89	0.73	3.19	0.73
LODG	20	0.79	0.19	1.92	0.49
MHAR	17	1.14	0.15	1.82	0.48
NAGA	16	1.15	0.13	2.19	0.76
RLGH	20	2.11	0.99	3.41	0.58
SCOATT	18	1.56	0.23	3.42	1.04
TINK	19	1.55	0.50	2.81	0.65
VNG9402	20	1.16	0.12	2.27	0.55

Table 3.11: Soil O horizon %C for 16 AWMN catchments (n_{tot}=296)

Sitecode	Count	Mean	Min	Max	SD
ARR	15	17.00	2.31	43.3	14.51
BEAH	20	43.64	27.40	59.6	7.58
BENC	18	32.87	10.10	52.4	11.47
BLU	17	27.78	16.20	48.4	9.28
BURNMT	19	31.88	14.30	44.3	9.65
DARG	19	18.40	1.36	31.9	9.12
ETHR	20	48.74	9.08	61.3	11.18
GWY	20	21.06	4.51	46.3	12.85
LAG	18	31.07	10.50	49.5	14.18
LODG	20	15.46	2.33	41.3	10.92
MHAR	17	28.14	4.02	43.7	11.84
NAGA	16	26.52	2.28	50	19.42
RLGH	20	37.77	12.20	51.2	10.26
SCOATT	18	21.61	3.61	48.8	13.62
TINK	19	36.82	9.36	59.9	12.77
VNG9402	20	25.87	2.68	47.4	13.54

Table 3.12: Soil O horizon C:N ratio for 16 AWMN catchments (n_{tot}=296)

Sitecode	Count	Mean	Min	Max	SD
ARR	15	19.69	12.53	29.50	4.58
BEAH	20	26.08	16.81	31.07	3.63
BENC	18	18.99	12.44	23.33	3.27
BLU	17	21.51	15.10	36.95	6.07
BURNMT	19	15.74	10.92	33.33	5.46
DARG	19	12.15	9.95	14.80	1.41
ETHR	20	30.09	15.09	42.88	8.07
GWY	20	14.03	10.00	23.50	3.13
LAG	18	16.15	8.81	22.71	4.02
LODG	20	18.91	11.10	31.50	4.70
MHAR	17	25.33	17.81	35.29	4.54
NAGA	16	21.67	14.22	34.01	5.56
RLGH	20	17.98	12.32	23.23	3.04
SCOATT	18	14.37	9.39	21.90	3.53
TINK	19	24.78	11.81	42.32	6.52
VNG9402	20	22.32	10.00	39.50	5.66

However, inspection of the data suggests that peat erosion may be an important factor here - four sites with significant erosion observed during the fieldwork all lie in the top right hand corner of the plots (i.e. high C:N ratio and high NO_3^- concentrations/leaching); River Etherow, Bencrom River, Blue Lough and Lochnagar. If these sites are removed from the plot the relationship is much more convincing and appears to show that both NO_3^- concentrations and proportion leached increase as C:N ratio declines below 15-20 (Figs. 3.22-3.23). However, peat erosion is known to be present in other catchments and future work will aim to better quantify this.

The best relationship between NO_3^- concentrations and measures of N inputs/production is found for N deposition (Fig. 3.24). It appears that deposition is still the major determinant of leaching but preliminary data analysis suggests that catchment specific factors such as vegetation cover and soil type (e.g. eroding peat) are also important. Future work will further explore these catchment-based controls on NO_3^- leaching with a view to improving models to predict leaching under different deposition scenarios.

Figure 3.18: Soil O horizon %N versus total modelled mean annual N deposition for 2002-2005

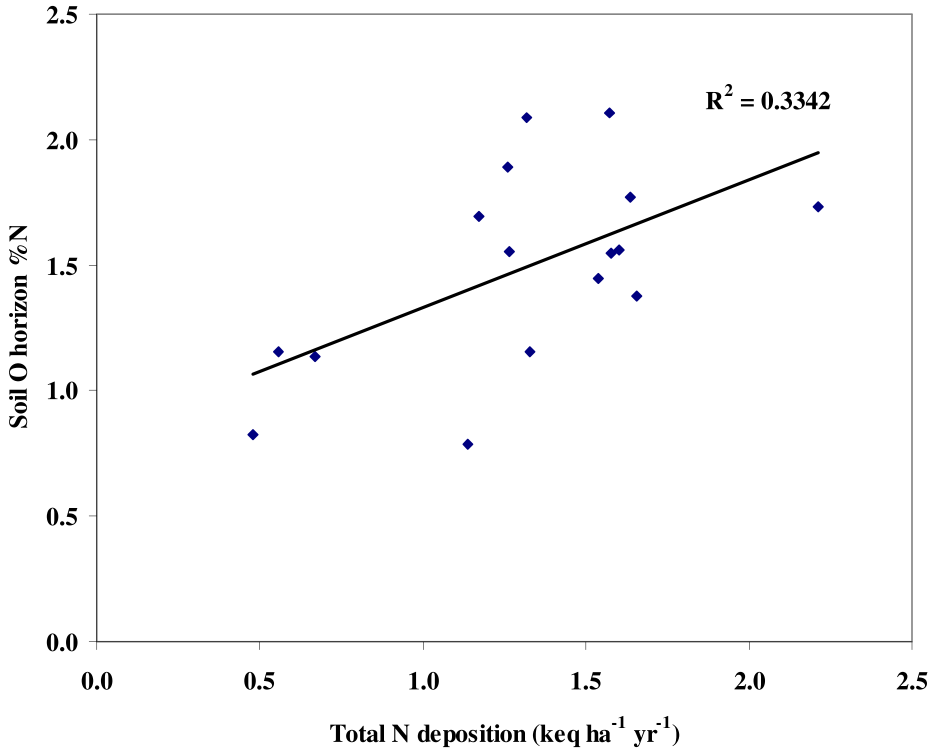


Figure 3.19: Soil O horizon C:N ratio versus long-term mean annual runoff

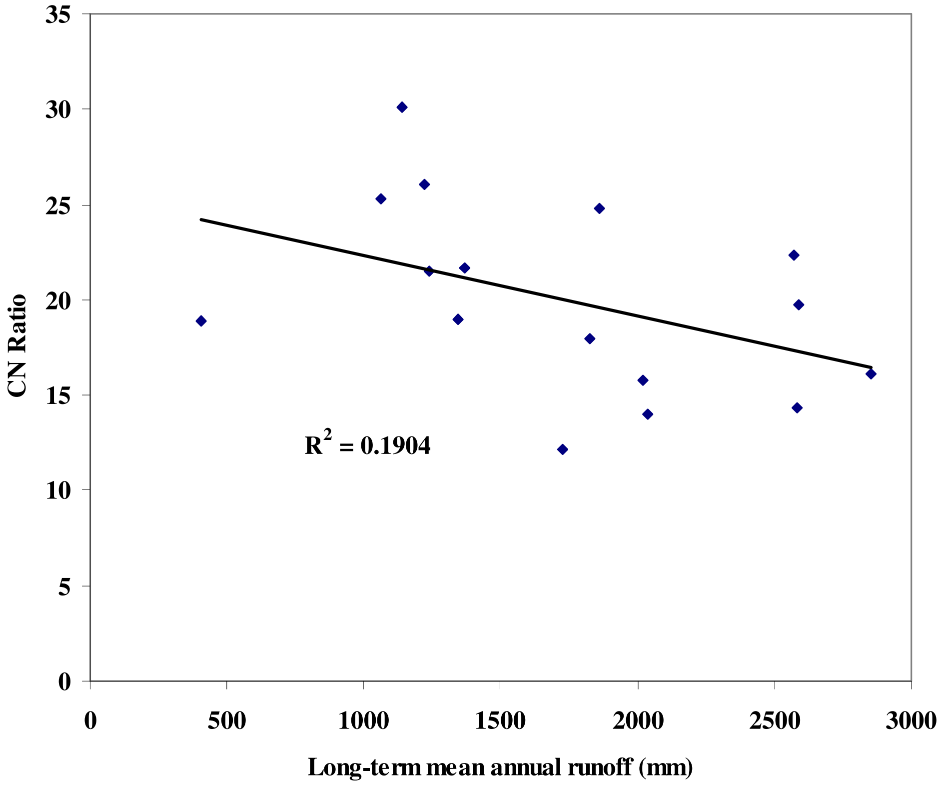


Figure 3.20: Relationship between long-term mean NO_3^- concentrations and soil C:N ratio

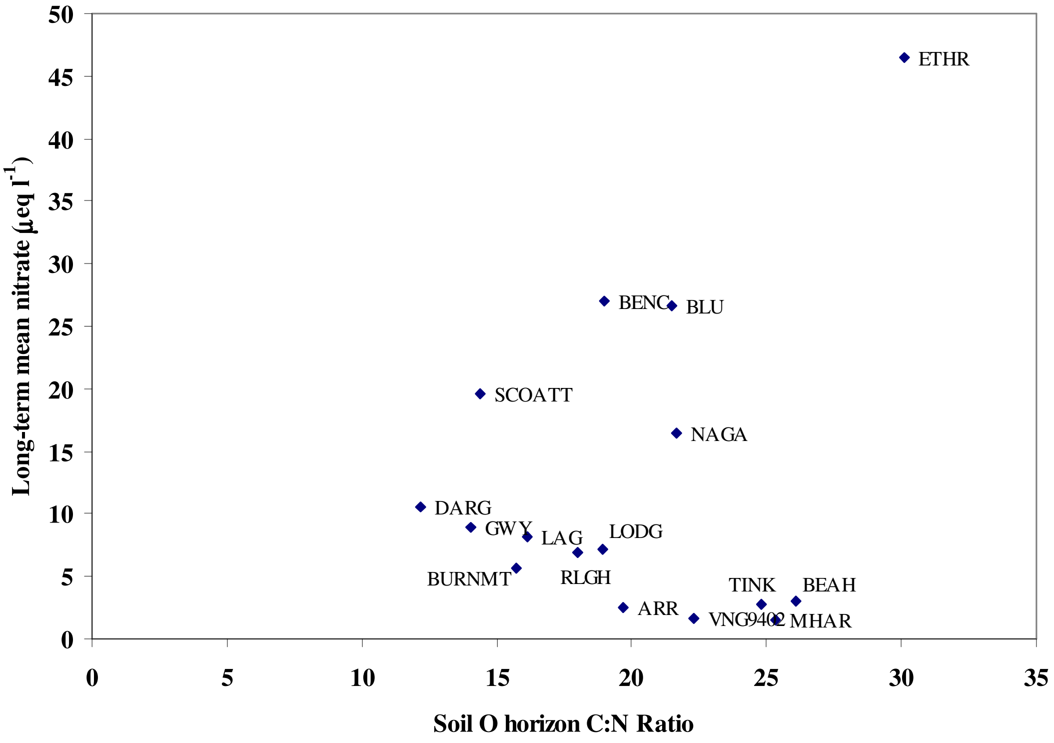


Figure 3.21: Relationship between proportion of N deposition leached and soil C:N ratio

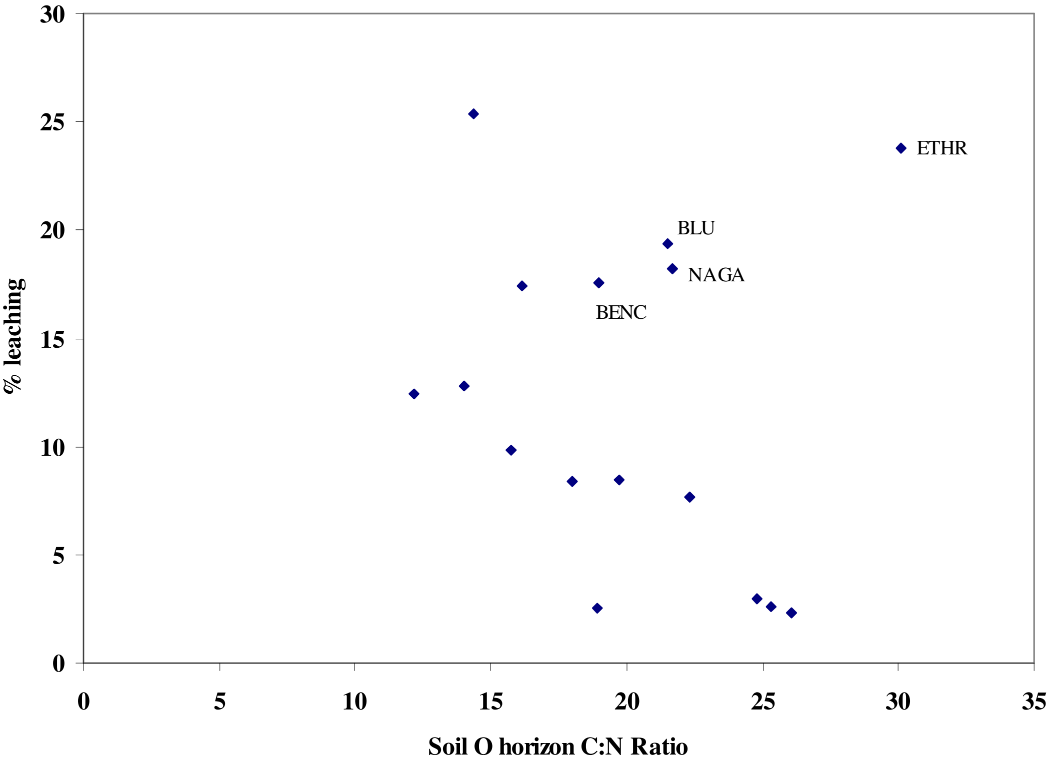


Figure 3.22: Relationship between long-term mean NO_3^- concentrations and soil C:N ratio excluding sites with significant peat erosion (ETHR, NAGA, BENC, BLU)

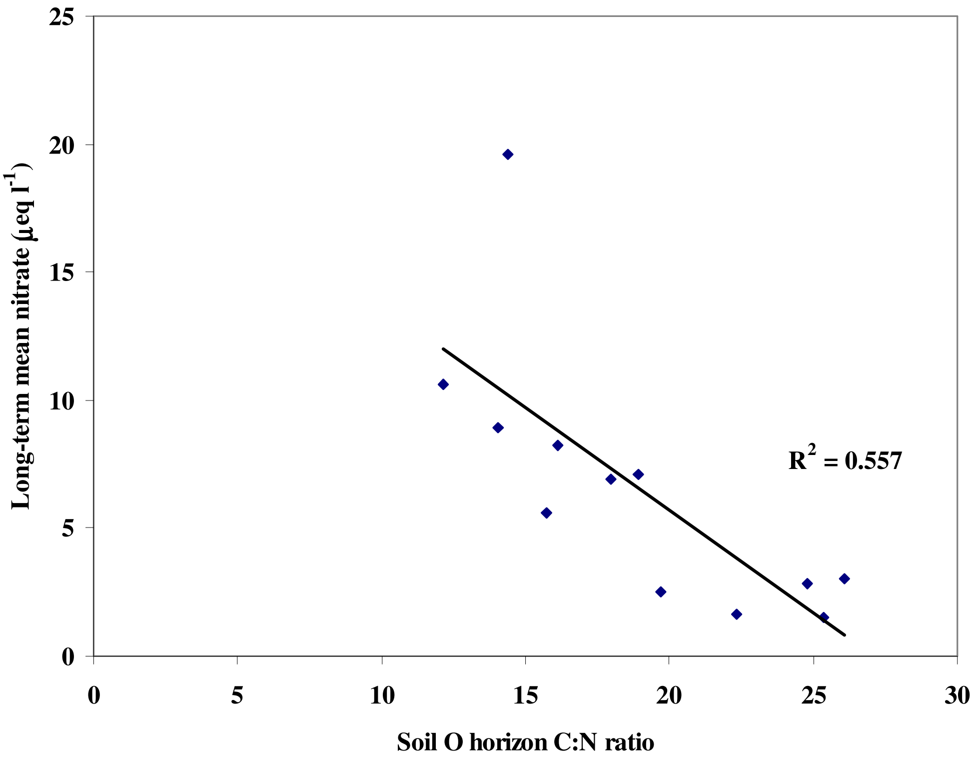


Figure 3.23: Relationship between proportion of N deposition leached and soil C:N ratio excluding sites with significant peat erosion (ETHR, NAGA, BENC, BLU)

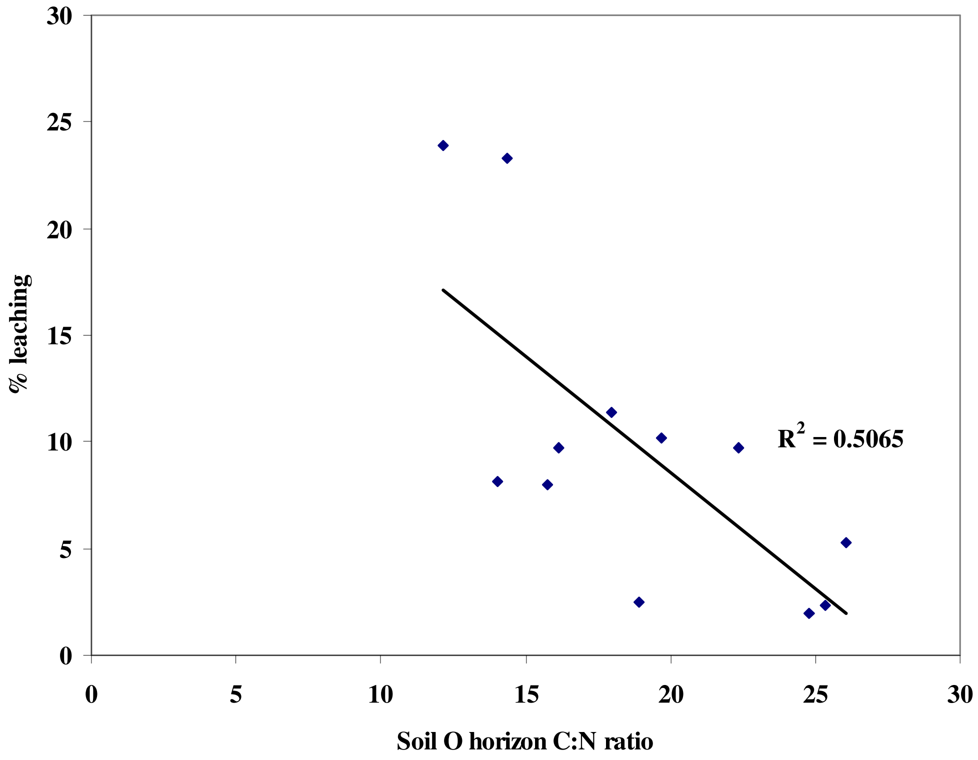
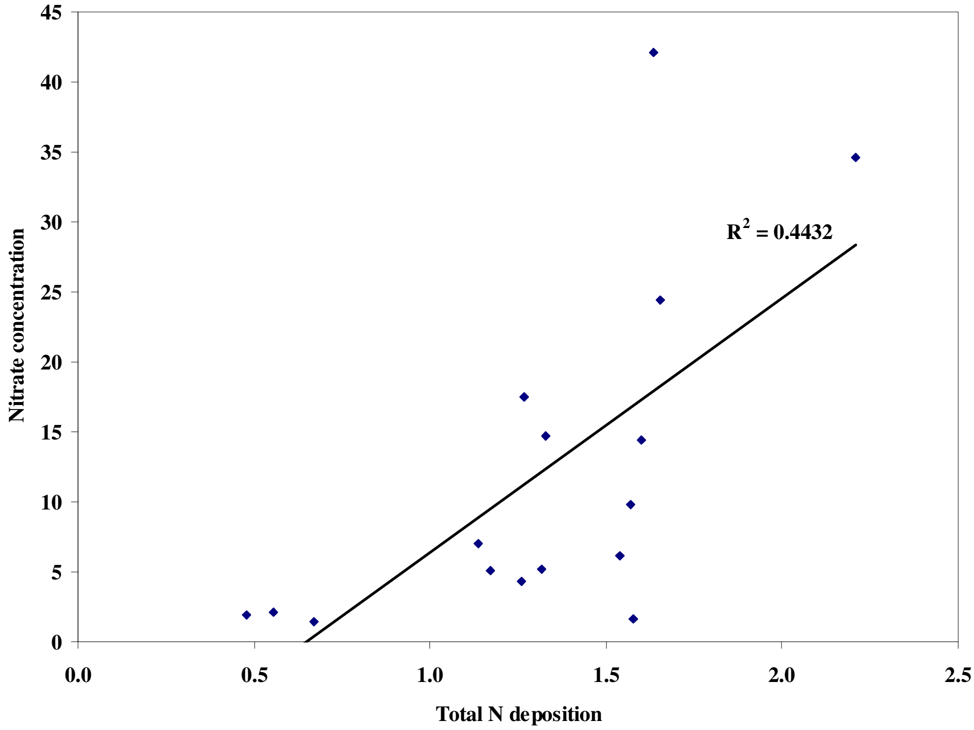


Figure 3.24: Relationship between mean NO_3^- concentration for 2005 and total annual mean N deposition for the period 2002-2005



Results - Task 3.4: Moss survey of AWMN sites

Summary statistics from the moss survey are presented in Table 3.13. Mean biomass varies between 13.4 and 142.1 g dry wt per $0.25m^2$ quadrat. Within-site variation is high, with standard deviations similar to or greater than the mean value at most sites.

Table 3.13: Summary data for bryophyte and lichen biomass (g dry wt per $0.25m^2$) at 16 AWMN catchments ($n_{tot} = 318$)

SITE	Count	Mean	Minimum	Maximum	SD
ARR	19	56.3	0.0	237.2	63.6
BEAH	20	81.4	9.6	291.39	69.3
BENC	15	13.4	0.0	57.6	18.7
BLU	20	40.5	0.4	144.63	38.0
BURNMT	20	20.0	0.4	76.28	24.2
DARG	20	44.9	0.0	241.49	59.7
ETHR	20	29.7	0.0	235.78	55.9
GWY	20	120.9	2.8	710	202.0
LAG	20	37.4	0.0	172.3	46.2
LODG	19	14.1	0.0	121.54	32.0
MHAR	20	142.1	2.8	448.73	108.8
NAGA	18	71.1	8.5	189.21	49.3
RLGH	20	26.6	0.0	247.03	57.1
SCOATT	23	31.1	0.2	151.78	50.5
TINK	20	94.3	1.3	284.22	84.9
VNG9402	24	78.4	2.7	217.05	58.8

There is only a weak relationship between long-term mean NO_3^- concentration or proportion of N deposition leached and moss biomass (Figs. 3.25-3.26). However, if Old Lodge is removed from the plots as an outlier on the basis of being a lowland catchment with much lower precipitation and runoff than all the other sites (see Table 3.9), stronger relationships are observed (NO_3^-, $R^2 = 0.27$; % leaching, $R^2 = 0.43$). This site has one of the lowest values for both proportion of NO_3^- leached and for mean moss biomass.

Figure 3.25: Relationship between mean moss biomass and long-term mean NO_3^- concentrations

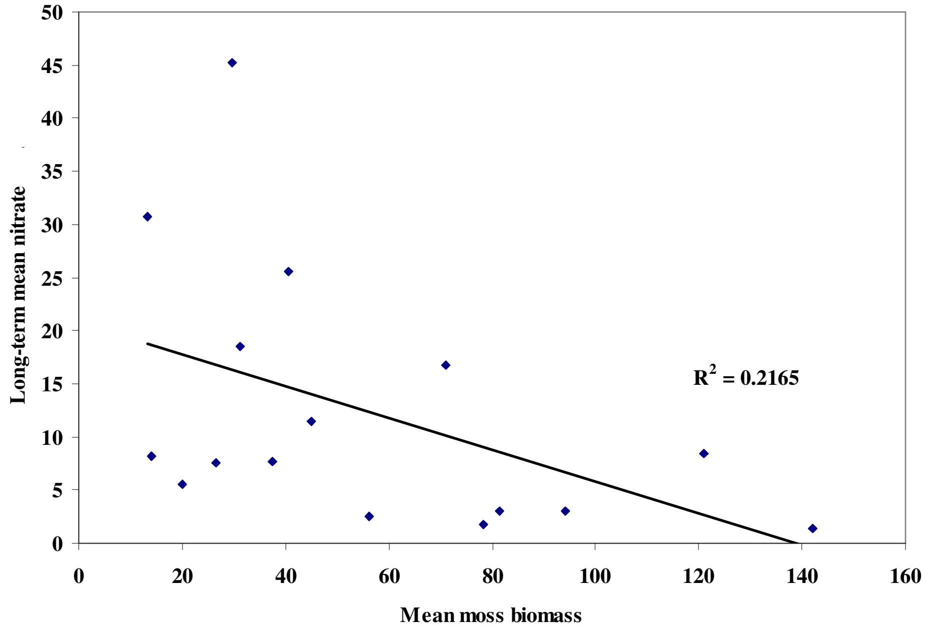
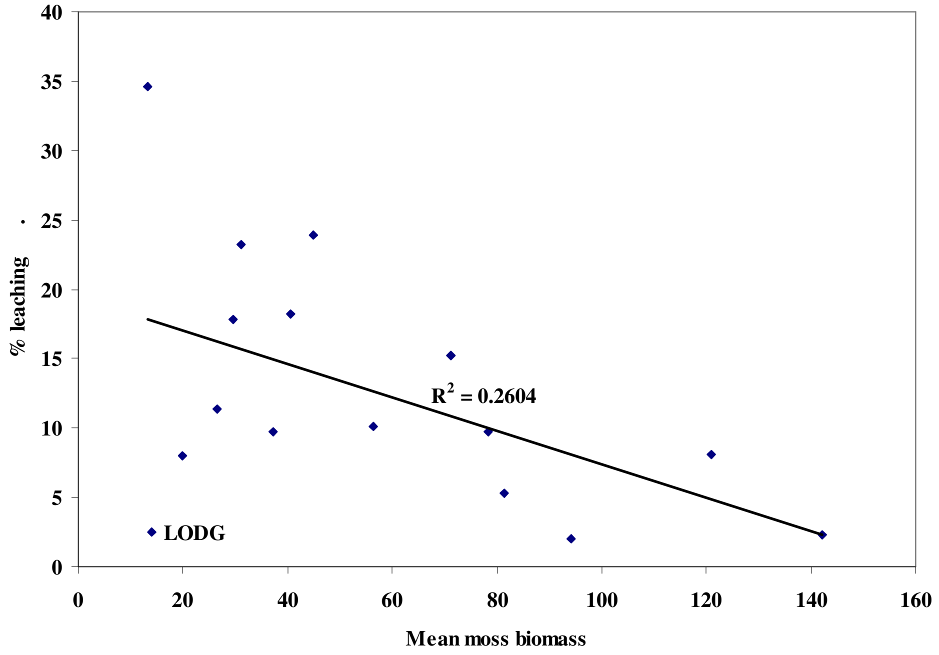


Figure 3.26: Relationship between mean moss biomass and proportion of total N deposition leached as NO_3^-



Statistical analysis and regression modelling

Following the exploratory data analysis of results described above, detailed statistical analysis of organic soil C:N ratio and moss biomass data was performed.

Statistical methods

One-way analysis of variance (ANOVA) was applied to the moss biomass and soil C:N data to determine whether there were significant differences in group mean values for the 16 AWMN sites. "Site" was used as the sole explanatory variable in this case. Among the assumptions of ANOVA is the requirement for homogeneity of variances of the residuals. Plots of residuals versus fitted values and boxplots of residuals stratified by Site showed that there were considerable differences in the variances of the residuals between sites. This was confirmed using Levene's median test for homogeneity of variances.

To confirm the results of the one-way ANOVA, therefore, we used a permutation test to provide a distribution-free assessment of the null hypothesis (H_0) of no difference in the mean moss biomass or C:N ratio of the 16 study sites. We used the F ratio, the ratio of the within group to residual mean squares, as our test statistic. The F ratio is the statistic tested in ANOVA by reference to an F distribution with appropriate nominator and denominator degrees of freedom. Because of the different within group variances in the residuals of the ANOVA, the statistical theory underpinning the calculation of a p-value for the observed F ratio is violated and may therefore be unreliable. Instead, we produced an empirical randomisation distribution for the F ratio by randomly assigning the observations to the 16 sites whilst maintaining the same number of samples per site (group). A one-way ANOVA was applied to this random data and the F ratio recorded. This procedure was repeated 99999 times. The observed F ratio was then compared to the randomisation distribution for F to provide a p-value. The lowest p-value obtainable under this permutation test was 0.00001.

Least squares regression techniques were used to produce models relating water NO_3^- concentration to N deposition, moss biomass and soil C:N. Modelling was performed on the log scale (by a $\log_e$ transformation of water NO_3^- concentration) to stabilise variances and to avoid predicted water NO_3^- concentrations that are less than 0. The mean moss biomass and soil C:N ratio for each site was calculated from the within site replicate samples.

An initial full model was fitted to the data including all first, second and third order terms to allow for interactions between the three predictor variables. This model was then progressively pruned by the sequential dropping of the least important term. The importance of a model term was determined by calculating the change in BIC (Bayes Information Criterion) as a result of dropping each individual term. BIC strongly penalises model complexity and therefore helps to guard against overfitting the model to the data, and lower values of BIC indicate better models. After dropping a term, we also used an F-ratio test to assess the effect of dropping that term on model performance. Terms were sequentially pruned from the model until dropping a term would lead to an increase in BIC or to a significant change in model performance as assessed by the F-ratio test.

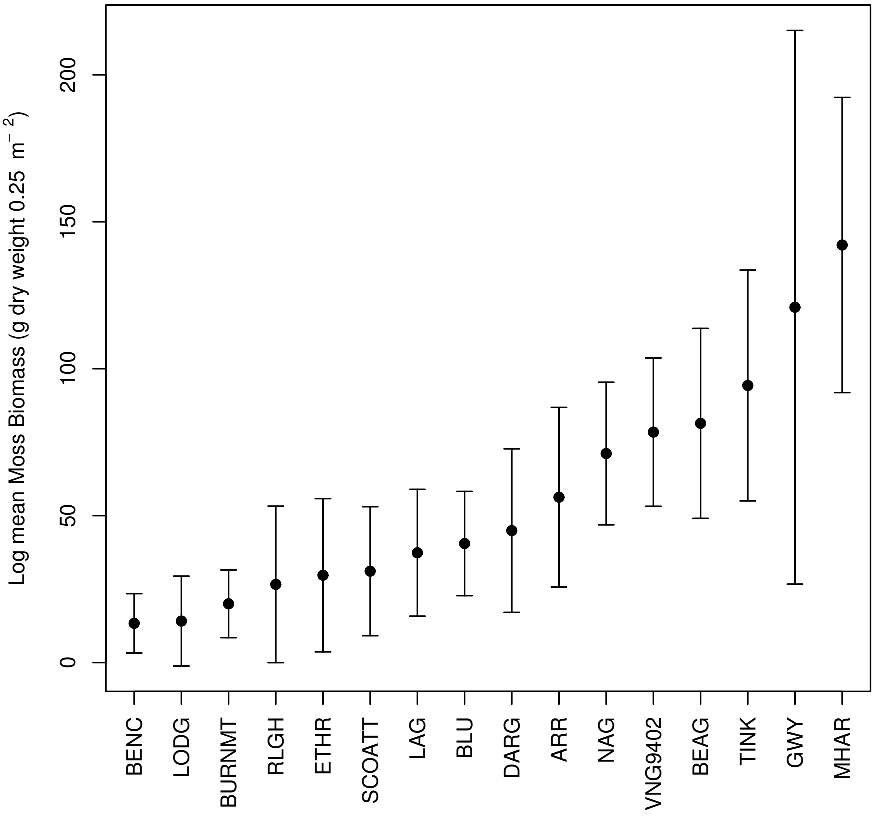
Results

Figures 3.27 and 3.28 show the site means and 95% confidence intervals for moss biomass and soil C:N ratio.

Results of the one-way ANOVA showed that there were large and significant differences between the 16 study sites in both mean moss biomass (F = 4.9671; P = 1.015e-08) and mean C:N ratio (F = 20.114; P < 2.2e-16). Plots of residuals versus fitted values and boxplots of residuals stratified by Site showed that there were considerable differences in the variances of the residuals between sites. This was confirmed using Levene's median test for homogeneity of variances applied to the actual moss biomass (F = 3.0848; P = 0.0001114) and soil C:N ratio (F = 2.8655; P = 0.0003313) data.

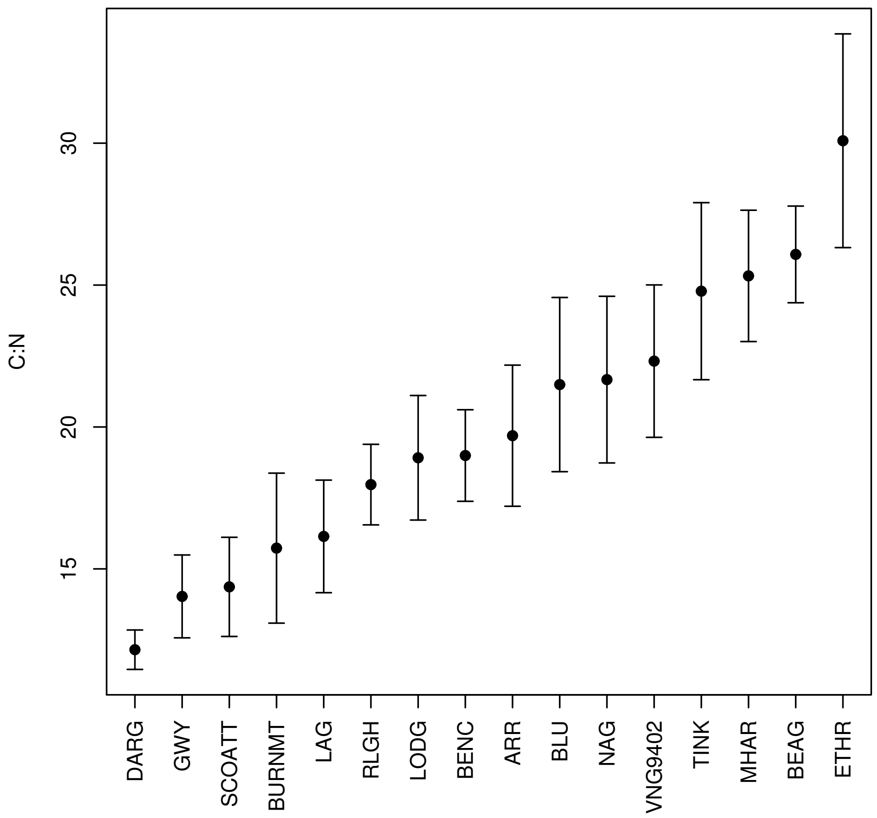
For both moss biomass and soil C:N ratio, the results of the one-way ANOVA were confirmed by the permutation test. In both cases, the permutation p-value for H_0 of no difference in site means was < 0.00001, the lowest obtainable p-value possible for the number of permutation used.

Figure 3.27: Mean moss biomass with 95% confidence intervals for each site



A two component model was selected as the best predictor of water NO_3^- concentration on the basis of BIC and the F-ratio tests. This model contained total N deposition and moss biomass as the two predictor variables. It was ascertained that C:N ratio and second or third order interaction terms did not add additional explanatory power to the model and they were consequently dropped from the full model to produce the final model.

Figure 3.28: Mean soil O horizon C:N ratio with 95% confidence intervals for each site

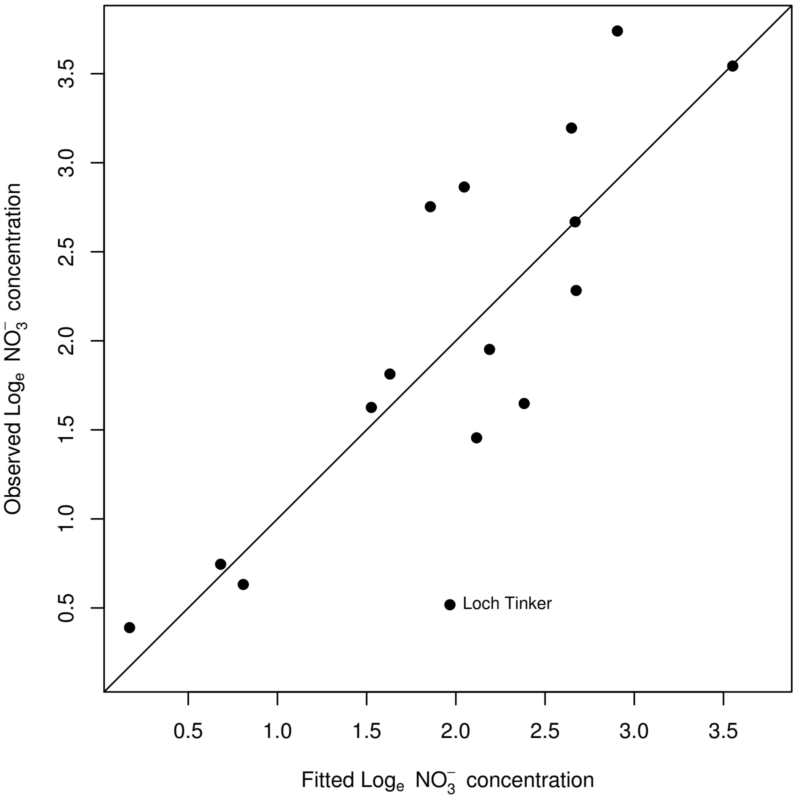


Total N deposition (β = 1.423782, s.e. = 0.418472, t = 3.402, P = 0.00472) is a better predictor of water NO_3^- concentration than moss biomass (β = -0.010594, s.e. = 0.004885, t = -2.169, P = 0.04924). The coefficient (β) for moss biomass is borderline significant at the 95% level, though both BIC and F-ratio tests demonstrate that the model with moss biomass included is significantly better than a model with total N deposition as the single predictor. The effects (β) of the two predictors are of opposite sign, with a unit increase in total N deposition leading to an approximate increase in water NO_3^- concentration of 1.4 $\log_e$ μeq L^{-1} (~4.15 μeq L^{-1}). A unit increase in moss biomass leads to an approximate reduction in water NO_3^- concentration of 0.01 $\log_e$ μeq L^{-1} (~1.0 μeq L^{-1}).

This model explains a large proportion of the variance in water NO_3^- concentrations across the 16 study sites (adjusted R^2 = 0.6127) and is highly significant (F = 12.86, P = 0.0008292).

Figure 3.29 shows observed water NO_3^- concentrations and model fitted values for the 16 study sites. There is a single outlier, Loch Tinker, indicated on Figure 3.29, with a large residual (error), having a fitted NO_3^- concentration of 1.967 $\log_e$ μeq L^{-1} (7.15 μeq L^{-1}) that is much higher than the observed value of 0.52 $\log_e$ μeq L^{-1} (1.68 μeq L^{-1}). The fitted values for the remaining sites all have smaller residuals which are uniformly distributed about the 1:1 line, with no indication of non-constant variance or patterns in the model residuals.

Figure 3.29: Observed versus fitted $\log_e NO_3^-$ using the total N deposition and moss biomass model



Conclusions

The 16 sampled AWMN catchments covering a large N deposition gradient show significant differences between sites in mean organic soil C:N ratio and moss biomass, even with the large within-site variation observed. Exploratory data analysis showed that both C:N ratio and moss biomass are important factors in regulating NO_3^- leaching. The weakness of these relationships does however indicate that other factors are important, probably related to land cover, dominant vegetation type, slope and other catchment variables.

Regression modelling showed that a simple model including only total N deposition and moss biomass terms explains a large proportion of the variation in observed NO_3^- concentrations (61%) while inclusion of the soil C:N ratio term adds no significant explanatory power.

The unexplained variation in NO_3^- concentrations is probably due to a combination of two factors;

1. the accuracy of the data used in modelling, and
2. the presence of other unquantified controls on catchment hydrology and NO_3^- leaching.

The sampling strategy employed in Tasks 3.4 and 3.5 was adequate to determine statistically significant differences between catchments but the small number of sample points provided only an approximate indication of catchment scale C:N ratios and moss biomass, as illustrated by the large confidence intervals in Figs. 3.27 and 3.28. Mean NO_3^- concentrations are based on only 12 monthly samples for streams and four quarterly samples for lake sites; better estimates of annual mean values could be obtained with more frequent sampling. The greatest source of uncertainty is probably associated with the total N deposition data which are based on national scale modelled data on a 5km grid.

The omission of soil C:N ratio from the final regression model was contrary to expectations and it is possible that one reason for the poor relationship between soil C:N ratio and NO_3^- concentrations is the presence of peat erosion in a number of catchments. Future work will include the collection of more detailed catchment scale data on vegetation cover, slope and presence of bare rock which may provide an improved model which explains more of the variation in NO_3^- concentrations between sites. While the model described here explains a relatively high proportion of the variation between sites, the moss biomass variable is not easily upscalable to the national level required for critical load modelling and policy development.

Policy relevance

The relationship between N deposition and NO_3^- leaching demonstrated here provides strong evidence that NO_3^- leaching is driven largely by the total deposition load, even if the controlling processes are only partly understood. Taken together with the findings of the dual isotope study in Tasks 3.2 and 3.3 it is clear that reductions in total N deposition should results in reduced NO_3^- leaching and hence a reduction in the exceedance of acidity critical loads and nutrient N impacts. Moss biomass adds significant explanatory power to the regression model and this work demonstrates that it is possible to identify characteristics which make catchments vulnerable to NO_3^- leaching. Hence it should be possible to further develop catchment models of vulnerability to the adverse effects of N deposition for scaling up across sensitive upland waters across the whole country.

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Curtis, C.J., Emmett, B.A., Grant, H., Kernan, M., Reynolds, B. and Shilland, E. (2005) Nitrogen saturation in UK moorlands: the critical role of bryophytes and lichens in determining retention of atmospheric N deposition. *Journal of Applied Ecology* **42**, 507-517.

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Work package 4: Influence of climate change on the impacts of atmospheric deposition in upland freshwaters

Task 4.1: Literature review of climate impacts on atmospheric pollutant effects, including liaison with Euro-limpacs

Chris Curtis, Don Monteith and Neil Rose

Background

Climate is changing rapidly, beyond the range of previous natural variability. The Inter-governmental Panel on Climate Change has recently reviewed the evidence for climate change and concluded that the increase in global mean air temperature, about 0.6°C since the end of the 19th century, is predicted to intensify during the 21st century. For Europe, regional climate models reveal an additional temperature increase of up to 6°C by the late 21st century and an increase in the number of extreme events, such as droughts, floods and storms. Thus natural ecosystems, already under stress from land-use change and pollution, now face additional pressures from climate change, both directly and through interaction with other drivers of change. Such changes would significantly affect the hydrology, chemistry and ecology of lakes and rivers.

Predictions of the direct effects of climate change on aquatic ecosystems are very complex, and predicting these in combination with other human impacts poses an even greater challenge. Climate change affects the hydrological, physical, chemical and biological characteristics of all freshwaters, and is thereby a key influence on element cycling (nutrients, major ions, DOC, organic pollutants, metals), food webs and biodiversity. A central question is *what are the likely changes to ecosystem structure and functioning that result from climate change that are independent of natural variability and the impact of other stressors?* For lakes a key impact of climate change will be the effect of changing air temperature and wind patterns on the physical structure of the lake water column (e.g. ice cover, stratification and mixing) and consequently on lake chemistry and biology. Additionally, substantial increases in the concentrations of dissolved organic carbon (DOC) have been observed in surface waters draining peaty catchments across north-west Europe and have been attributed to climatic factors such as increased temperature and the frequency and severity of droughts (Freeman *et al.*, 2001).

Despite major reductions in the emission of acidifying compounds, surface water acidification remains a serious threat to Europe's surface waters. Recovery is slow and recovery processes may increasingly be influenced by changing climatic patterns. The key issues are to determine the effects of long-term and seasonal changes in temperature and precipitation on the leaching of nitrogen and dissolved organic carbon (DOC), with subsequent effects on nutrient status and acidity and hence recovery from acidification.

The distribution of persistent organic pollutants (POPs) and metals may also be strongly influenced by future climate change. POPs are subject to a world-wide redistribution because of their volatility and chemical stability. In the last decade some organic pollutants have been observed to be transferred from temperate areas, where they were synthesised and used, to distant cold sites without significant dilution. Natural distillation and condensation processes are temperature dependent and that together with atmospheric transport leads to their deposition and accumulation in high altitude headwaters. A key question is the degree to which future climate change will influence the distribution patterns and mobility of organic pollutants in freshwater systems and lead to changes in the uptake and accumulation of these substances in freshwater food chains.

Within this Task, three literature reviews were carried out to incorporate the following issues:

1) changed rates of N cycling, immobilisation and release in terrestrial and aquatic ecosystems; implications of climate change for N mass balance, storage and transport;
2) trends in TOC (*cf.* TON) - how does this affect atmospheric pollutants? E.g. toxicity of organic pollutants and metals via complexation; changes in ANC_{crit} to protect biota from toxic effects of acidity and aluminium;
3) altered soil erosion (POPs and metals transport) and weathering rates (ANC generation).

The key findings from the literature are considered in the context of sensitive UK surface waters impacted primarily by atmospheric pollutant sources, using the UK Acid Waters Monitoring Network sites as examples.

Introduction - the climate change context

In February 2007 the Intergovernmental Panel on Climate Change (IPCC) issued a summary for policymakers of its Fourth Assessment Report (not yet published in July 2007), including several key statements on the likely causes, nature and degree of climate change in the coming decades. In particular, the IPCC stated the following:

1) The probability that human action, through increasing emissions and atmospheric concentrations of greenhouse gases (GHG), has contributed to recent observed climate change is greater than 90%.
2) Warming of the climate system is unequivocal and demonstrated by increases in global average air and ocean temperatures, widespread melting of snow and ice and rising global mean sea level.
3) Over the 12 year period from 1995-2006, 11 years rank amongst the 12 warmest years found in instrumental records going back to 1850.
4) Projected global warming over the next 20 years under a range of scenarios is c. 0.2°C per decade.
5) The probability of a continued increase in the frequency of hot extreme temperatures, heatwaves and heavy precipitation events is greater than 90%.

While the remit of the IPCC is global, the UK Climate Impacts Programme (UKCIP: www.ukcip.org.uk) provides national climate change scenario data for the UK under a DEFRA funded programme. At a recent conference on "Climate Change and Aquatic Ecosystems in the UK: Science, Policy & Management" (University College London, 16th May 2007), Anna Steynor of UKCIP pointed out that average UK temperatures for the period May 2006 to April 2007 were 0.8°C higher than the average for 1970 to 2000 and that average temperatures for January, February, March and April 2007 were all the highest on record for those months.

The current UKCIP scenarios for the UK (UKCIP02 - published April 2002) indicate that:

1) High summer temperatures will become more frequent, whilst very cold winters will become increasingly rare.
2) Winters will become wetter and summers may become drier throughout the UK.
3) Snowfall amounts will decrease throughout the UK.
4) Heavy winter precipitation will become more frequent.

Outputs from UKCIP include data and maps of predicted change in mean temperature and precipitation on 50km and 5km grids from a baseline of annual average observed values over the period 1961-1990 using official UK Meteorological Office data. Projections are made for decadal spans in the 2020s, 2050s and 2080s using a range of GHG emissions scenarios (low, medium-low, medium-high and high).

On a regional level within the UK, predicted climate changes may be summarized as follows:

1) At the mean annual scale, the greatest temperature increases are found in south-east England, ranging from a best-case rise of 0.5-1.0°C in the 2020s to 2.0-2.5°C by the 2080s under the low emission scenario and a worst-case rise of 1.0-1.5°C in the 2020s to 4.0-4.5°C in the 2080s under the high emissions scenario.
2) The greatest temperature increases are found in the summer, reaching a maximum of >4.5°C in the whole of southern England and Wales under the worst-case high emissions scenario by 2080. While there is seasonal variation in the average increase in temperature, the general spatial pattern of increase is constant, with the greatest increases in south-east England and the smallest increases in north-west Scotland and Northern Ireland. There is therefore a general gradient from the south-east to the north-west.
3) While the whole of the UK is subjected to increasing temperatures, patterns of precipitation change vary between regions, with some increasing and some decreasing on a seasonal basis. Overall on an annual basis precipitation will decrease by a minimum of 0-10% by the 2020s and 2080s under the low emissions scenario and by 10-20% in the 2080s under the high emissions scenario. However, these relatively minor annual mean changes mask much larger seasonal changes in opposite directions.
4) Winter precipitation (December to February) under the low emissions scenario is predicted to increase by 0-10% in most of England and Wales by the 2020s and up to 15-20% in eastern England by the 2080s, with no significant change beyond natural variability in much of Scotland. Under the high emissions scenario the pattern is very similar for the 2020s but increases in winter precipitation of up to 35% will occur on the eastern coast of the UK by the 2080s, with increases of up to 15% also occurring in north-west Scotland.
5) Summer precipitation will decrease across most of the UK, with low emission scenario decreases of up to 10% in Scotland, Northern Ireland and north-west England and 10-20% elsewhere by the 2020s. These figures rise to 20-30% decreases by the 2080s in all regions except the Scottish Highlands where the decline is only 0-20%.

6) In the spring and autumn periods, projected changes in precipitation are generally smaller in magnitude than the summer decreases and winter increases, but vary in direction between regions.

Specific examples of UKCIP projections of change in temperature and precipitation from the 50km grid data are summarized for the UK AWMN sites in Tables 4.1-4.3. While these tables include too many data to summarise, a few key points are detailed below.

Temperature changes

Consistent patterns are found in the sites showing the largest and smallest increases in temperature under all scenarios. Old Lodge stream in south-east England shows the greatest increases, from an annual mean increase of +0.9°C in the 2020s under a low emission scenario to a worst case predicted increase of +4.4°C by 2080 under a high emission scenario. These increases are most pronounced at all sites in the summer, but at Old Lodge range from +1.1°C by the 2020s under a low emission scenario to +5.6°C by the 2080s under a high emission scenario.

The smallest increases in temperature are found in Northern Ireland and north-west Scotland, with annual means ranging from +0.6°C in the 2020s under a low emission scenario to +2.8°C in the 2080s under a high emission scenario.

Precipitation changes

The greatest decreases in precipitation are found in the southernmost AWMN sites of Old Lodge and Narrator Brook, with minor annual declines of 2.2 and 2.8% (low emissions) increasing to 2.7 and 3.4% respectively (high emissions) for the 2020s. While these changes are small overall, they are much greater in summer, from 10-12% declines depending on the emissions scenario. By the 2080s these annual declines in precipitation have increased to 6-7% (low emissions) and under high emissions reach 11% at Old Lodge and 14% at Narrator Brook. These translate into very large decreases in summer precipitation of over 50% in both cases, with most other AWMN sites also experiencing a summer decrease of up to 30-50% by 2080.

While all sites show increases in winter precipitation, only two sites in the same UKCIP grid cell (Lochs Coire nan Arr and Coire Fionnaraich) show mean annual increases in precipitation, albeit of only +0.3% by 2020 under the low emissions scenario. These sites do not show the biggest absolute increase on a seasonal basis - Burnmoor Tarn shows a 5.4% increase in winter - but they show the most consistent increase across seasons (winter, spring and autumn). By the 2080s the increase is still only +1.6% on an annual basis under the high emissions scenario but most sites show a winter increase of 10-25% with the highest value again at Burnmoor Tarn (+26.7%).

Table 4.1: UKCIP projected changes in precipitation (%) and temperature (°C) for 2020 based on 50km grid cells

A: PRECIPITATION CHANGE SCENARIOS FOR 2020

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	-0.1	2.4	1.0	-4.3	0.6	-0.1	2.7	1.1	-4.8	0.6	-0.1	2.7	1.1	-4.8	0.6	-0.1	2.9	1.1	-5.1	0.7
1	ARR	Loch Coire nan Arr	180800	842200	SCO	0.3	1.6	0.7	-2.2	1.3	0.4	1.8	0.7	-2.5	1.4	0.4	1.8	0.7	-2.5	1.4	0.4	1.9	0.8	-2.6	1.5
19	BEAH	Beaghs Burn	317700	429700	IR	-1.4	4.1	-0.5	-8.5	-0.8	-1.6	4.5	-0.5	-9.5	-0.8	-1.6	4.5	-0.5	-9.5	-0.8	-1.7	4.9	-0.6	-10.1	-0.9
20	BENC	Bencrom River	330400	324500	IR	-1.2	4.3	-0.1	-7.9	-1.1	-1.3	4.8	-0.1	-8.8	-1.2	-1.3	4.8	-0.1	-8.8	-1.2	-1.4	5.1	-0.1	-9.4	-1.3
21	BLU	Blue Lough	332700	325200	IR	-1.2	4.3	-0.1	-7.9	-1.1	-1.3	4.8	-0.1	-8.8	-1.2	-1.3	4.8	-0.1	-8.8	-1.2	-1.4	5.1	-0.1	-9.4	-1.3
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	-0.8	5.4	0.2	-8.0	-0.7	-0.9	6.1	0.3	-8.9	-0.8	-0.9	6.1	0.3	-8.9	-0.8	-0.9	6.5	0.3	-9.5	-0.9
5	CHN	Loch Chon	242100	705100	SCO	-1.5	2.6	-0.9	-7.2	-0.6	-1.7	2.9	-1.0	-8.0	-0.7	-1.7	2.9	-1.0	-8.0	-0.7	-1.8	3.1	-1.0	-8.5	-0.7
22	CONY	Coneyglen Burn	264000	388500	IR	-1.4	3.0	-0.5	-7.7	-0.6	-1.6	3.4	-0.6	-8.6	-0.7	-1.6	3.4	-0.6	-8.6	-0.7	-1.7	3.6	-0.6	-9.1	-0.7
9	DARG	Dargall Lane	244900	578600	SCO	-0.4	4.8	0.7	-7.0	-0.1	-0.5	5.3	0.7	-7.8	-0.1	-0.5	5.3	0.7	-7.8	-0.1	-0.5	5.7	0.8	-8.3	-0.1
12	ETHR	River Etherow	411600	399600	ENG	-2.0	4.2	-1.3	-8.7	-2.3	-2.2	4.7	-1.5	-9.7	-2.5	-2.2	4.7	-1.5	-9.7	-2.5	-2.4	5.0	-1.6	-10.3	-2.7
24	GWY	Afon Gwy	282400	285400	WAL	-2.1	4.1	-1.3	-8.8	-2.3	-2.3	4.6	-1.4	-9.7	-2.5	-2.3	4.6	-1.4	-9.7	-2.5	-2.4	4.9	-1.5	-10.4	-2.7
17	HAFR	Afon Hafren	284400	287600	WAL	-2.1	4.1	-1.3	-8.8	-2.3	-2.3	4.6	-1.4	-9.7	-2.5	-2.3	4.6	-1.4	-9.7	-2.5	-2.4	4.9	-1.5	-10.4	-2.7
15	LAG	Llyn Llagi	264800	348400	WAL	-1.7	4.4	-0.6	-8.5	-2.1	-1.9	4.9	-0.7	-9.4	-2.3	-1.9	4.9	-0.7	-9.4	-2.3	-2.0	5.2	-0.7	-10.1	-2.5
8	LGR	Loch Grannoch	254100	569800	SCO	-0.6	4.7	0.4	-7.3	0.0	-0.6	5.3	0.5	-8.2	0.0	-0.6	5.3	0.5	-8.2	0.0	-0.7	5.6	0.5	-8.7	-0.1
13	LODG	Old Lodge Stream	545600	129400	ENG	-2.2	5.1	-0.2	-10.2	-3.7	-2.5	5.7	-0.2	-11.4	-4.1	-2.5	5.7	-0.2	-11.4	-4.1	-2.7	6.1	-0.3	-12.1	-4.4
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	-1.6	2.1	-0.9	-6.0	-1.6	-1.8	2.4	-1.1	-6.7	-1.8	-1.8	2.4	-1.1	-6.7	-1.8	-1.9	2.5	-1.1	-7.2	-1.9
16	MYN	Llyn cwm Mynach	267800	323800	WAL	-2.0	4.2	-1.1	-8.8	-2.2	-2.2	4.7	-1.2	-9.9	-2.5	-2.2	4.7	-1.2	-9.9	-2.5	-2.4	5.0	-1.3	-10.5	-2.7
4	NAGA	Lochnagar	325200	785900	SCO	-0.9	4.3	-0.5	-6.7	-0.8	-1.0	4.8	-0.5	-7.4	-0.9	-1.0	4.8	-0.5	-7.4	-0.9	-1.1	5.1	-0.6	-7.9	-1.0
23	NART	Narrator Brook	256800	69200	ENG	-2.8	4.0	-1.7	-10.5	-3.1	-3.2	4.5	-1.9	-11.7	-3.5	-3.2	4.5	-1.9	-11.7	-3.5	-3.4	4.8	-2.1	-12.5	-3.7
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	-0.4	4.8	0.7	-7.0	-0.1	-0.5	5.3	0.7	-7.8	-0.1	-0.5	5.3	0.7	-7.8	-0.1	-0.5	5.7	0.8	-8.3	-0.1
10	SCOATT	Scoat Tarn	315900	510400	ENG	-0.3	5.1	0.7	-6.7	-0.1	-0.3	5.7	0.8	-7.5	-0.1	-0.3	5.7	0.8	-7.5	-0.1	-0.3	6.0	0.8	-8.0	-0.1
6	TINK	Loch Tinker	244500	706800	SCO	-1.5	2.6	-0.9	-7.2	-0.6	-1.7	2.9	-1.0	-8.0	-0.7	-1.7	2.9	-1.0	-8.0	-0.7	-1.8	3.1	-1.0	-8.5	-0.7
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	0.3	1.6	0.7	-2.2	1.3	0.4	1.8	0.7	-2.5	1.4	0.4	1.8	0.7	-2.5	1.4	0.4	1.9	0.8	-2.6	1.5
					MEAN:	**-1.2**	**3.8**	**-0.3**	**-7.3**	**-1.0**	**-1.3**	**4.2**	**-0.3**	**-8.1**	**-1.1**	**-1.3**	**4.2**	**-0.3**	**-8.1**	**-1.1**	**-1.4**	**4.5**	**-0.4**	**-8.7**	**-1.2**

B: TEMPERATURE CHANGE SCENARIOS FOR 2020

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	0.7	0.5	0.6	0.7	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.8	0.9
1	ARR	Loch Coire nan Arr	180800	842200	SCO	0.6	0.5	0.5	0.6	0.7	0.7	0.6	0.6	0.6	0.8	0.7	0.6	0.6	0.6	0.8	0.7	0.6	0.6	0.7	0.9
19	BEAH	Beaghs Burn	317700	429700	IR	0.6	0.5	0.5	0.6	0.7	0.6	0.5	0.6	0.6	0.8	0.6	0.5	0.6	0.6	0.8	0.7	0.6	0.6	0.7	0.8
20	BENC	Bencrom River	330400	324500	IR	0.6	0.5	0.5	0.7	0.7	0.7	0.5	0.6	0.8	0.8	0.7	0.5	0.6	0.8	0.8	0.7	0.6	0.6	0.8	0.9
21	BLU	Blue Lough	332700	325200	IR	0.6	0.5	0.5	0.7	0.7	0.7	0.5	0.6	0.8	0.8	0.7	0.5	0.6	0.8	0.8	0.7	0.6	0.6	0.8	0.9
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	0.7	0.6	0.6	0.8	0.9	0.8	0.7	0.7	0.9	1.0	0.8	0.7	0.7	0.9	1.0	0.9	0.7	0.8	1.0	1.0
5	CHN	Loch Chon	242100	705100	SCO	0.7	0.5	0.6	0.8	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.9	0.9
22	CONY	Coneyglen Burn	264000	388500	IR	0.6	0.5	0.5	0.7	0.7	0.7	0.5	0.6	0.7	0.8	0.7	0.5	0.6	0.7	0.8	0.7	0.6	0.6	0.8	0.9
9	DARG	Dargall Lane	244900	578600	SCO	0.7	0.5	0.6	0.7	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.8	0.9
12	ETHR	River Etherow	411600	399600	ENG	0.8	0.6	0.7	0.9	0.9	0.8	0.7	0.7	1.0	1.0	0.8	0.7	0.7	1.0	1.0	0.9	0.7	0.8	1.1	1.1
24	GWY	Afon Gwy	282400	285400	WAL	0.8	0.6	0.6	0.9	0.9	0.9	0.7	0.7	1.0	1.0	0.9	0.7	0.7	1.0	1.0	0.9	0.7	0.8	1.1	1.1
17	HAFR	Afon Hafren	284400	287600	WAL	0.8	0.6	0.6	0.9	0.9	0.9	0.7	0.7	1.0	1.0	0.9	0.7	0.7	1.0	1.0	0.9	0.7	0.8	1.1	1.1
15	LAG	Llyn Llagi	264800	348400	WAL	0.7	0.6	0.6	0.8	0.8	0.8	0.6	0.7	0.9	0.9	0.8	0.6	0.7	0.9	0.9	0.8	0.7	0.7	0.9	1.0
8	LGR	Loch Grannoch	254100	569800	SCO	0.7	0.5	0.6	0.7	0.8	0.8	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.9	1.0
13	LODG	Old Lodge Stream	545600	129400	ENG	0.9	0.7	0.7	1.1	1.0	1.0	0.8	0.8	1.3	1.1	1.0	0.8	0.8	1.3	1.1	1.1	0.8	0.9	1.3	1.2
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	0.7	0.5	0.6	0.7	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.9	0.9
16	MYN	Llyn cwm Mynach	267800	323800	WAL	0.8	0.6	0.6	0.9	0.9	0.8	0.7	0.7	1.0	1.0	0.8	0.7	0.7	1.0	1.0	0.9	0.7	0.8	1.1	1.1
4	NAGA	Lochnagar	325200	785900	SCO	0.7	0.5	0.6	0.8	0.8	0.8	0.6	0.7	0.9	0.9	0.8	0.6	0.7	0.9	0.9	0.8	0.7	0.8	0.9	0.9
23	NART	Narrator Brook	256800	69200	ENG	0.8	0.6	0.6	1.0	0.9	0.9	0.6	0.7	1.1	1.0	0.9	0.6	0.7	1.1	1.0	0.9	0.7	0.8	1.2	1.1
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	0.7	0.5	0.6	0.7	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.8	0.9
10	SCOATT	Scoat Tarn	315900	510400	ENG	0.7	0.6	0.6	0.8	0.8	0.8	0.7	0.7	0.9	0.9	0.8	0.7	0.7	0.9	0.9	0.8	0.7	0.7	0.9	1.0
6	TINK	Loch Tinker	244500	706800	SCO	0.7	0.5	0.6	0.8	0.8	0.7	0.6	0.7	0.8	0.9	0.7	0.6	0.7	0.8	0.9	0.8	0.6	0.7	0.9	0.9
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	0.6	0.5	0.5	0.6	0.7	0.7	0.6	0.6	0.6	0.8	0.7	0.6	0.6	0.6	0.8	0.7	0.6	0.6	0.7	0.9
					MEAN:	**0.7**	**0.5**	**0.6**	**0.8**	**0.8**	**0.8**	**0.6**	**0.7**	**0.9**	**0.9**	**0.8**	**0.6**	**0.7**	**0.9**	**0.9**	**0.8**	**0.6**	**0.7**	**0.9**	**1.0**

Table 4.2: UKCIP projected changes in precipitation (%) and temperature (°C) for 2050 based on 50km grid cells

A: PRECIPITATION CHANGE SCENARIOS FOR 2050

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	-0.2	4.3	1.7	-7.6	1.0	-0.2	5.1	2.0	-9.0	1.2	-0.2	5.7	2.3	-10.1	1.4	-0.2	6.8	2.7	-12.1	1.6
1	ARR	Loch Coire nan Arr	180800	842200	SCO	0.6	2.8	1.2	-4.0	2.3	0.7	3.3	1.4	-4.7	2.7	0.8	3.7	1.6	-5.2	3.0	0.9	4.4	1.9	-6.3	3.6
19	BEAH	Beaghs Burn	317700	429700	IR	-2.5	7.3	-0.8	-15.2	-1.4	-3.0	8.6	-1.0	-18.0	-1.6	-3.3	9.7	-1.1	-20.1	-1.8	-4.0	11.6	-1.3	-24.1	-2.1
20	BENC	Bencrom River	330400	324500	IR	-2.1	7.6	-0.2	-14.1	-1.9	-2.5	9.0	-0.2	-16.7	-2.2	-2.8	10.1	-0.2	-18.7	-2.5	-3.4	12.1	-0.3	-22.4	-3.0
21	BLU	Blue Lough	332700	325200	IR	-2.1	7.6	-0.2	-14.1	-1.9	-2.5	9.0	-0.2	-16.7	-2.2	-2.8	10.1	-0.2	-18.7	-2.5	-3.4	12.1	-0.3	-22.4	-3.0
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	-1.4	9.7	0.4	-14.3	-1.3	-1.6	11.5	0.5	-16.9	-1.6	-1.8	12.9	0.6	-18.9	-1.7	-2.2	15.4	0.7	-22.7	-2.1
5	CHN	Loch Chon	242100	705100	SCO	-2.7	4.6	-1.5	-12.8	-1.1	-3.2	5.4	-1.8	-15.1	-1.3	-3.6	6.1	-2.0	-16.9	-1.5	-4.3	7.3	-2.4	-20.3	-1.8
22	CONY	Coneyglen Burn	264000	388500	IR	-2.6	5.4	-0.9	-13.7	-1.1	-3.0	6.4	-1.1	-16.2	-1.3	-3.4	7.2	-1.2	-18.2	-1.4	-4.1	8.6	-1.5	-21.8	-1.7
9	DARG	Dargall Lane	244900	578600	SCO	-0.7	8.5	1.2	-12.4	-0.2	-0.9	10.0	1.4	-14.7	-0.2	-1.0	11.2	1.6	-16.5	-0.3	-1.2	13.5	1.9	-19.8	-0.3
12	ETHR	River Etherow	411600	399600	ENG	-3.6	7.6	-2.4	-15.5	-4.1	-4.3	9.0	-2.8	-18.3	-4.8	-4.8	10.0	-3.1	-20.5	-5.4	-5.7	12.0	-3.7	-24.6	-6.5
24	GWY	Afon Gwy	282400	285400	WAL	-3.7	7.3	-2.3	-15.6	-4.1	-4.3	8.7	-2.7	-18.5	-4.8	-4.9	9.7	-3.0	-20.7	-5.4	-5.8	11.7	-3.6	-24.8	-6.4
17	HAFR	Afon Hafren	284400	287600	WAL	-3.7	7.3	-2.3	-15.6	-4.1	-4.3	8.7	-2.7	-18.5	-4.8	-4.9	9.7	-3.0	-20.7	-5.4	-5.8	11.7	-3.6	-24.8	-6.4
15	LAG	Llyn Llagi	264800	348400	WAL	-3.0	7.8	-1.1	-15.1	-3.7	-3.6	9.2	-1.3	-17.9	-4.4	-4.0	10.3	-1.4	-20.1	-4.9	-4.8	12.4	-1.7	-24.0	-5.9
8	LGR	Loch Grannoch	254100	569800	SCO	-1.0	8.5	0.8	-13.1	-0.1	-1.2	10.0	0.9	-15.5	-0.1	-1.3	11.2	1.0	-17.4	-0.1	-1.6	13.4	1.2	-20.8	-0.1
13	LODG	Old Lodge Stream	545600	129400	ENG	-4.0	9.1	-0.4	-18.2	-6.5	-4.7	10.8	-0.5	-21.5	-7.7	-5.3	12.1	-0.5	-24.1	-8.7	-6.3	14.5	-0.6	-28.9	-10.4
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	-2.9	3.8	-1.7	-10.8	-2.8	-3.4	4.5	-2.0	-12.8	-3.4	-3.8	5.0	-2.2	-14.3	-3.8	-4.6	6.0	-2.7	-17.1	-4.5
16	MYN	Llyn cwm Mynach	267800	323800	WAL	-3.5	7.5	-1.9	-15.8	-4.0	-4.2	8.9	-2.3	-18.7	-4.7	-4.7	10.0	-2.5	-20.9	-5.3	-5.6	12.0	-3.0	-25.1	-6.3
4	NAGA	Lochnagar	325200	785900	SCO	-1.6	7.7	-0.9	-11.9	-1.4	-1.9	9.1	-1.0	-14.1	-1.7	-2.2	10.2	-1.2	-15.7	-1.9	-2.6	12.2	-1.4	-18.9	-2.3
23	NART	Narrator Brook	256800	69200	ENG	-5.1	7.2	-3.1	-18.8	-5.6	-6.0	8.5	-3.7	-22.2	-6.7	-6.7	9.5	-4.1	-24.9	-7.4	-8.1	11.4	-4.9	-29.8	-8.9
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	-0.7	8.5	1.2	-12.4	-0.2	-0.9	10.0	1.4	-14.7	-0.2	-1.0	11.2	1.6	-16.5	-0.3	-1.2	13.5	1.9	-19.8	-0.3
10	SCOATT	Scoat Tarn	315900	510400	ENG	-0.5	9.1	1.3	-12.0	-0.1	-0.5	10.7	1.5	-14.2	-0.1	-0.6	12.0	1.7	-15.9	-0.1	-0.7	14.4	2.0	-19.1	-0.1
6	TINK	Loch Tinker	244500	706800	SCO	-2.7	4.6	-1.5	-12.8	-1.1	-3.2	5.4	-1.8	-15.1	-1.3	-3.6	6.1	-2.0	-16.9	-1.5	-4.3	7.3	-2.4	-20.3	-1.8
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	0.6	2.8	1.2	-4.0	2.3	0.7	3.3	1.4	-4.7	2.7	0.8	3.7	1.6	-5.2	3.0	0.9	4.4	1.9	-6.3	3.6
					MEAN:	**-2.1**	**6.8**	**-0.5**	**-13.0**	**-1.8**	**-2.5**	**8.1**	**-0.6**	**-15.4**	**-2.1**	**-2.8**	**9.0**	**-0.7**	**-17.3**	**-2.4**	**-3.4**	**10.8**	**-0.8**	**-20.7**	**-2.8**

B: TEMPERATURE CHANGE SCENARIOS FOR 2050

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	1.2	0.9	1.0	1.2	1.4	1.4	1.1	1.2	1.5	1.7	1.5	1.3	1.4	1.7	1.9	1.8	1.5	1.7	2.0	2.3
1	ARR	Loch Coire nan Arr	180800	842200	SCO	1.1	0.9	1.0	1.0	1.3	1.2	1.1	1.1	1.2	1.6	1.4	1.2	1.3	1.3	1.7	1.7	1.4	1.5	1.6	2.1
19	BEAH	Beaghs Burn	317700	429700	IR	1.0	0.8	0.9	1.0	1.2	1.2	1.0	1.0	1.2	1.4	1.3	1.1	1.2	1.4	1.6	1.6	1.3	1.4	1.6	1.9
20	BENC	Bencrom River	330400	324500	IR	1.1	0.8	1.0	1.2	1.3	1.3	1.0	1.1	1.4	1.5	1.4	1.1	1.3	1.6	1.7	1.7	1.3	1.5	1.9	2.1
21	BLU	Blue Lough	332700	325200	IR	1.1	0.8	1.0	1.2	1.3	1.3	1.0	1.1	1.4	1.5	1.4	1.1	1.3	1.6	1.7	1.7	1.3	1.5	1.9	2.1
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	1.3	1.1	1.1	1.4	1.5	1.5	1.3	1.3	1.7	1.8	1.7	1.4	1.5	1.9	2.1	2.1	1.7	1.8	2.3	2.5
5	CHN	Loch Chon	242100	705100	SCO	1.2	1.0	1.1	1.4	1.4	1.4	1.1	1.3	1.6	1.7	1.6	1.3	1.4	1.8	1.9	1.9	1.5	1.7	2.1	2.2
22	CONY	Coneyglen Burn	264000	388500	IR	1.1	0.8	0.9	1.2	1.3	1.3	1.0	1.1	1.4	1.5	1.4	1.1	1.3	1.5	1.7	1.7	1.3	1.5	1.8	2.1
9	DARG	Dargall Lane	244900	578600	SCO	1.2	1.0	1.0	1.3	1.4	1.4	1.1	1.2	1.5	1.7	1.5	1.3	1.4	1.7	1.9	1.9	1.5	1.7	2.0	2.3
12	ETHR	River Etherow	411600	399600	ENG	1.4	1.1	1.2	1.6	1.6	1.6	1.3	1.4	1.9	1.9	1.8	1.4	1.5	2.1	2.1	2.2	1.7	1.9	2.5	2.5
24	GWY	Afon Gwy	282400	285400	WAL	1.4	1.1	1.2	1.7	1.6	1.6	1.3	1.4	2.0	1.9	1.8	1.4	1.5	2.2	2.1	2.2	1.7	1.8	2.6	2.5
17	HAFR	Afon Hafren	284400	287600	WAL	1.4	1.1	1.2	1.7	1.6	1.6	1.3	1.4	2.0	1.9	1.8	1.4	1.5	2.2	2.1	2.2	1.7	1.8	2.6	2.5
15	LAG	Llyn Llagi	264800	348400	WAL	1.2	1.0	1.1	1.4	1.4	1.4	1.2	1.3	1.6	1.7	1.6	1.3	1.4	1.8	1.9	1.9	1.6	1.7	2.2	2.3
8	LGR	Loch Grannoch	254100	569800	SCO	1.2	1.0	1.1	1.3	1.4	1.4	1.2	1.3	1.6	1.7	1.6	1.3	1.4	1.8	1.9	1.9	1.5	1.7	2.1	2.3
13	LODG	Old Lodge Stream	545600	129400	ENG	1.6	1.2	1.3	2.0	1.8	1.9	1.4	1.5	2.4	2.2	2.1	1.6	1.7	2.7	2.4	2.5	1.9	2.1	3.2	2.9
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	1.2	0.9	1.1	1.3	1.4	1.4	1.1	1.3	1.6	1.7	1.6	1.2	1.4	1.8	1.9	1.9	1.5	1.7	2.1	2.2
16	MYN	Llyn cwm Mynach	267800	323800	WAL	1.3	1.1	1.1	1.6	1.6	1.6	1.3	1.4	1.9	1.9	1.8	1.4	1.5	2.1	2.1	2.1	1.7	1.8	2.5	2.5
4	NAGA	Lochnagar	325200	785900	SCO	1.2	1.0	1.1	1.4	1.4	1.4	1.2	1.3	1.6	1.6	1.6	1.3	1.5	1.8	1.8	1.9	1.5	1.8	2.2	2.2
23	NART	Narrator Brook	256800	69200	ENG	1.4	1.0	1.1	1.7	1.6	1.6	1.2	1.3	2.0	1.9	1.8	1.4	1.5	2.3	2.1	2.2	1.6	1.8	2.7	2.5
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	1.2	1.0	1.0	1.3	1.4	1.4	1.1	1.2	1.5	1.7	1.5	1.3	1.4	1.7	1.9	1.9	1.5	1.7	2.0	2.3
10	SCOATT	Scoat Tarn	315900	510400	ENG	1.3	1.0	1.1	1.4	1.5	1.5	1.2	1.3	1.7	1.8	1.7	1.4	1.5	1.9	2.0	2.0	1.7	1.8	2.2	2.4
6	TINK	Loch Tinker	244500	706800	SCO	1.2	1.0	1.1	1.4	1.4	1.4	1.1	1.3	1.6	1.7	1.6	1.3	1.4	1.8	1.9	1.9	1.5	1.7	2.1	2.2
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	1.1	0.9	1.0	1.0	1.3	1.2	1.1	1.1	1.2	1.6	1.4	1.2	1.3	1.3	1.7	1.7	1.4	1.5	1.6	2.1
					MEAN:	**1.2**	**1.0**	**1.1**	**1.4**	**1.4**	**1.4**	**1.2**	**1.3**	**1.6**	**1.7**	**1.6**	**1.3**	**1.4**	**1.8**	**1.9**	**1.9**	**1.5**	**1.7**	**2.2**	**2.3**

Table 4.3: UKCIP projected changes in precipitation (%) and temperature (°C) for 2080 based on 50km grid cells

A: PRECIPITATION CHANGE SCENARIOS FOR 2080

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	-0.2	6.1	2.4	-10.8	1.4	-0.3	7.1	2.8	-12.6	1.7	-0.4	10.0	4.0	-17.8	2.4	-0.4	11.8	4.7	-21.0	2.8
1	ARR	Loch Coire nan Arr	180800	842200	SCO	0.8	4.0	1.7	-5.6	3.2	0.9	4.6	1.9	-6.6	3.8	1.3	6.5	2.7	-9.2	5.3	1.6	7.7	3.2	-10.9	6.2
19	BEAH	Beaghs Burn	317700	429700	IR	-3.6	10.3	-1.2	-21.5	-1.9	-4.2	12.1	-1.4	-25.2	-2.2	-5.9	17.0	-1.9	-35.4	-3.2	-6.9	20.0	-2.3	-41.7	-3.7
20	BENC	Bencrom River	330400	324500	IR	-3.0	10.8	-0.2	-20.0	-2.7	-3.6	12.7	-0.3	-23.4	-3.1	-5.0	17.8	-0.4	-33.0	-4.4	-5.9	21.0	-0.5	-38.9	-5.2
21	BLU	Blue Lough	332700	325200	IR	-3.0	10.8	-0.2	-20.0	-2.7	-3.6	12.7	-0.3	-23.4	-3.1	-5.0	17.8	-0.4	-33.0	-4.4	-5.9	21.0	-0.5	-38.9	-5.2
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	-1.9	13.8	0.6	-20.3	-1.9	-2.3	16.1	0.7	-23.7	-2.2	-3.2	22.7	1.0	-33.3	-3.1	-3.8	26.7	1.2	-39.3	-3.6
5	CHN	Loch Chon	242100	705100	SCO	-3.8	6.5	-2.2	-18.1	-1.6	-4.5	7.6	-2.5	-21.2	-1.9	-6.3	10.7	-3.6	-29.8	-2.6	-7.4	12.6	-4.2	-35.1	-3.1
22	CONY	Coneyglen Burn	264000	388500	IR	-3.7	7.6	-1.3	-19.4	-1.5	-4.3	8.9	-1.5	-22.7	-1.8	-6.0	12.6	-2.2	-32.0	-2.5	-7.1	14.8	-2.5	-37.7	-2.9
9	DARG	Dargall Lane	244900	578600	SCO	-1.1	12.0	1.7	-17.7	-0.3	-1.2	14.1	2.0	-20.7	-0.3	-1.7	19.8	2.8	-29.0	-0.4	-2.0	23.3	3.3	-34.2	-0.5
12	ETHR	River Etherow	411600	399600	ENG	-5.1	10.7	-3.3	-22.0	-5.8	-6.0	12.6	-3.9	-25.7	-6.8	-8.4	17.7	-5.5	-36.1	-9.5	-9.9	20.8	-6.5	-42.6	-11.2
24	GWY	Afon Gwy	282400	285400	WAL	-5.2	10.4	-3.3	-22.1	-5.7	-6.1	12.2	-3.8	-25.9	-6.7	-8.5	17.1	-5.4	-36.4	-9.5	-10.1	20.2	-6.3	-43.0	-11.1
17	HAFR	Afon Hafren	284400	287600	WAL	-5.2	10.4	-3.3	-22.1	-5.7	-6.1	12.2	-3.8	-25.9	-6.7	-8.5	17.1	-5.4	-36.4	-9.5	-10.1	20.2	-6.3	-43.0	-11.1
15	LAG	Llyn Llagi	264800	348400	WAL	-4.3	11.0	-1.5	-21.5	-5.3	-5.0	12.9	-1.8	-25.1	-6.2	-7.1	18.2	-2.5	-35.3	-8.7	-8.4	21.4	-2.9	-41.6	-10.3
8	LGR	Loch Grannoch	254100	569800	SCO	-1.4	12.0	1.1	-18.6	-0.1	-1.6	14.0	1.3	-21.7	-0.1	-2.3	19.7	1.8	-30.5	-0.2	-2.7	23.3	2.1	-36.0	-0.2
13	LODG	Old Lodge Stream	545600	129400	ENG	-5.7	13.0	-0.5	-25.8	-9.3	-6.6	15.2	-0.6	-30.2	-10.8	-9.3	21.3	-0.9	-42.4	-15.2	-11.0	25.1	-1.0	-50.0	-18.0
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	-4.1	5.3	-2.4	-15.3	-4.0	-4.8	6.3	-2.8	-17.9	-4.7	-6.7	8.8	-3.9	-25.2	-6.6	-7.9	10.4	-4.6	-29.7	-7.8
16	MYN	Llyn cwm Mynach	267800	323800	WAL	-5.0	10.7	-2.7	-22.4	-5.6	-5.9	12.5	-3.2	-26.2	-6.6	-8.2	17.6	-4.4	-36.8	-9.3	-9.7	20.7	-5.2	-43.4	-11.0
4	NAGA	Lochnagar	325200	785900	SCO	-2.3	10.9	-1.2	-16.8	-2.0	-2.7	12.7	-1.4	-19.7	-2.4	-3.8	17.9	-2.0	-27.7	-3.3	-4.5	21.1	-2.4	-32.7	-3.9
23	NART	Narrator Brook	256800	69200	ENG	-7.2	10.1	-4.4	-26.6	-8.0	-8.4	11.9	-5.1	-31.1	-9.3	-11.8	16.7	-7.2	-43.8	-13.1	-14.0	19.7	-8.5	-51.6	-15.4
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	-1.1	12.0	1.7	-17.7	-0.3	-1.2	14.1	2.0	-20.7	-0.3	-1.7	19.8	2.8	-29.0	-0.4	-2.0	23.3	3.3	-34.2	-0.5
10	SCOATT	Scoat Tarn	315900	510400	ENG	-0.6	12.8	1.8	-17.0	-0.1	-0.7	15.0	2.1	-19.9	-0.2	-1.0	21.1	2.9	-28.0	-0.2	-1.2	24.9	3.4	-33.0	-0.3
6	TINK	Loch Tinker	244500	706800	SCO	-3.8	6.5	-2.2	-18.1	-1.6	-4.5	7.6	-2.5	-21.2	-1.9	-6.3	10.7	-3.6	-29.8	-2.6	-7.4	12.6	-4.2	-35.1	-3.1
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	0.8	4.0	1.7	-5.6	3.2	0.9	4.6	1.9	-6.6	3.8	1.3	6.5	2.7	-9.2	5.3	1.6	7.7	3.2	-10.9	6.2
					MEAN:	**-3.0**	**9.6**	**-0.8**	**-18.5**	**-2.5**	**-3.5**	**11.3**	**-0.9**	**-21.6**	**-3.0**	**-5.0**	**15.9**	**-1.2**	**-30.4**	**-4.2**	**-5.9**	**18.7**	**-1.5**	**-35.8**	**-4.9**

B: TEMPERATURE CHANGE SCENARIOS FOR 2080

AWMN No.	Site Code	Sitename	Easting	Northing	Country	LOW Annual	LOW DJF	LOW MAM	LOW JJA	LOW SON	MLOW Annual	MLOW DJF	MLOW MAM	MLOW JJA	MLOW SON	MHIGH Annual	MHIGH DJF	MHIGH MAM	MHIGH JJA	MHIGH SON	HIGH Annual	HIGH DJF	HIGH MAM	HIGH JJA	HIGH SON
3	ANCC	Allt na Coire nan Con	179300	768800	SCO	1.7	1.3	1.5	1.8	2.0	1.9	1.6	1.7	2.1	2.4	2.7	2.2	2.4	2.9	3.3	3.2	2.6	2.9	3.4	3.9
1	ARR	Loch Coire nan Arr	180800	842200	SCO	1.5	1.3	1.4	1.4	1.9	1.7	1.5	1.6	1.7	2.2	2.4	2.1	2.2	2.4	3.1	2.9	2.5	2.6	2.8	3.6
19	BEAH	Beaghs Burn	317700	429700	IR	1.4	1.2	1.2	1.4	1.7	1.6	1.4	1.5	1.7	2.0	2.3	1.9	2.0	2.4	2.8	2.7	2.3	2.4	2.8	3.4
20	BENC	Bencrom River	330400	324500	IR	1.5	1.2	1.4	1.7	1.8	1.8	1.4	1.6	2.0	2.1	2.5	2.0	2.2	2.8	3.0	3.0	2.3	2.6	3.3	3.6
21	BLU	Blue Lough	332700	325200	IR	1.5	1.2	1.4	1.7	1.8	1.8	1.4	1.6	2.0	2.1	2.5	2.0	2.2	2.8	3.0	3.0	2.3	2.6	3.3	3.6
11	BURNMT	Burnmoor Tarn	318400	504300	ENG	1.8	1.5	1.6	2.0	2.2	2.2	1.8	1.9	2.4	2.6	3.0	2.5	2.6	3.4	3.6	3.6	3.0	3.1	4.0	4.3
5	CHN	Loch Chon	242100	705100	SCO	1.7	1.3	1.5	1.9	2.0	2.0	1.6	1.8	2.2	2.3	2.8	2.2	2.5	3.2	3.3	3.3	2.6	2.9	3.7	3.8
22	CONY	Coneyglen Burn	264000	388500	IR	1.5	1.2	1.3	1.6	1.8	1.8	1.4	1.6	1.9	2.2	2.5	2.0	2.2	2.7	3.0	2.9	2.3	2.6	3.2	3.6
9	DARG	Dargall Lane	244900	578600	SCO	1.7	1.4	1.5	1.8	2.0	1.9	1.6	1.7	2.1	2.4	2.7	2.2	2.4	2.9	3.3	3.2	2.6	2.9	3.4	3.9
12	ETHR	River Etherow	411600	399600	ENG	1.9	1.5	1.7	2.3	2.2	2.2	1.8	1.9	2.6	2.6	3.2	2.5	2.7	3.7	3.7	3.7	3.0	3.2	4.4	4.3
24	GWY	Afon Gwy	282400	285400	WAL	1.9	1.5	1.6	2.3	2.3	2.3	1.8	1.9	2.7	2.7	3.2	2.5	2.7	3.8	3.7	3.8	2.9	3.2	4.5	4.4
17	HAFR	Afon Hafren	284400	287600	WAL	1.9	1.5	1.6	2.3	2.3	2.3	1.8	1.9	2.7	2.7	3.2	2.5	2.7	3.8	3.7	3.8	2.9	3.2	4.5	4.4
15	LAG	Llyn Llagi	264800	348400	WAL	1.7	1.4	1.5	1.9	2.0	2.0	1.7	1.8	2.3	2.4	2.8	2.3	2.5	3.2	3.4	3.4	2.8	2.9	3.8	4.0
8	LGR	Loch Grannoch	254100	569800	SCO	1.7	1.4	1.5	1.9	2.0	2.0	1.6	1.8	2.2	2.4	2.8	2.3	2.5	3.1	3.4	3.3	2.7	2.9	3.7	4.0
13	LODG	Old Lodge Stream	545600	129400	ENG	2.3	1.7	1.8	2.9	2.6	2.6	2.0	2.1	3.4	3.0	3.7	2.8	3.0	4.7	4.3	4.4	3.4	3.6	5.6	5.0
2	MHAR	Allt a'Mharcaidh	288100	804500	SCO	1.7	1.3	1.5	1.9	2.0	2.0	1.6	1.8	2.2	2.3	2.8	2.2	2.5	3.1	3.3	3.3	2.6	3.0	3.6	3.9
16	MYN	Llyn cwm Mynach	267800	323800	WAL	1.9	1.5	1.6	2.2	2.2	2.2	1.8	1.9	2.6	2.6	3.1	2.5	2.7	3.7	3.7	3.7	2.9	3.1	4.3	4.3
4	NAGA	Lochnagar	325200	785900	SCO	1.7	1.4	1.6	1.9	2.0	2.0	1.6	1.9	2.3	2.3	2.8	2.3	2.6	3.2	3.2	3.3	2.7	3.1	3.7	3.8
23	NART	Narrator Brook	256800	69200	ENG	1.9	1.5	1.6	2.4	2.2	2.3	1.7	1.9	2.9	2.6	3.2	2.4	2.6	4.0	3.7	3.8	2.8	3.1	4.7	4.3
7	RLGH	Round Loch of Glenhead	245000	580400	SCO	1.7	1.4	1.5	1.8	2.0	1.9	1.6	1.7	2.1	2.4	2.7	2.2	2.4	2.9	3.3	3.2	2.6	2.9	3.4	3.9
10	SCOATT	Scoat Tarn	315900	510400	ENG	1.8	1.5	1.6	2.0	2.1	2.1	1.7	1.8	2.3	2.5	2.9	2.4	2.6	3.3	3.5	3.5	2.9	3.0	3.9	4.1
6	TINK	Loch Tinker	244500	706800	SCO	1.7	1.3	1.5	1.9	2.0	2.0	1.6	1.8	2.2	2.3	2.8	2.2	2.5	3.2	3.3	3.3	2.6	2.9	3.7	3.8
26	VNG9402	Loch Coire Fionnaraich	194500	849800	SCO	1.5	1.3	1.4	1.4	1.9	1.7	1.5	1.6	1.7	2.2	2.4	2.1	2.2	2.4	3.1	2.9	2.5	2.6	2.8	3.6
					MEAN:	**1.7**	**1.4**	**1.5**	**1.9**	**2.0**	**2.0**	**1.6**	**1.8**	**2.3**	**2.4**	**2.8**	**2.3**	**2.5**	**3.2**	**3.4**	**3.3**	**2.7**	**2.9**	**3.8**	**4.0**

SECTION 1: CLIMATE CHANGE, N CYCLING AND N LEACHING

Chris Curtis

Introduction - the NO_3^- leaching problem

The two key environmental problems associated with NO_3^- leaching into surface waters are acidification and eutrophication. The aim of this review is to describe the potential impacts of climate change on NO_3^- leaching in surface water catchments where the main input of N is through atmospheric deposition. Hence the main focus of the review is on upland catchments where large N inputs from agriculture (fertilizer additions) or major point sources (sewage, urban runoff etc.) are absent, but certain semi-natural lowland aquatic systems may also be included. Elevated NO_3^- concentrations in upland lakes and streams are widespread in the UK uplands where atmospheric deposition is the major source (e.g. Allott *et al.*, 1995).

The contribution of NO_3^- to acidification in surface waters is well established and it will surpass SO_4^{2-} in importance as the major cause of ongoing acidification and critical load exceedance in many UK upland waters within the next five years (Curtis *et al.*, 2005). In some lakes and streams, NO_3^- concentrations already exceed SO_4^{2-} on a seasonal basis.

The effects of N deposition in terms of nutrient cycling and eutrophication are less well established although the current work programme has made major progress in this regard (see Work Package 2). Phytoplankton bioassays were previously used by Maberly *et al.* (2002) to demonstrate that N limitation of production was much more common than previously assumed in upland lakes, and further work in this programme has confirmed this assertion (Task 2.3.2).

An independent strand of evidence for nutrient N effects in upland lakes has come from palaeolimnological studies of lake sediments in remote areas, where changes in N isotopes and fossil plankton assemblages show changes over the last 50-150 years that are not related to acidification. In alpine and arctic lakes, the relative importance of climate change and N deposition in explaining observed changes in lake sediment cores (including bulk sediment $\delta^{15}N$ and assemblages of diatoms and other organisms) is still a contentious issue. While some authors claim that climate alone is likely to be responsible given the timescales of observed changes and remoteness (and hence very low N deposition) of these sites (e.g. Birks *et al.*, 2004; Smol *et al.*, 2005), other authors cite isotopic evidence of changes in N inputs and nutrient cycling (e.g. Wolfe *et al.*, 2001, 2003, 2006; Saros *et al.*, 2003). However, this question is distinct from the issue of how climatic changes may affect NO_3^- leaching in future and is not considered further in this review; development of this work under the current programme is described under Tasks 2.3.1 and 2.3.3. Furthermore it has also been argued that climate change may exacerbate eutrophication through changes in water residence times in lakes (Schindler, 2006) but in-lake processes are beyond the scope of this review.

In pristine or semi-natural forest sites unimpacted by N deposition, total N leaching tends to be dominated by dissolved organic N (DON: Kortelainen *et al.*, 1997; Perakis

& Hedin, 2002) which accounted on average for 80% of N losses in pristine South American Forests, although a smaller fraction of 50% was found for a larger range of American watersheds (Lewis *et al.*, 1999, Scott *et al.*, 2007). It has been argued that in these low N areas, DON leaching may contribute to N limitation in terrestrial ecosystems as the major flux of N from catchments (Hedin *et al.*, 1995; Goodale *et al.*, 2000; Hood *et al.,* 2003). This argument has been described as the "leaky faucet" hypothesis, as DON leaks from what would otherwise be a closed system of internal N cycling. Under elevated anthropogenic N deposition, this closed system under which the only N losses may be through DON changes to a more open system whereby inorganic N, mainly NO_3^-, may leach into surface waters despite its importance as a major nutrient for plants and soil microbes. The severity and temporal patterns of NO_3^- leaching have been described under schemes of N saturation, for example by Stoddard (1994), but first we consider the seasonal nature of NO_3^- leaching and the relevant climatic and biological controls on this process.

Natural temporal variations and climatic controls on NO_3^- leaching

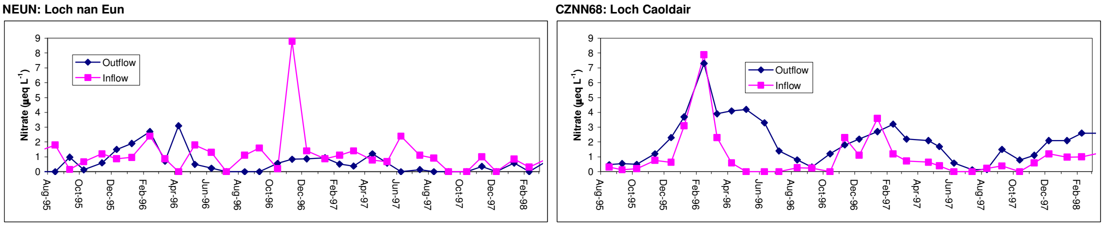
In catchments subject to anthropogenic N deposition, export of inorganic N species, especially NO_3^-, increases in importance relative to the organic N forms exported from more pristine systems. Where NO_3^- leaching from upland catchments is observed, it generally follows a distinct seasonal pattern with maximum concentrations in winter and lowest values in summer (Reynolds et al., 1992, Reynolds & Edwards, 1995; Hessen *et al.*, 1997; Murdoch & Stoddard, 1992; Williams *et al.*, 1996; Clarke *et al.*, 2004), often below detection limits (Fig. 4.1). A widely cited reason for this seasonal pattern is the variation in N demand by terrestrial plants, with maximum uptake during the summer growing season (e.g. Mitchell *et al.*, 1996). Hence the climatic controls on the length of the vegetation growing season are a key determinant of seasonal NO_3^- leaching patterns.

However, the actual processes regulating NO_3^- leaching are more complex than simple plant N uptake and while published studies with direct measurements of biological controls on retention and leaching of N species are very rare for upland systems in the UK, much work has been done in forested watersheds of North America. Microbial processes are very important, with key processes including N uptake, immobilization, mineralization (ammonification) and nitrification. Abiotic processes may also be important and the significance of hydrological controls on NO_3^- leaching is the subject of ongoing research efforts under the DEFRA Freshwater Umbrella programme and elsewhere. Clearly, hydrological controls will be tightly linked to seasonal patterns of rainfall and runoff. While some authors have suggested abiotic immobilization processes may be significant (e.g. Dittman *et al.*, 2007), a recent study ruled this out as an important NO_3^- sink in acid forest soils (Colman *et al.*, 2007).

A large proportion of leached NO_3^- has been microbially produced, as demonstrated in the UK under the Freshwater Umbrella programme using the dual isotope approach, and in other similar studies in Germany and North America (Durka *et al.*, 1994; Spoelstra *et al.*, 2001; Williard *et al.*, 2001; Burns & Kendall, 2002; Campbell *et al.*, 2002; Rock & Mayer, 2004). Hence the seasonal winter increase in NO_3^- leaching commonly observed is not due simply to a decline in biological activity and uptake with decreasing temperatures, allowing a greater proportion of deposited NO_3^- to be leached. Plant N uptake may decline while microbial production of NO_3^- may continue and it is only outside the growing season that this microbial NO_3^- is not immediately utilized by plants. In northern hardwood forests of the USA, NO_3^- loss typically peaks in early spring when microbial mineralization and nitrification can precede tree uptake by fine roots (Groffman *et al.*, 2001a).

Figure 4.1: Seasonal patterns of NO_3^- leaching in lake inflows and outflows across the UK total N deposition gradient (selected CLAG Nitrogen Network sites), 1995-1998

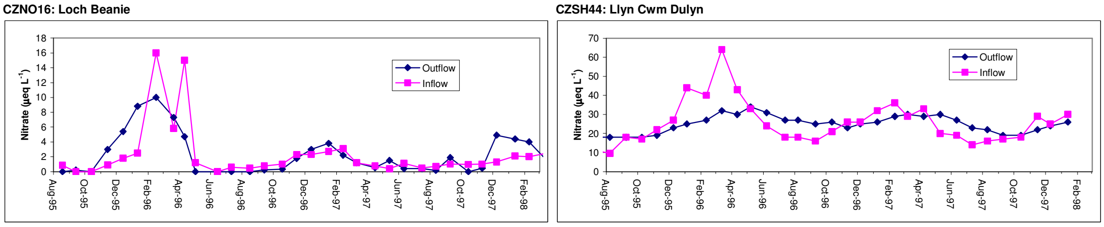
a) North-west and central Scotland, low N deposition (6.5-8.0 kgN/ha/yr)



NEUN: Loch nan Eun

CZNN68: Loch Caoldair

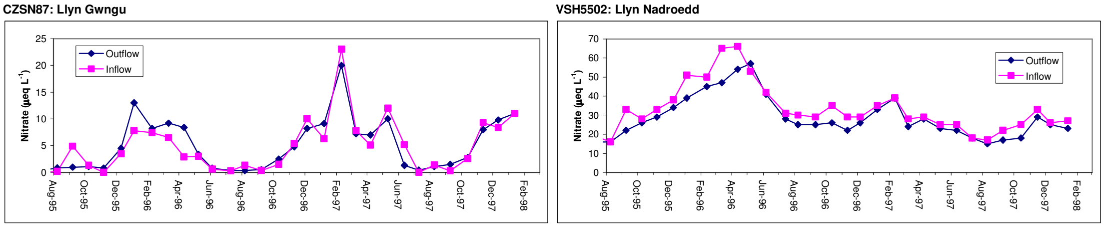
b) Grampian Mountains and north-west Wales, moderate N deposition (12.6-17.6 kgN/ha/yr)



CZNO16: Loch Beanie

CZSH44: Llyn Cwm Dulyn

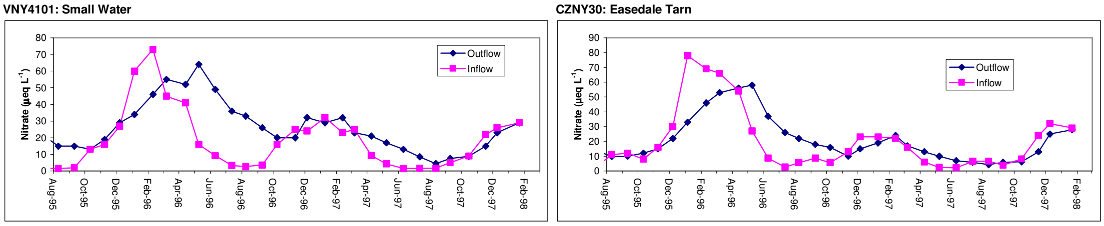
c) Mid-Wales and Snowdonia, high N deposition (20.2-25.3 kgN/ha/yr)



CZSN87: Llyn Gwngu

VSH5502: Llyn Nadroedd

d) Lake District, very high N deposition (37.0-37.4 khN/ha/yr)



VNY4101: Small Water

CZNY30: Easedale Tarn

An elegant conceptual model of NO_3^- leaching from forested catchments was proposed by Creed *et al.* (1996), termed the "N flushing hypothesis". Their argument was that NO_3^-, like DOC, accumulates in the upper soil layers when both soil moisture (the soil saturation deficit) and biological demand are low. During autumn or winter rainfall and spring snowmelt events, the soil saturation deficit decreases and a saturated subsurface layer forms in the soil, providing a hydrological flowpath for flushing of accumulated NO_3^- into surface waters. Some of this NO_3^- rich soilwater drains into deeper groundwaters which may then release NO_3^- into surface waters more slowly throughout the year. This mechanism would be consistent with the seasonal patterns of NO_3^- leaching frequently observed (Fig. 4.1), while the vertical and horizontal transport of NO_3^- in soilwaters will be strongly regulated by biological processes and demand for N. This mechanism is also largely supported by the high proportion of microbial NO_3^- found in isotopic studies

The importance of soil C:N ratio as a control on NO_3^- leaching via nitrification has been the subject of many studies over the last decade and they seem to be well correlated for European forests (e.g. Dise & Wright, 1995; Gundersen *et al.*, 1998; Dise *et al.*, 1998) but less so for moorlands (Curtis *et al.*, 2004). Vegetation type seems to be a key determinant of the relationship between C:N ratio and NO_3^- leaching (Rowe *et al.*, 2006). While cumulative N deposition load as well as vegetation type are important controls on C:N ratio, Yoh (2001) further suggested that climate is a major factor through regulation of the relative importance of mineralization and organic matter accumulation. The inter-relationships between these factors are therefore clearly complex.

Most biological processes are strongly affected by temperature and moisture, including the processes responsible for the retention or release of inorganic N compounds (Reynolds *et al.*, 1992; Reynolds & Edwards, 1995; Williard *et al.*, 1997). The key biological processes responsible for the retention of deposited N inputs are identified in mass-balance critical load models like the simple mass balance (SMB) model for terrestrial critical loads and the related First-order acidity balance (FAB: Posch *et al.*, 1997; Henriksen & Posch, 2001) model for freshwater critical loads. Net biological uptake in biomass, N immobilization in refractory soil organic matter and denitrification are all key processes which are affected by climatic factors. Reynolds and Edwards (1995) explicitly listed the climatic factors which influence NO_3^- leaching from moorland catchments: seasonality, drought, freeze-thaw and snowmelt processes. More direct measures such as temperature, precipitation and discharge may also be added to this list. While these factors are clearly not independent, they may be considered separately as many previous studies have focused on just one or two aspects. Seasonal controls linked to the length of the growing season have already been discussed above.

1. Temperature

Temperature has been correlated both directly and inversely with NO_3^- leaching in a number of studies.

In their study of a Welsh upland stream, Reynolds *et al.* (1992) found a significant within-year inverse correlation between NO_3^- concentration and soil/stream temperature which explained 36-78% of variance. This was attributed to increased terrestrial and in-stream uptake at higher temperatures. Clark *et al.* (2004) found that monthly mean temperature was the best predictor of mean NO_3^- concentration from a suite of catchment and meteorological predictors in upland river catchments of northern Scotland, with an inverse relationship. Kolb (1998) suggested that N sequestration in soil organic matter in the Bavarian Alps was reduced at lower temperature because of a decrease in microbial activity, while higher temperatures accelerate N accumulation.

Conversely, Murdoch *et al.* (1998) found a significant positive relationship between mean annual temperature and NO_3^- leaching at Biscuit Brook in the Catskill Mountains, while Park *et al.* (2003) found the same positive relationship at Arbutus Lake in the Adirondacks. Lawrence *et al.* (2000) suggested that increases in temperature were likely to decrease N retention in forest soils. Joslin and Wolfe (1993) concluded that increasing temperature resulted in higher net mineralization and nitrification rates in high altitude red spruce forest soils, leading to greater release of NO_3^-.

The available literature therefore suggests an inverse relationship between NO_3^- leaching and temperature for moorland or Alpine catchments in European studies and a direct correlation for forested catchments in North American studies. These differences may be due to differing characteristic rates of net mineralization, nitrification and uptake/immobilization in the two types of systems. However, the moorland studies focused on within-year relationships between NO_3^- and temperature (i.e. seasonality) while the longer-term North American studies considered year to year variations which are probably more relevant in the context of global climate warming. On a seasonal basis the North American studies would also show an inverse rather than a direct correlation between NO_3^- and temperature.

2. Precipitation and discharge

Although the effects of precipitation and discharge are sometimes difficult to separate from antecedent conditions (especially drought - see below) most studies report increased fluxes of N species, especially NO_3^-, with increasing water flux.

In many upland catchments NO_3^- yields and sometimes concentrations may increase with stream discharge and/or annual runoff as NO_3^- produced within shallow organic soil horizons is flushed out by lateral flows (e.g. Stottlemeyer & Troendle, 1992; Creed *et al.*, 1996; Andersson & Lepistö, 1998; Lewis *et al.*, 1999; Lewis, 2002; Park *et al.*, 2003; Murdoch & Shanley, 2006; Mitchell *et al.*, 2006, Stottlemyer & Toczydlowski, 2006; Dittman *et al.*, 2007). Higher precipitation in winter was associated with reduced N retention in montane forest of the Bavarian Alps by Kolb (1998). Annual yield of both inorganic and organic N was found to be a linear function of runoff for alpine lakes in the Sierra Nevada of California (Sickman *et al.*, 2001). NO_3^- was mainly mobilized during high flows in a forested Mediterranean catchment, with one single large storm contributing 80% of the annual NO_3^- flux (Bernal *et al.*, 2002).

The relationship between NO_3^- yield and discharge does, however, vary on a seasonal basis (Inamdar *et al.*, 2006). Winter flushing of accumulated total inorganic N pools during the dormant season results in steeper NO_3^- to discharge relationships than summer (Murdoch & Stoddard, 1992). Furthermore, in their study of NO_3^- - discharge relationships over four consecutive storms during a two week period, Murdoch & Stoddard (1992) found decreasing peak concentrations in successive storms and by the third storm, NO_3^- changes with discharge were negligible. The increase in NO_3^-

during high flow events may therefore partly reflect the period of NO_3^- accumulation since the previous high-flow event, i.e. accumulated NO_3^- may be effectively washed out during storm events. In a study comparing the chemistry of lakes in high elevation national parks of the western USA, lower NO_3^- in 1999 relative to 1985 was attributed to rain prior to the earlier sampling which had elevated NO_3^- concentrations (Clow *et al.*, 2003). Murdoch and Shanley (2006) found that for long-term monitoring datasets in the northeastern USA, responses to deposition and climatic change were more rapid at high flows than at low flows when groundwater inputs caused a time lag in response.

Leaching of dissolved organic compounds is also sensitive to water fluxes and long-term changes in precipitation will affect net export of DOC and DON species from catchments. Reductions in precipitation and runoff will result in less productive lakes with clearer water, while increased runoff could result in more coloured waters and higher productivity in lakes (Dillon & Molot, 2005).

3. Drought

Enhanced NO_3^- leaching has been found in many studies to result from re-wetting of soils after periods of drought (e.g. Reynolds *et al.*., 1992; Holloway & Dahlgren, 2001; Bernal *et al.*, 2002; Mitchell *et al.*, 2006) although some studies in European coniferous forests did not find this anticipated response (e.g. Tietema *et al.*, 1997). Watmough *et al.* (2004) found summer drought duration to be the best predictor of NO_3^- leaching in both wetland and lowland groups of streams in central Ontario. Freeman *et al.* (1994) found increased autotrophic biomass but decreased diversity of biofilms and increased NO_3^- under simulated summer drought in a Welsh peatland stream.

Various mechanisms may be involved, including enhanced evaporation which concentrates solutes, vegetation damage which reduces N uptake leading to accumulation in the soil, and moisture stress reducing mineralisation of organic-N followed, during re-wetting, by flushes of mineralisation and nitrification. Leaching may persist into next season because of vegetation damage effects. Alternatively, the relationship between drought and elevated NO_3^- leaching may simply reflect the time factor, whereby mineralisation and nitrification products cannot be flushed out when there is very little movement of water within soils (see discharge section above).

4. Freeze-thaw

Freeze-thaw cycles can lead to increased nitrification and NO_3^- release into streams, possibly through biocidal effects on soil biomass and release of microbial lysis products upon thawing (Mitchell *et al.*, 1996; Fitzhugh *et al.*, 2001). Much experimental work using snow removal has been done in North America demonstrating that, counter-intuitively, climate warming may lead to more frequent soil freezing by reducing the depth and duration of snow cover (e.g. Fitzhugh *et al.*, 2001, 2003a). This phenomenon was summarised in the phrase "colder soils in a warmer world" by Groffman *et al.* (2001a). Even mild freezing above -5°C led to significant later pulses in NO_3^- concentrations following snowmelt relative to control soils where remaining snow cover had prevented freezing throughout the winter.

Several processes may result from soil freezing which may decouple the N mineralization and uptake cycle which is vital for nutrient conservation in forests (Fitzhugh *et al.*, 2001):

a) increased fine root and microbial mortality;
b) physical disruption of aggregates;
c) fragmentation of fresh litter; and
d) reduced N uptake in damaged fine roots and therefore reduced N assimilation.

These processes may result in increased total N leaching as well as NO_3^-. Since fine roots under snowpack have lower mortality than at other times of year and are more sensitive to freezing damage than leaves or twigs, fine root damage was deemed to be a likely major contributor to increased NO_3^- leaching in the snow removal experiments at Hubbard Brook (Fitzhugh *et al.*, 2001; Groffman *et al.*, 2001a). The subsequent experiments showed that while important, the other factors listed above are also significant and that the frequency of soil freezing may be a key determinant of N losses from freeze/thaw action (Groffman *et al.*, 2001b). Later studies confirmed that the NO_3^- peak following an ice-storm in 1998 was due primarily to reduced plant uptake (Dittman *et al.*, 2007).

Despite the apparently clear links between soil freezing and NO_3^- leaching described above, other studies have not found soil freezing to be a reliable predictor of NO_3^-. Measures of soil freezing were not correlated with NO_3^- leaching from upland streams in Ontario, even though cumulative frost depth was a predictor of NO_3^- in wetland streams (Watmough *et al.*, 2004). Furthermore, analysis of time-series data from the Hubbard Brook site of the snow removal experiments above found that the relationship between soil freezing and NO_3^- release held from 1970 to 1989, explaining 47% of short-term NO_3^- variability, but this relationship weakened significantly from 1990 to 1997 (Fitzhugh *et al.*, 2003b). The authors therefore concluded that the future impacts of warmer climate and changes in snow cover were unclear.

5. Snowmelt

The importance of snowmelt in annual leaching fluxes of NO_3^- and other solutes has long been recognised. Grennfelt and Hultberg (1986), writing about the potential water quality problems associated with future increases in NO_3^- leaching, optimistically suggested that it was only likely to become a problem during periods of snowmelt.

In mountain lakes, the highest concentrations of acid anions have often been found following snowmelt (e.g. Williams *et al.*, 1993, 1995, 1996; Johnson *et al.*, 1997; Sickman *et al.*, 2001) and the same pattern has been observed in forested catchments in North America (e.g. Inamdar *et al.*, 2006). In managed forest catchments in Finland, half of the annual runoff and leaching occur during the spring high flow period which represents only 10-15% of the year (Kortelainen *et al.*, 2006). Peak snowmelt runoff has also been found to account for flushing of regenerated nutrients (N and P) from conifer swamp wetlands in Canada (Devito & Dillon, 1993).

Nitrate flushes after snowmelt have been attributed to the sudden release of atmospherically derived N compounds from the snowpack, but it may be difficult to separate this process from the freeze-thaw effects above, plus hydrological changes in leaching pathways (e.g. Schaefer & Driscoll, 1993; Williams *et al.*, 1995; Sullivan *et al.*, 1997; Brooks *et al.*, 1999; Campbell *et al.*, 2000). Johannessen and Henriksen (1978) found that the first component of meltwater may contain a disproportionately large amount of total solutes, with up to 80% of SO_4^{2-} and NO_3^- released during melting of the first 30% of the snowpack. Stottlemyer and Toczydlowski (2006) suggested that the proportion of annual runoff transported as shallow lateral flow in the uppermost 25cm of soils could be a key determinant of solute fluxes in snowmelt dominated catchments.

Many studies of the biogeochemical importance of snowmelt have been carried out in alpine catchments in North America and Scandinavia. During snowmelt in an alpine/subalpine ecotone in the Rocky Mountains, alpine soils were found to be a net source of DIN while subalpine soils were a net sink (Heuer *et al.*, 1999; Hood *et al.*, 2003). The links between snowpack depth and duration, snowmelt and leaching of N species have even been used to classify catchment snow regimes into four zones (Brooks & Williams, 1999).

The key determinant of the importance of snowmelt in NO_3^- leaching fluxes is comparable to drought - the period of accumulation of NO_3^- in the snowpack (and also in soils under the snow) which is followed by rapid flushing and/or elution when snowmelt occurs (*cf.* storm events after drought).

Effects of climate change on patterns of NO_3^- leaching and N speciation

Climate exerts a strong influence on the retention of atmospherically deposited N, with the highest retention occurring under cold and dry conditions (Grant & Scheeringa, 2002). Climatic extremes that limit primary productivity and microbial activity are key determinants of N retention and release (Campbell *et al.*, 2000). The individual controls and processes responsible for these links have already been discussed above.

Interpretation of climatic interactions with patterns of NO_3^- leaching is complicated by the presence of climatic oscillations superimposed on the general trend of climate warming. Monteith *et al.* (2000) proposed a possible link between climatic oscillations, described by the North Atlantic Oscillation (NAO) Index, and temporal variations in NO_3^- leaching on a roughly decadal timescale in the UK Acid Waters Monitoring Network, while Park *et al.* (2003) proposed a similar decadal pattern in the northeastern USA. The interactions between the NAO and NO_3^- are not always in the same direction, however. George *et al.* (2004) found a negative correlation between the NAO and NO_3^- in Windermere, UK, attributed to enhanced terrestrial N uptake in mild winters, while the correlation was positive at Paajarvi in Finland because of an earlier flush of NO_3^- rich meltwater from the catchment.

Jennings and Allott (2006) found no such relationship with the NAO for lakes in south-west Ireland but did find a positive relationship with the position of the Gulf Stream as measured by the Gulf Stream North Wall (GSNW) index. Winter NO_3^- was significantly related to the GSNW Index in the previous April, the suggested link being the influence of early summer weather on soil moisture deficit and hence NO_3^- production and storage in soils.

It is not just NO_3^- that is influenced by these climatic oscillations; the other major anthropogenic acid anion SO_4^{2-} may also be affected. Similar large-scale climatically driven patterns in SO_4^{2-} concentrations have been found in Norway (NAO and Arctic Oscillation Index; Dillon *et al.*, 2003a) and Canada (Southern Oscillation Index - El Nino Southern Oscillation and NAO; Dillon *et al.*, 2003b).

While not necessarily associated with large-scale climatic oscillations, variation in climatic factors has been linked to surface water chemical trends (or lack of) in various studies, mostly emanating from North America. Climate variability and its relative effects on microbial N mineralization and plant uptake can explain much of the interannual variation in N retention and leaching at Hubbard Brook in the northeastern USA (Aber & Driscoll, 1997; Goodale *et al.*, 2000) and may obscure longer term trends in NO_3^- leaching (Burns *et al.*, 2006). Some of this climate-induced change may be due to in-stream retention processes such as assimilation in algal biomass, with overall increases due to higher temperatures during spring peaks in NO_3^- leaching (Bernhardt *et al.*, 2005).

Declining NO_3^- concentrations in New Hampshire forest streams from the 1970s to the 1990s were unexpected given expectations of N saturation and climatic factors were deemed to be the most likely cause (Goodale *et al.*, 2003). There was little evidence that frosts were to blame as NO_3^- was lower in all seasons in the later survey. While no single climatic variable could explain the changes in NO_3^- it was suggested that more complex climatic interactions with uptake and mineralisation could be responsible, while climatic interactions with other perturbations were also found to be important (Aber *et al.*, 2002). At Arbutus Lake in the Adirondack Mountains of New York State, Park *et al.* (2003) found a similar decline in NO_3^- which they attributed to climatic drivers, but there was also a small but highly significant increasing trend in NH_4^+. Climate variations were cited as a major driver of inter-annual variations in water chemistry including NO_3^- losses in central Ontario forests by Watmough and Dillon (2003).

The effects of climate on N leaching may also be indirect. Studies in North American forests have found that N retention and leaching is regulated in part by tree species composition which could itself be affected by climate change, indirectly affecting the N leaching response (Lovett *et al.*, 2002; Christopher *et al.*, 2006). Plant species richness is also an important determinant of the response of soil microbes to both elevated CO_2 and N deposition (Chung *et al.*, 2007).

While climatic oscillations and random variations result in complex relationships with NO_3^- leaching, especially given the co-varying nature of different drivers of change, some studies have attempted to focus on one key aspect of climate change, whether increasing temperatures or changing patterns of precipitation and drought.

Increasing temperatures

The net effect of climate change on NO_3^- leaching depends on the new balance between production and retention processes which are both affected by temperature. Climatic warming could stimulate net mineralisation and nitrification rates and increase soil N availability but if net primary production increases then plant biomass storage will be greater (Fenn *et al.,* 1998). For temperate forests, Gundersen *et al.* (2006) suggested that

NO_3^- leaching only occurs when the sum of N deposition and net mineralization exceeds plant demand. The temperature increases predicted by the IPCC are likely to lead to short-term increases in NO_3^- leaching according to Murdoch *et al.* (1998), although longer-term impacts on N cycling and retention were uncertain.

The responses of Norwegian boreal forest catchments to climate change were tested experimentally under the CLIMEX Project (Lükewille & Wright, 1997; Wright, 1998) whereby catchments were covered by giant greenhouses and precipitation amount and chemistry, CO_2 and temperature were controlled. The covered KIM catchment received clean rain, CO_2 was elevated to 560ppm and air temperature was elevated by 3-5°C; NH_4^+ and NO_3^- both increased in runoff for the three years after treatment despite the decrease in N deposition inputs (Wright, 1998). The switching of catchment soils from a net sink to a net source of inorganic N was hypothesized to be due to accelerated decomposition and mineralization of soil organic matter at the higher temperatures.

As part of the NERC TIGER programme, two experimental approaches were used to assess the effects of increasing temperature on N dynamics in moorland soils, transplantation of intact lysimeter cores along a gradient of altitude at Great Dun Fell (Ineson *et al.*, 1998a) and soil warming (Ineson *et al.*, 1998b). The transplantation study found a decrease in leached NO_3^- for three contrasting soil types, attributed to increased vegetation uptake with increasing temperature. In the soil warming study only one soil type (brown earth) showed a significant decrease in NO_3^- leaching during the first five months of heating. Despite increases in mineralization and release of NO_3^-, a greater retention of NO_3^- was achieved through increased uptake and to a lesser degree by denitrification.

For alpine lakes where a deep, late-melting snowpack enhanced overall N losses, Sickman *et al.* (2001) concluded that increasing temperatures may lead to increased N retention, i.e. decreased leaching. These conclusions and results from the TIGER programme correspond with other studies which suggested an inverse relationship between NO_3^- leaching and temperature in moorland and alpine systems (see above), while the CLIMEX results in a boreal forest catchment show the opposite.

Precipitation and storminess

For the UK, predicted changes in precipitation patterns are variable but in general, drier summers with a higher incidence of prolonged droughts are expected to coincide with wetter, warmer winters. Hence while changes in annual mean precipitation will be relatively small, storminess is expected to increase substantially.

Mitchell *et al.* (2006) found increasing NO_3^- with discharge during storm events at Arbutus Lake Watershed in the northern USA, and attributed the high peak values to the exceptionally dry preceding period, in line with other studies in North America (above). In the UK, Cooper *et al.* (2007) described short-term controls on release of N species and DOC from a podzolic, moorland catchment in the Grampians (Birnie Burn at the ECN site Glensaugh) and found that for NO_3^- the combination of time since last flushing and rewetting of the H horizon most powerfully predicted its release in high flow events. They concluded that under climate change scenarios of hotter, more drought-prone summers and wetter winters with more extreme events, the release of DOC and N species would become much more variable and episodic in nature. Inamdar *et al.* (2006)

concluded that less frequent but more intense storms could increase exports of DOC, DON and NH_4^+ from forested watersheds but overall changes in NO_3^- export were uncertain due to the complex interactions between climatic and seasonal variations.

Overall, the few published studies on the subject have been equivocal about the net effect of predicted changes in precipitation and storminess on annual NO_3^- leaching fluxes.

Nitrogen saturation and climate change

N saturation has been defined as:

> *"the availability of ammonium and nitrate in excess of total combined plant and microbial nutritional demand (excluding the use of nitrate as a substrate for denitrification)"* (Aber *et al.*, 1989).

N saturation is therefore reached when its availability (from deposition and mineralisation) exceeds the biotic uptake capacity of the system, and this usually results from water, phosphorus or sometimes light limitation.

According to Aber (1992) N saturation need not occur at a point in time, but as a set of changes in ecosystem processes. In other words, the interpretation of N saturation as the first point of NO_3^- leaching is too narrow a definition. Prior to much of the work linking N leaching and climate, Stoddard (1994) proposed a scheme to describe stages of N saturation and associated NO_3^- leaching which was based on an earlier scheme for forests proposed by Aber *et al.* (1989). These catchment oriented stages assume that NO_3^- leaching (rather than denitrification) is the major export route for excess N and assume that forest is the dominant terrestrial ecosystem. They describe changes in the seasonal pattern of NO_3^- leaching associated with increasing levels of inorganic N deposition and availability, which are consistent with the N flushing hypothesis of Creed *et al.* (1996).

Stages of N saturation: the Stoddard classification

Stage 0

The dominance of plant/microbial uptake results in a seasonal pattern of NO_3^- leaching, with very low peak concentrations (less than that in deposition) occurring only during snowmelt or spring rainstorms. NO_3^- concentrations are <3 μeql^{-1} for more than 3 months of the growing season, with a peak value of <20 μeql^{-1}.

Stage 1

The seasonal pattern of NO_3^- leaching is amplified and prolonged. Surface water NO_3^- concentrations during leaching episodes may exceed those in deposition through preferential elution from melting snow or elevated mineralisation and nitrification in soils. NO_3^- concentration is <3 μeql^{-1} for up to 3 months of the growing season, or if below this threshold for more than 3 months, has a peak value of >20 μeql^{-1}.

Stage 2

Further delays in the onset of terrestrial N limitation result in a greater amplification and extension of the seasonal NO_3^- leaching period. Baseflow NO_3^- concentrations are elevated, approaching those found in deposition. Year round leaching of NO_3^- is therefore observed, but a strong seasonal pattern is still apparent. NO_3^- concentration is never <3 μeql^{-1} but is < 50 μeql^{-1} for more than 3 months of the growing season.

Stage 3

The catchment becomes a net source of N with elevated mineralisation and nitrification leading to surface water NO_3^- concentrations that often exceed those in deposition. The seasonal pattern in NO_3^- leaching breaks down as there are no longer any strong terrestrial sinks for N. High NO_3^- concentrations are therefore observed throughout the year. NO_3^- concentration is <50 μeql^{-1} for less than 3 months of the growing season.

Although developed for forested catchments in North America, these classes may be applied in general terms to UK moorland as well as forested catchments (Fig. 4.2). These examples from the UK AWMN show the full range of responses to N deposition in terms of N saturation class across the UK uplands.

- Stage 0: Three sites in north-west Scotland with very low N deposition show only sporadic NO_3^- leaching with low concentrations (Coire nan Arr, Allt a'Mharcaidh and Allt na Coire nan Con).
- Stage 1: This is a broad class containing 10 AWMN sites with moderate N deposition levels. Some sites are borderline Stage 2 (Burnmoor Tarn, Llyn Llagi, Narrator Brook, Old Lodge, Llyn Cwm Mynach).
- Stage 2: Five AWMN sites with moderate to high N deposition levels show NO_3^- leaching with a distinct seasonal pattern but occurring all year round, never declining to zero and indicating advanced N saturation (Round Loch of Glenhead, Loch Grannoch, Scoat Tarn, Afon Hafren and Blue Lough).
- Stage 3: Four sites fall into the most impacted class with high levels of year-round NO_3^- leaching and no evident seasonal pattern. Lochnagar and Loch Chon just fall into this category because seasonal patterns have become obscured in recent years. Two stream sites, River Etherow and Bencrom River, previously showed some seasonal pattern despite high variability but this has broken down in the recent part of the record.

While the absolute values for NO_3^- concentrations and timing of NO_3^- leaching are arbitrarily defined, it is clear than climate change could have a major impact on the N saturation status of a site described using such a scheme, through the direct effects of changes in snowpack accumulation, heavy rainfall and the summer growing season. It is likely that the climatic changes predicted for the UK under UKCIP and IPCC scenarios could result in an amplification of seasonal extremes in NO_3^- leaching, with prolonged periods of very low NO_3^- during the hotter, drier and longer summers, but larger peaks during wetter periods and heavy rainfall events which are predicted to increase in frequency. Sites in the two intermediate stages of N saturation (Stages 1 and 2) may show the most obvious changes to seasonal patterns, though the direction of change is difficult to predict.

Published studies have not attempted to predict changes in N saturation status in response to climate change, but have explored the confounding nature of climatic variability on schemes such as Stoddard's. Goodale *et al.* (2003) suggested that climatic variations could mask signals of N saturation in forested catchments of northeastern USA and Huntington (2005) suggested in response to this paper that N sequestration by soil microbes (i.e. N immobilization) could have increased due to elevated CO_2, N deposition inputs and longer growing seasons. It was suggested that effects would be manifested more rapidly in soil microbial biomass and that other factors (e.g. ozone stress) may have prevented tree growth responses as measured by stem biomass. Goodale *et al.* (2005) followed up the reply of Huntington (2005) by suggesting that observed DOC increases across North America and Europe might provide additional evidence of labile C production through stimulated soil microbial activity. Hence the inverse relationship between NO_3^- and DOC may be a result of soil microbial responses which liberate organic carbon and possibly organic nitrogen but more effectively convert or immobilize inorganic forms of N.

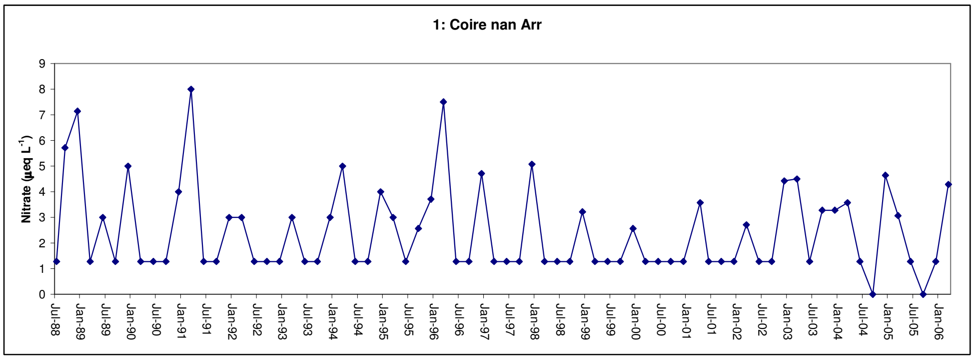
While Goodale *et al.* (2003) thought that evidence of N saturation might be obscured by climatic signals, Watmough *et al.* (2004) went further, stating that the strong climatic controls on NO_3^- leaching in Ontario streams meant that streamwater NO_3^- concentrations were a poor indicator of N saturation status. A similar issue may beset one of the most "NO_3^- - leaky" sites in the UK AWMN. Elevated NO_3^- concentrations in the last 10 years of monitoring at Lochnagar, with a step change in the mid-1990s taken at the time to be a possible indicator of the onset of N saturation, may instead be related to increasing winter duration and severity relative to the earlier period of monitoring from 1988-1995 (Rose *et al.*, 2004).

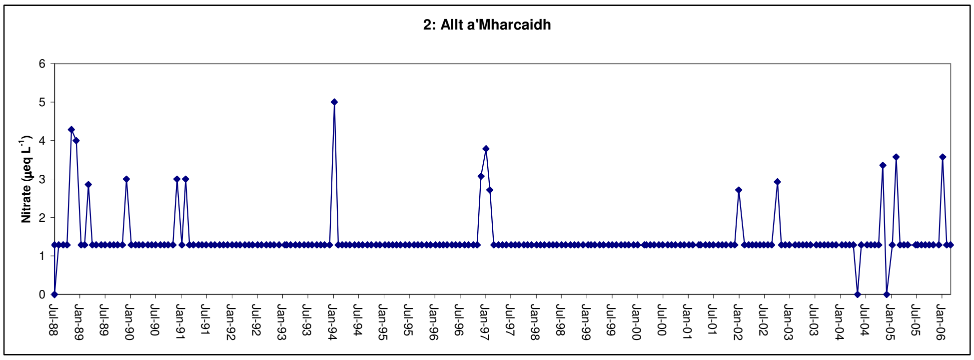
Understanding the future impacts of climate change on NO_3^- leaching is therefore confounded by the very complex interplay of several factors:

1. seasonal variations in leaching of N species, especially NO_3^-;
2. changes in these seasonal patterns due to progressive N saturation of terrestrial ecosystems;
3. changing N deposition loads through time;
4. periodic and random variations in climate superimposed on a general pattern of global warming; and
5. uncertainties associated with the regional impacts of global change in terms of precipitation patterns and storminess.

Despite these problems, several models have been developed and applied to attempt to predict the possible impacts of climate change on NO_3^- leaching.

Figure 4.2a: AWMN Sites at Stage 0 of N saturation


1: Coire nan Arr


2: Allt a'Mharcaidh

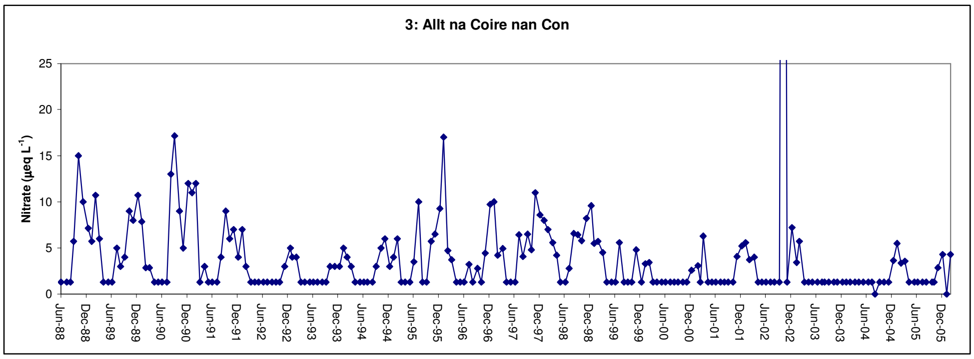

3: Allt na Coire nan Con

Figure 4.2b: AWMN Sites at Stage 1 of N saturation

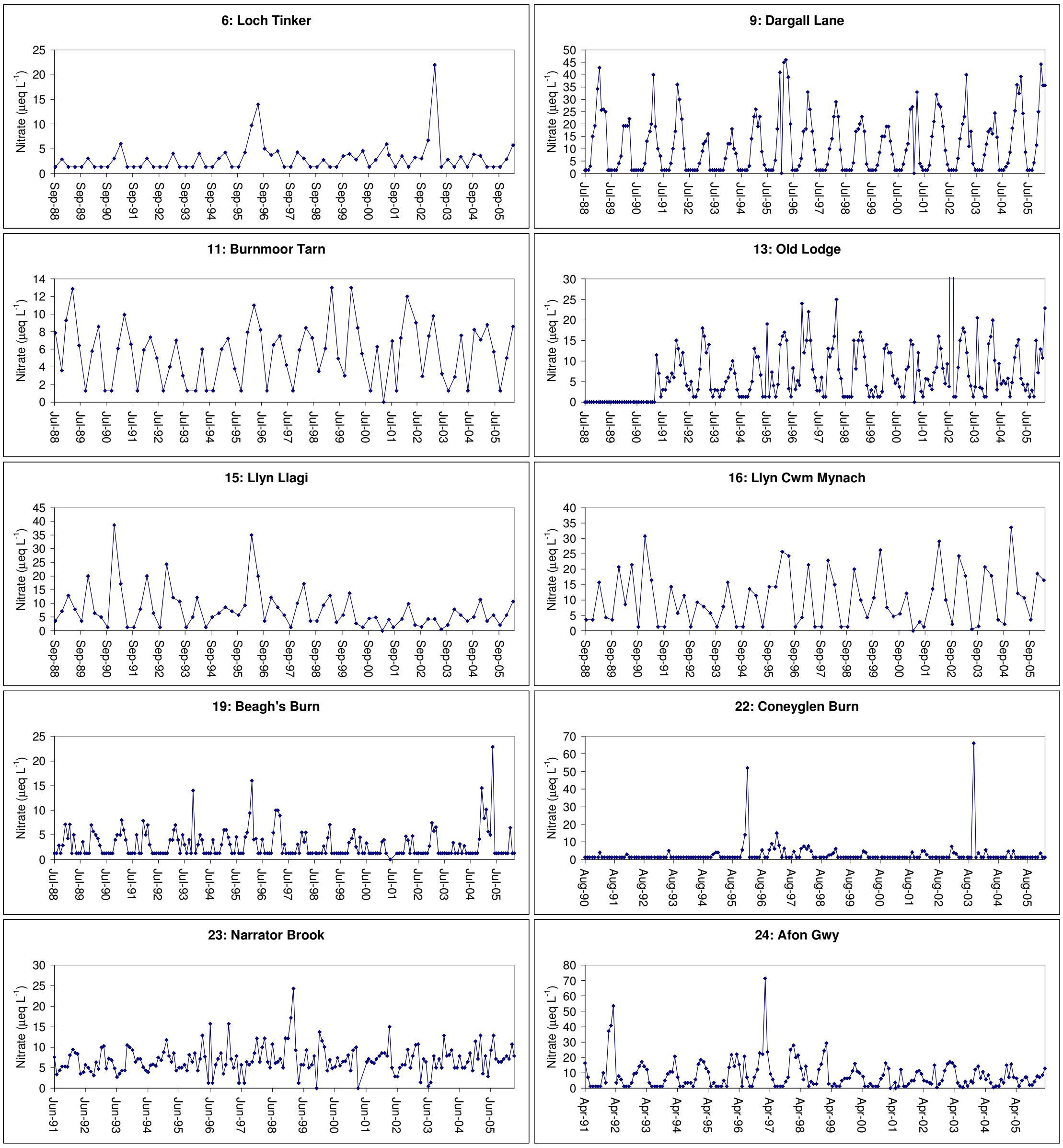
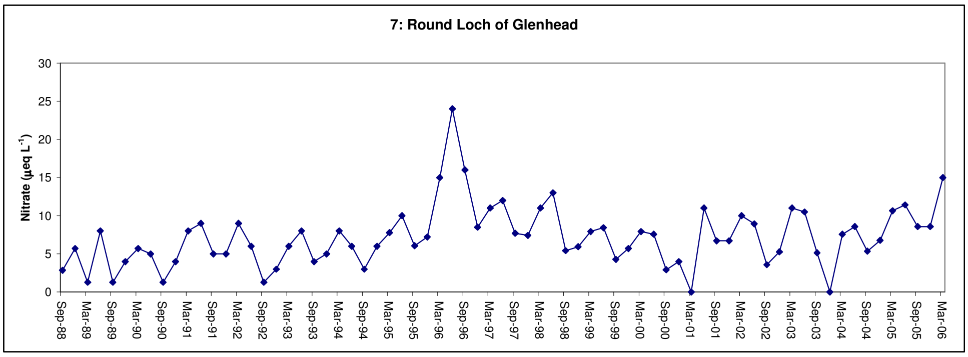
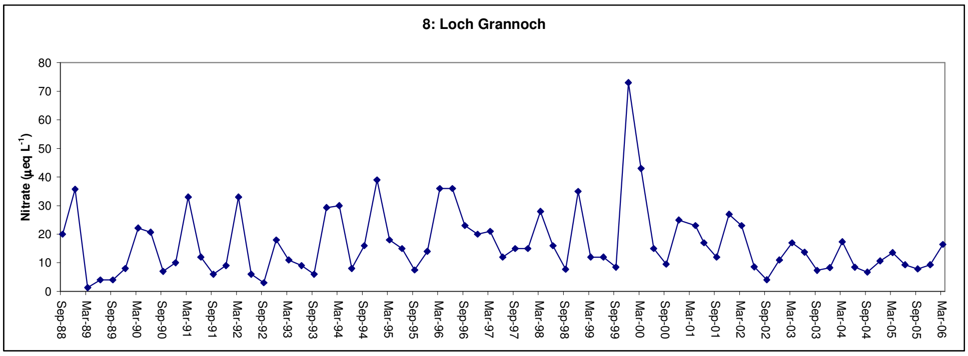
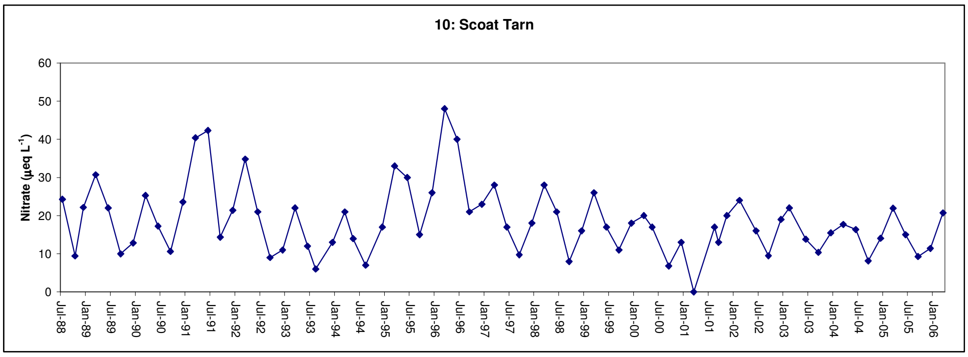
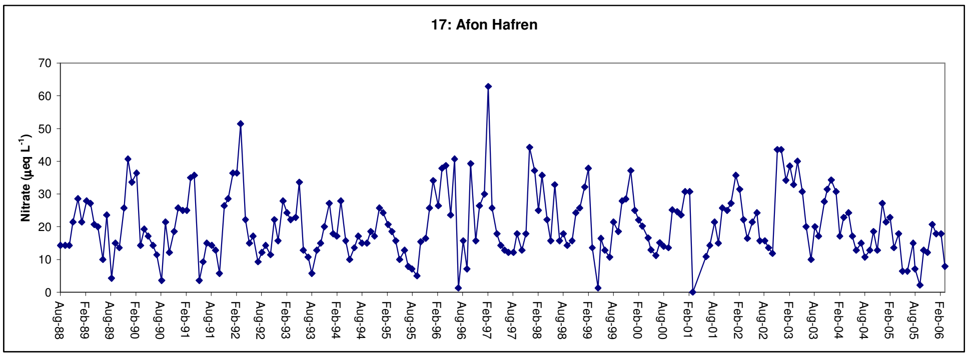


Figure 4.2c: AWMN Sites at Stage 2 of N saturation









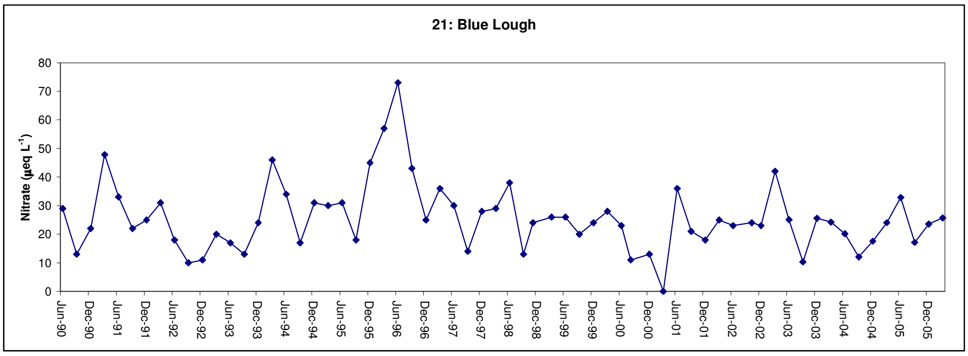
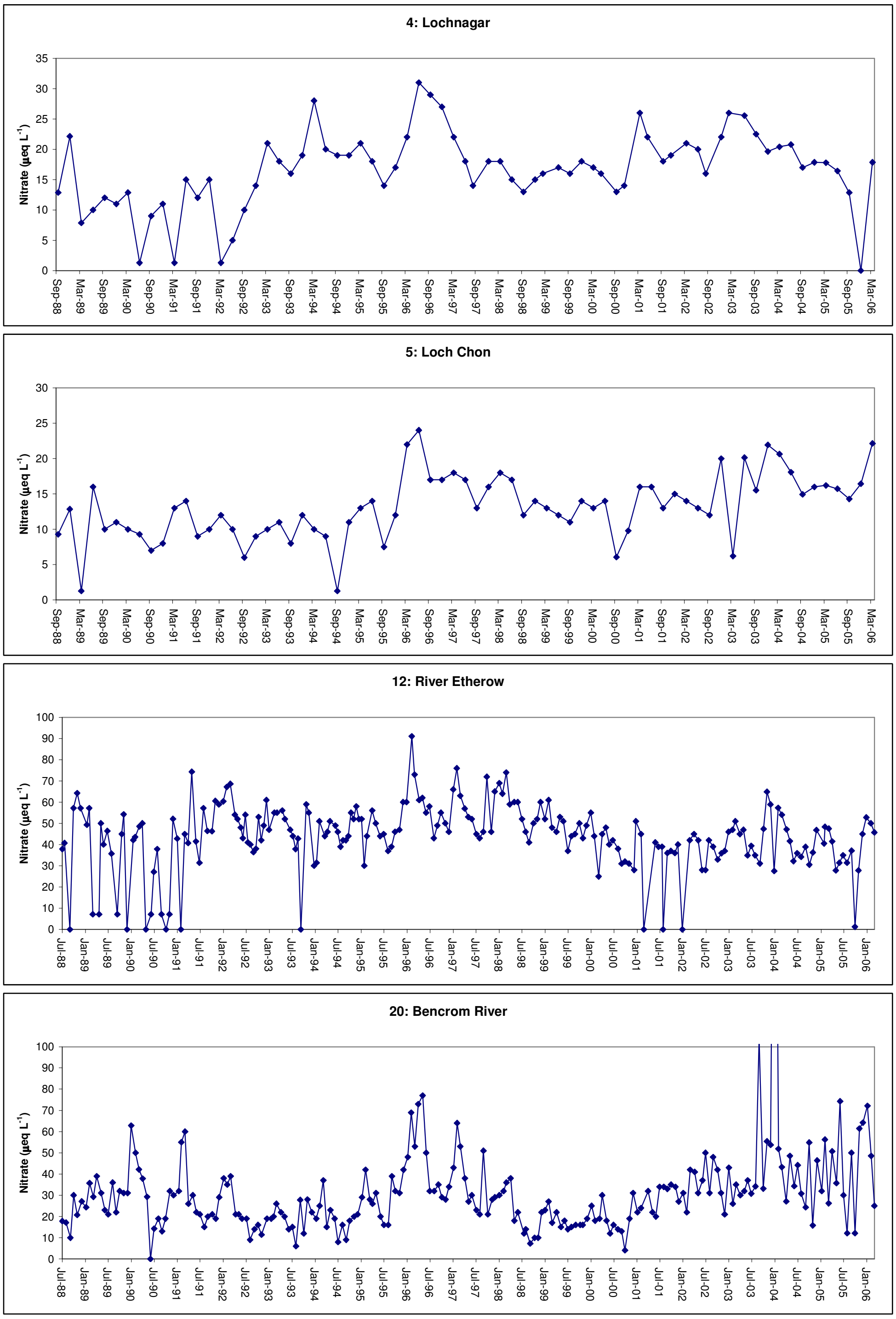


Figure 4.2d: AWMN Sites at Stage 3 of N saturation



Modelling the effects of climate change on NO_3^- leaching

Modelling the likely impacts of climate change on NO_3^- leaching from upland catchments requires complex biogeochemical models linking ecosystem changes with hydrochemical responses, e.g. DayCent-Chem (Hartman *et al.*, 2007), which successfully predicts short-term temporal patterns in an alpine catchment of the Rocky Mountains but has yet to be applied to longer-term modelling of responses to climate change. Several models have, however, been widely applied around Europe under EU research programmes to determine the effects of N deposition and climate change on surface waters, but the results are inconclusive.

As part of the EU DYNAMO project, MERLIN (Model of Ecosystem Retention and Loss of Inorganic Nitrogen; Cosby *et al.*, 1997) was used to test the possible effects of changing N deposition loads and climate on a boreal forest catchment (Wright *et al.*, 1998). MERLIN showed that a temperature-induced increase in decomposition of old soil organic matter by 5% was sufficient to produce the observed increases in NO_3^- leaching flux at the Norwegian CLIMEX experimental warming catchments (Lükewille & Wright, 1997; Wright, 1998). Verburg and Van Breemen (2000) found that net mineralisation increased especially in *Calluna vulgaris* dominated plots (compared with *Vaccinium myrtillus*) but there was no significant increase in nitrification with warming. However, in subsequent work under the EU RECOVER-2010 Project, Mol-Dijkstra & Kros (2001) applied the SMART2 model to the CLIMEX sites and found that the NO_3^- increases were predicted to be transient, with no longer-term increase being maintained. Hence the results of the CLIMEX work did not provide a clear indication of the likely response of boreal forest systems to global warming.

Kaste *et al.* (2004) used the INCA (Integrated Nitrogen Modelling in Catchments) model to demonstrate that the reduced duration and amount of snowcover and increase in temperatures predicted under climate change scenarios would increase NO_3^- supply in catchments of Norway and Finland, but concurrent increases in N retention meant that predicted increases in NO_3^- leaching were small. In the Eurolimpacs project, MAGIC and INCA-N were used to assess the likely changes to N fluxes at the Bjerkreim catchment in Norway under climate change scenarios, and large increases in concentrations with up to 50% increased fluxes were predicted for the Hadley A2 scenario by 2100 (Kaste *et al.*, 2006).

Overall, most of these studies agree that increased temperatures are likely to result in an increased supply of inorganic N in catchment soils but in most cases, corresponding increases in above-ground production and retention of N will mean there are no major net increases in NO_3^- leaching. The most important responses of upland catchments may therefore be related to precipitation and drought events, possibly with an increasing importance of episodic pulses of acidity and nutrients into surface waters.

Conclusions: effects of climate change on NO_3^- leaching in the UK

The main climatic changes predicted under UKCIP scenarios for the UK may be summarised as:

5) increasing temperatures, which will be most pronounced in southern England and smallest in Northern Ireland and north-west Scotland;

6) small decreases in annual mean precipitation which will be greatest in southern England but still only a few per cent overall;
7) major changes in the seasonal distribution of precipitation with worst-case predictions of more than 50% reductions during summer for southern England and 30-50% for the rest of the UK, and increases of at most 10-25% in winter;
8) increasing incidence of extreme precipitation events and drought but reduced snowfall as a result of the above changes.

The implications of these changes for upland waters in the UK are complex and sometimes unpredictable but some general statements may be made.

Increasing temperature

On a seasonal basis there is usually an inverse correlation between temperature and NO_3^- leaching but the relationship between annual mean temperatures and fluxes of N species is less well understood, with few clear predictions in terms of NO_3^- leaching. There is a general consensus that higher temperatures lead to higher rates of mineralization and nitrification in soils but there is usually a corresponding increase in vegetation production and N immobilization and the balance between NO_3^- production and retention will be very specific to local vegetation, soils, N deposition and climatic conditions.

Experimental manipulations have included:

1) warming in the field using greenhouses or electric cables, and
2) soil mesocosm transplants along altitudinal gradients to replicate temperature changes.

Warming under greenhouses in boreal forest (CLIMEX) demonstrated initial increases in NO_3^- leaching at raised temperatures but later modelling work found this to be a short-term, transient effect. Soil warming and transplant experiments in a UK moorland (TIGER) found reduced NO_3^- leaching, although this was also a short-term study.

Hence there is no clear prediction of the net overall effect of increasing annual temperatures on NO_3^- leaching in the UK or elsewhere.

Reduced annual mean precipitation

The great majority of studies in upland systems have found that NO_3^- fluxes, and sometimes concentrations, tend to increase with discharge. Hence a reduction in annual mean runoff due to lower precipitation could on this basis result in lower annual leaching fluxes of NO_3^-.

However, this relationship is not constant throughout the year because NO_3^- concentrations and fluxes tend to be greatest during the dormant season (autumn/winter) and smallest during the summer, and the relationship between discharge and NO_3^- yield is steepest in winter when there is less biological demand. Furthermore, predicted changes in precipitation are in opposite directions for winter and summer so the seasonal responses will be very different.

Summer responses to reduced precipitation and increased drought

In all but the most N impacted catchments of the UK uplands, summertime NO_3^- concentrations tend to be very low or undetectable. With reduced rainfall and prolonged droughts it is likely that summer NO_3^- leaching will remain low but production and storage in soils may increase so that the scope for event-based NO_3^- pulses is much greater. If droughts are very severe then vegetation damage could result in large increases in NO_3^- leaching through the following dormant season and effects may last several years. The effects of summertime storms such as those causing the recent flooding across much of northern England are unknown but there may be scope for summertime leaching pulses of NO_3^- if vegetation uptake is reduced by drought damage.

Overall, the increased likelihood of low summer precipitation, drought and vegetation damage may result in the greatest impacts during the dormant season.

Winter responses to increased precipitation and reduced snowfall

Given that maximum NO_3^- leaching fluxes and concentrations already occur during winter and early spring and that discharge-yield relationships are steepest at this time of year, the predicted increases in winter precipitation and storms is likely to result in larger seasonal fluxes of NO_3^-. This effect may be compounded by summer drought and vegetation damage which will allow inorganic N to accumulate in soils for longer periods prior to flushing during rainfall events. In lakes and especially streams, episodic inputs of NO_3^- leading to acid pulses may increase in frequency and magnitude.

An unexpected consequence of reduced snowcover may be an increase in soil freezing events despite the higher temperatures, as demonstrated in snow removal experiments in North America. While extremely cold events will become less frequent, thereby reducing the serious damage to fine roots and larger flushes of inorganic N associated with severe freeze-thaw action, an increased frequency of mild freezing events may occur. The net effect on NO_3^- leaching associated with freeze-thaw action is therefore difficult to predict.

Spring peaks in NO_3^- concentrations

Concentrations of NO_3^- in UK upland waters start to increase in the autumn and reach peak values in early spring, usually February or March in streams and a month or two later in lakes due to their residence time (Fig. 4.1). These peaks are associated with increasing microbial generation of NO_3^- in soils prior to the onset of vegetation growth, combined with thawing of frozen soils or snowmelt and flushing of accumulated inorganic N in soils. Climate warming is likely to alter the timing of this seasonal pattern but the impact on peak fluxes is uncertain. Predicted changes in springtime precipitation are very minor so any changes are more likely to be associated with the spring thaw and snowmelt.

In a UK context the proportion of the annual solute flux arising during snowmelt is small compared with Scandinavian, North American and high mountain lakes so the effect of reduced snowcover and duration is likely to be rather minor. However, there may be a reduction in the spring pulse of NO_3^- that is associated with snowmelt in the higher altitude regions of the UK. It is possible that spring peak yields may decrease while overall dormant season yields increase, i.e. the winter concentration curve may be flatter but broader.

Effects on patterns of NO_3^- leaching and N saturation class in AWMN sites

The predicted climate changes for the UK are likely to enhance seasonal patterns of NO_3^- leaching and will probably increase annual NO_3^- leaching fluxes. For the most unimpacted sites at Stage 0 the incidence of small leaching episodes is likely to increase especially in winter. If peak concentrations following drought or winter storms increase and exceed 20 μeq l^{-1}, some sites at Stage 0 will move to Stage 1of N saturation. Allt na Coire nan Con is the most likely candidate, as it is already borderline with peak NO_3^- concentrations approaching 20 μeq l^{-1}.

Some sites at Stage 1 of N saturation may experience higher summer NO_3^- concentrations as a result of greater NO_3^- inputs to groundwater during winter which feed into streams and lakes throughout the year. However, reduced summer rainfall and possible droughts may result in longer periods of very little NO_3^- leaching and perhaps lower concentrations. Hence the impacts on Stage 1 sites will depend on the balance between slow groundwater inputs and rapid runoff contributions to NO_3^- fluxes. If peak NO_3^- concentrations decrease even with larger fluxes of NO_3^- in winter, for example because of reduced snowmelt inputs at the end of the season, then Stage 1 catchments may move to Stage 0 (e.g. Loch Tinker). Conversely, raised year-round groundwater inputs could move a Stage 1 site into a Stage 2 pattern of constantly elevated NO_3^- levels (e.g. Burnmoor Tarn, Llyn Llagi, Narrator Brook).

Elevated annual fluxes of NO_3^- and enhanced seasonal patterns of leaching would be unlikely to move Stage 2 catchments into another pattern of leaching. It is possible that a responsive stream site like the Afon Hafren may see a much-more storm driven response which obscures seasonal patterns and might result in a Stage 3 pattern of leaching, but this is highly uncertain. Similarly, the worst N impacted sites at Stage 3 of N saturation are unlikely to see an improvement in NO_3^- leaching status although the imposition of stronger seasonal drivers (higher winter and lower summer precipitation and leaching) could in theory re-impose a seasonal pattern where it had previously broken down (e.g. Lochnagar, Loch Chon).

The stages of N saturation proposed by Stoddard (1994) are used here only as a convenient illustrative scheme of potential changes in seasonal, within-year patterns of leaching. The most significant aspects of increased NO_3^- leaching will, however, be determined by two factors overall:

1. changes to the frequency and severity of acid pulses during storm events (acidification), which may both increase under UK climate change scenarios, and
2. the magnitude and seasonal distribution of increases in mean NO_3^- leaching which will exacerbate both chronic acidification and potentially nutrient N effects in N-limited lakes and streams.

While the likelihood of either of these responses is unknown, given the uncertainty in the precise pattern of predicted climate change on a regional basis, the balance of probabilities is that problems associated with NO_3^- leaching in the uplands will deteriorate in the coming decades.

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SECTION 2: THE POTENTIAL IMPORTANCE OF CLIMATE CHANGE FOR THE FUTURE DISSOLVED ORGANIC CARBON CONCENTRATIONS IN UPLAND WATERS

Don Monteith

Introduction

Definition

Soils contain more carbon than either vegetation or the atmosphere (Davidson and Jannssens, 2006), and the bulk of this is held in organically rich soils, such as peats and organo-mineral soils, that dominate much of the world's more remote landscapes. Waters draining these "carbon stores" often exhibit relatively high concentrations of dissolved organic carbon (DOC) and therefore represent significant pathways by which organically fixed carbon is removed from the land. DOC influences the character of surface waters by imparting acidity, changing its transparency to photosynthetically active and UV-B radiation, and acting as a conveyor of nutrients (such as nitrogen, phosphorus) and organic and inorganic contaminants.

Operationally, DOC is a term for all organic carbon that passes through a 0.45 µm filter and may be considered to represent the potentially chemically reactive portion of the total organic carbon content of waters. Normally it is determined by the infrared spectrometric analysis of the carbon dioxide generated by its oxidation. The fraction of organic carbon that is retained by a 0.45 µm filter is known as particulate organic carbon, but this can be broken down my microbial activity to increase DOC concentrations.

Surface waters contain several classes of DOC compounds including humic substances (fulvic and humic acids), hydrophilic acids, carboxylic acids, amino acids, carbohydrates and hydrocarbons. Aquatic humic substances are defined as coloured polyelectrolytic acids which are isolated by sorption onto XAD resins, weak-base resins or similar methods (Thurman, 1985).

On average humic substances comprise about half of all DOC in river water (Thurman, 1985) but the fraction is often much greater in waters draining wetland areas, such as marshes and bogs and other wet peatlands that characterise much of the UK uplands. Streams and lakes draining peaty catchments normally show concentrations of between 0.5 to 10 mg l^{-1} DOC, of which up to 90% may be humic substances.

Humic substances may be categorised by their tendency to precipitate in acid. Fulvic acids remain in solution at low pH. This solubility is due to their relatively low molecular weight (800 - 2000) and the high density of carboxylic and hydroxyl functional groups. Humic acids have higher molecular weight (>2000) and fewer carboxylic and hydroxyl functional groups (see below), and they interact with clay minerals and iron and aluminium oxides. These characteristics render them susceptible to precipitation in strongly acidic solutions.

The importance of DOC for aquatic ecosystems

DOC exerts many biologically influential physical and chemical effects on surface waters. Depending on the chemistry of the soil solution, DOC molecules have the capacity to either donate or accept hydrogen ions, and thus either contribute to, or ameliorate, acidity. They also complex with potentially toxic metal species and organic pollutants, rendering them less harmful while also contributing to their transport (see next section). Biologically, complexation with aluminium in acidified waters improves survival rates of salmonids and other acid-sensitive biota at low pH.

Physically DOC absorbs solar radiation across much of the visible spectrum. In upland waters it is often the dominant influence on the vertical distribution of light and heat in the water column. Elevated DOC concentrations, therefore, restrict the photic zone, i.e. the vertical zone within which photosynthesis may occur, increase protection for some surface dwelling aquatic organisms against the harmful effects of UV-B radiation, reduce photo-inhibitory effects of high levels of photosynthetically active radiation (PAR) on algal photosynthesis in shallow water, and raise surface temperatures while reducing bottom water temperatures.

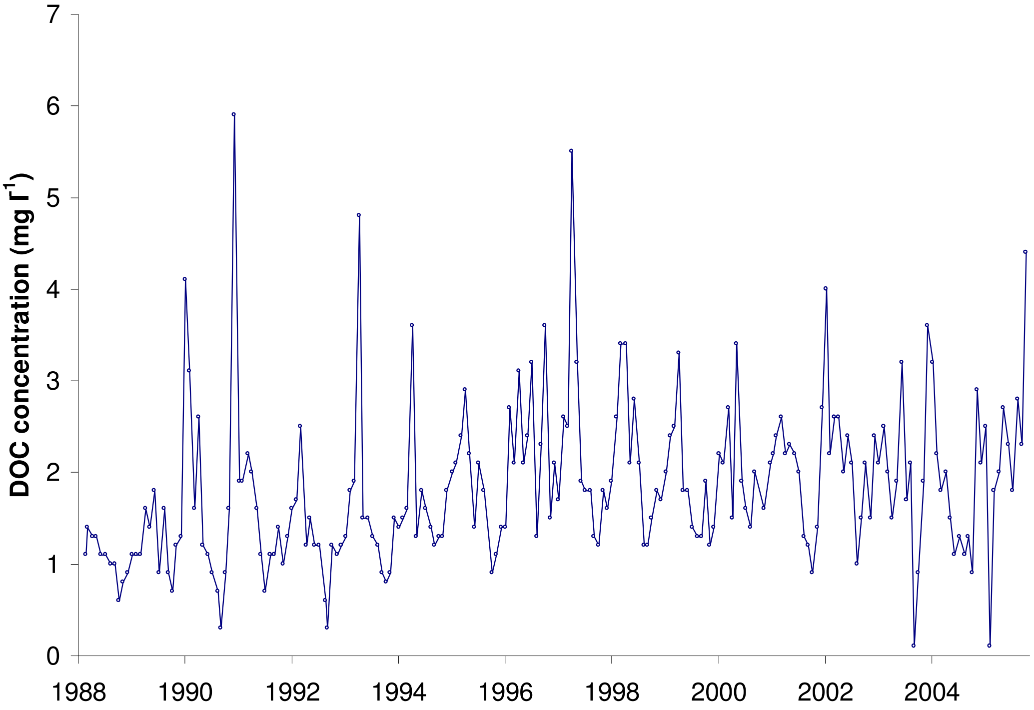
DOC has a direct role in aquatic food chains as it is utilised by heterotrophic bacteria, although more labile, low molecular weight material is more important than are the more refractory humic substances (Romani *et al.*, 2004) that are the primary focus of this review.

Temporal variation in DOC

DOC concentrations in surface waters vary over a range of time-scales, reflecting variation in: the supply of organic matter from organisms living above and within the soil; organic matter decomposition (to soluble organic matter - SOM); dissolution of SOM; hydrological removal (i.e. flow); and hydrological pathways. In streams and lakes with short residence times in northern boreal landscapes, DOC concentrations often show strong seasonality (Fig. 4.3), with peak concentrations occurring either in the autumn or in spring. This is normally accounted for by the relationship between the availability of SOM at the end of the summer growing season and flushing by autumn rainfall or after winter snowmelt.

Over the past two decades several freshwater monitoring initiatives in North America, southern Scandinavia and the UK have reported strong increases in DOC (Freeman *et al.*, 2001; Stoddard, 2003; Worrall *et al.*, 2004; Evans *et al.*, 2005). These trends continue in some regions. In the UK, DOC concentrations in the streams and rivers of the UK Acid Waters Monitoring Network increased by an average of 65% between 1988 and 2000. Freeman *et al.* (2001) postulated that the UK trends might be linked to the effects of a gradual rise in air temperatures (since the 1970s) on soil processes (see later). This paper sparked a debate with regard to alternative explanations for DOC trends (e.g. Tranvik & Jansson, 2002; Evans *et al.*, 2002) and has widened more recently following suggestions that increased nitrogen deposition or ambient CO_2 concentrations may be key factors, and the identification of clear links between declining levels of acid deposition and DOC increases (e.g. Stoddard *et al.*, 2003; Evans *et al.*, 2006; Monteith *et al.*, in review).

Figure 4.3: Concentration of dissolved organic carbon (DOC) in the UK Acid Waters Monitoring Network site, the Dargall Lane Burn, 1988-2006. Concentrations show a distinct seasonal cycle with peaks in autumn and troughs during spring.



In a broad sense, therefore, a dichotomy persists between the argument that recent trends in DOC are linked in some way to global warming or other anthropogenic disturbance - the implication being that current levels are "unnatural" and are set to continue to rise - and the argument that the dominant trend represents a return to pre-acidification conditions, i.e. that higher DOC concentrations represent the natural state. These different explanations have very different implications for the future response of DOC in surface waters to changes in climate and consequent ecological effects.

The main aims of this section are to:

1) review briefly the current understanding of processes which govern DOC concentration and how these may be linked to climate;
2) consider the various hypotheses which have been raised to explain DOC trends; and,
3) in the light of 1) and 2), consider the likely implications of forecast changes in climate for future DOC behaviour in upland waters across the UK

Processes governing DOC concentration

DOC concentrations in surface waters can be considered to be a function of:

i) net primary production (NPP);
ii) decomposition of organic matter (via fungal and microbial pathways) to SOM;
iii) solubility of SOM; and

iv) transport and removal (by hydrological, photo-oxidative and biological processes)

Below we consider how each of these components is influenced by variability in climate and consider likely future behaviour in concentration trends with respect to UKCIP projections.

Net primary production

DOC is a by-product of the decay of organic material, including plant litter, root exudates and microbial biomass. Concentrations in surface waters have been shown to be closely related to the extent to which the catchment constitutes wetland (Hope, 1997; Curtis, 1998). This is often argued to reflect the relatively high net primary production (NPP) of wetland plants, and the slow movement of water which leaches organic detritus and flushes interstitial soil waters (Thurman, 1985). However, while water draining the peat landscapes that characterise much of the UK uplands is also often strongly coloured by DOC, these cool, nutrient poor environments are not noted for their productivity. Rather, the same processes responsible for the development of peat, i.e. slow decomposition rates due to low oxygen availability, low pH, low nutrient supply and low temperatures, also determine a greater availability of organic material for potential removal as DOC.

Ultimately though, productivity rates in these landscapes are clearly important for DOC generation, given observations of the distribution of DOC in soil profiles and estimates of the age of DOC in runoff. Soil water DOC concentrations tend to be highest close to the soil surface and decline sharply with depth, suggesting a dominant role for recently formed plant organic matter in the composition of DOC. Radio-isotopic (i.e. ^{14}C-based) studies often support this by showing that the age of organic carbon in northern peatland surface waters is predominantly modern (e.g. Palmer *et al.*, 2001; Benner *et al.*, 2004; Evans *et al.*, 2006). An ongoing study of dissolved organic ^{14}C in streams and soil solutions draining a range of soil and land-use types in North Wales (Dr Chris Evans pers. comm) indicates that most of the DOC exported from organic soils today was fixed after the 1950s, especially at high flow when the majority of DOC flux export occurs. Others have pointed to a significant contribution from an older component (Raymond & Bauer, 2001), or a shift from a dominance of older to newer material with increasing flow (Schiff *et al.*, 1997). On balance though, it would seem that recent DOC trends are more likely to be indicative of an accelerated loss of carbon that has only recently been fixed from the atmosphere, than of destabilisation of 'old' soil carbon (as suggested, for example, by the results of Bellamy *et al.*, 2005).

The future behaviour of DOC in upland waters, therefore, is likely to be sensitive to the future NPP response of upland vegetation to changes in climate, both directly and indirectly as a result of changes in land management that might follow. Boer *et al.* (1990) considered that the most important effect of global CO_2 increase on Fennoscandivanian vegetation would be to increase rates of productivity through rising temperatures, but they recognised that other limiting factors, such as nitrogen availability, might become established.

The vegetation of upland landscapes in the UK and high latitude landscapes elsewhere is adapted to a cool thermal regime. However, there is evidence to suggest that the productivity of many plants common to the UK uplands is limited by temperatures and the length of the thermal growing season. Manley (1952), on the assumption that NPP was normally restricted to temperatures above 6 °C, postulated that growth at higher altitudes would be slower and over a shorter growing season. This was supported by observations of Gore (1963) who compared the performance of the common and often dominant upland grass *Molinia caerulea* in upland Moor House with a site closer to sea level. He found that growth at Moor House occurred over a shorter part of the year and that net carbon assimilation rates were substantially lower. Grace and Woolhouse (1970) found that light saturated photosynthesis of one common species (*Calluna vulgaris*) was optimised at temperatures between 18-20°C (considerably higher than average summer temperatures experienced today). Application of their findings in a growth model (Grace & Woolhouse, 1974) were in good agreement with observations of *C. vulgaris* in the field, suggesting pronounced temperature sensitivity in the natural environment. Application of the model to the effects of increasing altitude concluded that in environments higher than Moor House *C. vulgaris* stands would not be sustainable and this was supported by the observation of only rare and isolated plants on the summit of nearby Great Dun Fell (847 m).

Despite these detailed studies, Gordon *et al.* (1999) found no evidence of any significant effect on the productivity of either *C. vulgaris* or bracken (*Pteridium aquilinum*) with an increase in air temperature of between 0.5-1.5 °C. Studies by Shaver *et al.* (1986) (on cotton grass, *Eriophorum vaginatum,* in Alaska) and Wookey *et al.* (1994) (on the Alpine bistort, *Polyganum viviparum*), are also equivocal, suggesting that warmer temperatures may change biomass allocation without necessarily affecting NPP.

Wetland plants are generally adapted to the problems of oxygen stress caused by waterlogging (Wheeler, 1999) and it therefore seems unlikely that forecast increases in winter precipitation will have a major bearing on NPP. However, many are sensitive to drought, due to inefficient stomata, high cuticular water loss and poorly developed root systems. Increased drought frequency would therefore be expected to have a negative effect on productivity, and could result in the loss of some species if the water table is sufficiently depressed (Moore, 2002). Gordon *et al.* (1999) found that summer drought had a particularly marked negative effect on the photosynthesis, growth and reproduction of both *P. aquilinum* and *C. vulgaris*. They showed that the timing of drought relative to the growth stage was critical; these taxa being vulnerable to early summer and late summer drought respectively.

Ultimately however, the primary importance of climate change on NPP may depend on the future frequency of drought events. Alm *et al.* (1999) suggested that a prolonged lowering of the water table in peatlands would encourage the establishment of tree growth which might increase the amount of litterfall and the production of fine roots (Laine & Minkkinen, 1996) - thus increasing NPP. On the other hand, tree establishment would be unlikely if the future trend was for occasional droughts interrupted by periods of high precipitation and water tables.

Atmospheric CO_2 concentration *per se* may also limit NPP in some situations. Globally, concentrations have increased by circa 20% in the last 50 years and are predicted to continue to rise through the first half of the 21st century. Oechel *et al.* (2004) demonstrated that carbon fixation by *Eriophorum vaginatum* in an Alaskan bog was stimulated by doubling the ambient CO_2 concentration, while Freeman *et al.* (2004) showed that elevated ambient CO_2 raised the DOC concentration of leachate slightly for various organically rich soil types. No evidence for an increase in open ground biomass was presented in the latter study, but ^{13}C tracer experiments indicated that the increase in DOC was driven by newly fixed carbon; the predominant effect was suggested to be an increase in root exudates.

The Oechel *et al.* (2004) study also hints at the possible importance of nitrogen and phosphorus availability for NPP; the effect of CO_2 increase was short-lived, possibly due to a rapid onset of nutrient limitation. Productivity in northern boreal ecosystems is often considered to be nitrogen limited, and the TEM process-based model predicted that temperature mediated nitrogen availability would cap the influence of CO_2 on NPP in these environments (Melillo *et al.*, 1993). While many upland plants are adapted to low nitrogen availability NPP could be boosted through vegetational succession as a result of enhanced nitrogen deposition. However, an increase in nitrogen availability against a background of rising air temperatures will not necessarily have positive synergistic influence on upland productivity. Gordon *et al.* (1999) found that nitrogen addition stimulated the growth of *Calluna vulgaris* to a point which was not sustainable under drought conditions, leading to wilting, reduced shoot growth and acclimation of water-use efficiency that would restrict NPP.

In summary, primary productivity provides the organic substrate from which DOC is derived. There is increasing evidence to suggest that the most DOC draining upland waters in the UK is derived from recent photosynthesis. Global changes in atmospheric CO_2 and its indirect effect on air temperatures and precipitation will undoubtedly influence the NPP of upland environments in the UK. A combination of rising ambient CO_2 concentration, rising summer temperatures, enhanced atmospheric nitrogen deposition and sufficient rainfall in the growing season, would be expected to increase NPP and hence the potential pool for leaching as DOC. However, nutrient availability and increased summer drought might limit the response, while the latter could potentially reduce NPP depending on future drought frequency and seasonal timing.

Decomposition

The potential pool of organic carbon available for export as DOC depends on the balance between rates of NPP and decomposition, by which organic matter from plant and animal remains, faeces and the microbial biomass is broken down by a range of soil invertebrates, fungi and bacteria. Organic matter decomposition comprises two largely concomitant phases. In a largely mechanical process, invertebrates shred particles into finer size classes, thus increasing the surface area of the substrate to further attack. Biochemically, through numerous food-chain pathways, enzymes secreted by the guts of invertebrates, fungi and bacteria, break down particles to potentially soluble forms (i.e. soluble organic matter or SOM), which may be exported hydrologically, or eventually to simple sugars which may be respired. Both phases are sensitive to temperature and soil moisture.

Cole *et al.* (2000) studied the activity of enchytraeid worms (ubiquitous oligochaetes and primary consumers of organic material in peatlands) in soil samples taken from the Moor House National Nature reserve. The invertebrates increased microbial respiration in surface horizons by 35% and the DOC concentrations of leachate by almost 100%. They concluded that the primary effect of the animals on DOC concentrations was to increase the availability of organic substrate for microbial breakdown. Cole *et al.* (2002a), went on to show that enchytraeid density was positively correlated with soil temperature and estimated that a mean monthly air temperature increase of 2.5 °C would increase abundance by 43% and soil DOC concentration by 11% as a result of their influence on microbial activity, litter fragmentation and soil aeration. However, Springett (1970) showed that enchytraeids respond to soil drying by burying deeper into the profile; Cole *et al.* (2002b) pointed out that since enchytraeid activity is largely confined to the top 4 cm of the soil profile, drought might reduce the influence of these animals on decomposition in this zone, where litter is most abundant.

All biochemical processes are temperature dependent and it has been proposed that, at a global scale, climate warming will cause a greater acceleration in decomposition than NPP and hence a net loss of carbon from soils to the atmosphere (Jenkinson, 1991; Anderson, 1992). In the short-term at least heightened decomposition would be expected to increase fluxes of CO_2 to the atmosphere and DOC in runoff unless or until NPP became limiting.

Davidson and Janssens (2006) in their thorough review of the temperature sensitivity of soil carbon decomposition concluded that, although individual biochemical reaction rates can be predicted from theoretical kinetics, the thermal response of the entire soil system is extreme difficult to model. Soils contain a vast range of organic carbon compounds which have greatly differing thermal sensitivities. Equally important though, a large range of factors (many climate-related and thus potentially subject to long-term change) determine the extent to which enzymic decomposition can realise optimal rates - because of physical or chemical barriers between enzymes and reaction "microsites". Of these potential barriers, Davidson and Janssens (2006) cited physical protection of organic matter (e.g. oxygen limitation, extent of aggregate formation, low water solubility), chemical protection (through adsorption of organic matter onto surfaces), drought (decreasing soil water films inhibits diffusion of both enzymes and substrates), flooding (e.g. anaerobic conditions restrict the number of potential enzymatic decomposition pathways) and freezing (substrate and enzyme diffusion rates greatly restricted in frozen soils.

Soil moisture is clearly critical in determining the relative roles of aerobic and anaerobic respiration on decomposition, and it follows that changes in precipitation patterns could influence decomposition rates. Most fungi are aerobic and their activity is therefore restricted to soil horizons above the water table. Alm *et al.* (1999) demonstrated that the lowering of the water table in an ombrotrophic bog resulted in respiration (as determined by the measurement of CO_2 and CH_4 fluxes) exceeding gross production (i.e. the bog switched from being a carbon sink to carbon source).

Microbial organic matter decomposition in peatlands is inhibited by cyclic phenolic compounds. In aerobic conditions the enzyme phenol oxidase is able to break these down, thus increasing decomposition rates. Freeman *et al.* (2001) proposed that an increase in aeration of peat under a scenario of global warming would increase phenol oxidase activity, thus lifting a "latch" on organic matter decomposition and potentially turning peatlands from sinks to sources of carbon. The link between phenol oxidase and potential climatic effects on these environments was extended by Freeman *et al.* (2001a) to explain the widespread increase in DOC concentrations in UK Acid Waters Monitoring Network sites over the period 1988-2000. They demonstrated that phenol oxidase activity was also temperature dependent. Laboratory studies showed that warming not only increased activity ($Q_{10} = 1.36$) but also resulted in an equivalent increase in DOC concentration ($Q_{10} = 1.33$) and an even greater release of phenolic compounds ($Q_{10} = 1.72$). In response, Tranvik *et al.* (2002) pointed out that DOC concentrations had increased in Swedish waters during the 1970s and 1980s despite a negative trend in air temperature over the same period. Subsequently it has become clear that the reported Q_{10} values were too small to explain the size of observed DOC trends; there was no trend in UK air temperatures over the 1988-2000 period, while over the longer term Central England Temperatures were only 0.66 °C higher in the 1990s than in the three preceding decades (Freeman *et al.*, 2004).

Predictions of the magnitude of the effect of rising temperature are often based on the assumption that decomposition rate sensitivity to temperature in the soil litter is representative of the whole soil profile. Liski *et al.* (1999), challenged this view, by examining the amount and age of soil carbon and the decomposition rate of litter on north European geographical temperature gradients. They concluded that the decomposition of older carbon was considerably more resistant to changes in temperature and that estimates of temperature effects on whole soil profiles would be considerably smaller than previously suggested. This has been proposed as one explanation as to why warming experiments in the field often provide indications of a short term increase in decomposition only (Davidson & Janssens, 2006) and is supported by modelling studies (e.g. Knorr *et al.*, 2005). In an assessment of the temperature sensitivity of Scottish soils under Sitka spruce, however, Fang *et al.* (2005) found no evidence for differing sensitivity of "resistant" and "labile" pools of organic matter.

It is clear that biochemical decomposition will be accelerated under a scenario of rising temperatures, at least when aerobic conditions may be maintained. However, it is important to consider not only the relative temperature sensitivity of different organic carbon pools but also the effect a temperature rise could have on absolute decomposition rates. Hence Davidson and Janssens (2006) provide a comparison of the potential effect of a 2 °C rise on the absolute decomposition of two contrasting organic compounds. Under current climatic conditions glucose is estimated to decompose 6.5 million times faster than tannin. The latter has a higher temperature sensitivity, so the temperature rise would increase its decomposition twice as much as that for glucose, but the latter would still decompose 5.8 million times faster. Tannins are far more abundant in soils than glucose so the influence of temperature cannot be ignored at the ecosystem scale. Nevertheless, the effect of small increases in temperature on the decomposition of recalcitrant compounds such as tannins may be subtle and possibly only detectable over multi-decadal time-scales.

To summarise, rising temperatures, in the absence of any change in soil moisture, will inevitably increase biochemical decomposition rates leading to larger loss of CO_2 to the atmosphere and SOM available for export as DOC. The more mechanical primary breakdown of organic matter is also likely to respond positively to increased temperature, providing this is not accompanied by rising water tables. However, estimates of the likely absolute change to decomposition rates are complicated hugely by an array of factors that restrict the ability of enzymes to operate optimally. Among these are soil moisture and the effects of flooding and drought. Finally, it is feasible that the effect on absolute rates for the more recalcitrant compounds that dominate peat soils will be so small that it may take decades for temperature dependent decomposition effects on DOC to be identified.

Solubility

During oxidative bacterial decomposition, carboxylic acids and other "functional groups" are formed within the modified soil organic matter. Carboxylic acids, particularly, exert a major effect on the acidity and solubility of organic molecules. In soil waters between pH 6-8 these acids are dissociated, and electrostatic repulsion between like charges of these dissociated functional groups renders their organic molecules highly soluble. As pH declines however, dissociation decreases, charge repulsion weakens and water is expelled from within the macromolecular structures causing them to contract and precipitate (Ghosh & Schnitzer, 1980; Ritchie & Posner, 1982). The relationship with pH is described by an acid dissociation constant (Ka) or its negative log (pKa). For an organic acid with a pKa of 4.2 (the average for dissolved humic substances), approximately 50% of carboxylic acid groups will be dissociated at pH 4.2. Tipping and Hurley (1988) have demonstrated through mechanistic models that soils in acidified parts of the UK that were recovering from acidification were finely poised in this respect.

Organic matter solubility has also been shown to be dependent on ionic strength. In a gel filtration experiment de Haan *et al.* (1987) found that increasing the ionic strength of water from small Finnish forest lakes either reduced the size or changed the shape of the humic acid molecules.

It is feasible, therefore, that changes in acid deposition, i.e. the very large reduction in sulphur deposition over the past 20 years, will have increased the solubility of DOC through both increasing the pH of soil and decreasing the ionic strength of soil solutions. Such relationships have been demonstrated in a range of laboratory experiments by Kalbitz *et al.* (2000). Clark *et al.* (2005) identified a strong inverse logarithmic relationship between sulphate concentration and the amount by which ambient DOC concentrations were reduced during drought conditions, due to the oxidation of reduced sulphur. Similar results were later shown for natural drought at Moor House (Evans *et al.*, 2006).

Evans *et al.* (2005) found that changes not only in sulphate but also in chloride concentration could explain variability and trends in DOC at UK sites. This is important with respect to AWMN time series since chloride concentrations were elevated in the first few years of monitoring as a result of large seasalt inputs during persistently stormy conditions over the period (Evans *et al.*, 2001). Like sulphate, seasalt also has the potential to both acidify soils (at least in the short term) and increase the ionic strength of soil solutions. Vuorenmaa *et al.* (2006), investigating

DOC trends in Finland concluded that decreasing sulphur deposition and the associated mineral acid input appeared to be the main driver.

The possible importance of both sulphur and seasalt deposition on DOC trends have been developed by Monteith *et al.* (in review) who compiled DOC trend data for the period 1990-2004 for lakes and streams across eastern North America and northeast Europe where reports of recent DOC increase are widespread. They concluded that changes in sulphur and seasalt deposition are sufficient to explain DOC trends in all the investigated regions, including parts of Atlantic Canada where DOC concentrations have unusually declined (in this region sulphur deposition is close to background and seasalt deposition has increased over the period). This study also shows that factors proposed previously to explain DOC trends, including rising temperature, rising ambient CO_2, changes in hydrology and changes in land-use did not show the appropriate geographical distribution to explain the widespread occurrence of trends.

To date there is less evidence to suggest that nitrogen deposition also influences DOC concentration through changing soil pH and ionic strength. Indeed it has been proposed that nitrogen deposition may actually be the driver of DOC trends in the Hudson River (Findlay, 2005) through its stimulation of soil bacteria. However, unlike sulphate and chloride, nitrate is not conservative in soils and, therefore, it is not possible to use its concentrations in runoff to infer the current deposition load. Further assessment of DOC data at sites with deposition chemistry data will be necessary to explore this further.

The primary influence on SOM solubility is the chemistry of precipitation. There is strong and mounting evidence to suggest that the solubility of SOM is not only influenced by changes in inputs of acid anions (particularly sulphur and seasalts) but has been the dominant factor influencing DOC trends throughout northwest Europe and eastern North America over the past two decades. The implications of the likely impact of climate change, therefore, on solubility rest predominantly with likely future trajectories and "wash-out" zones for polluted air masses. However, the dominant effect on DOC concentrations is likely to be anthropogenic. Providing further controls are placed on sulphur emissions, DOC concentrations in UK fresh waters are set to continue to rise in the foreseeable future. The anticipated increase in the North Atlantic Oscillation, and consequences of more frequent and more intense seasalt episodes should increase medium term (i.e. decadal scale) variability at sites in coastal areas.

Transport

Providing that the supply of DOC in soil water is not limiting, concentrations and fluxes of DOC in runoff will be strongly dependent on hydrology. Changes in water flowpath from (low-DOC) mineral horizons into (high-DOC) organic horizons during rain or snowmelt events (e.g. McDowell & Likens, 1988; Hongve *et al.*, 2004) increase concentrations at least initially. Tranvik and Jansson (2002) proposed changes in hydrology as the most plausible explanation for recent trends in Swedish rivers in recent decades.

However, changes in stream discharge in the absence of changing DOC flux can lead either to decreased DOC values (through dilution) or to increased DOC levels (through concentration). DOC concentrations have been shown to peak on stream hydrographs, prior to peak flow being reached, suggesting a relatively rapid onset of supply limitation. However, it is feasible that in a future climate scenario where NPP, decomposition rates and solubility (through lower sulphur deposition) are all increased, that limitation will occur later and DOC concentration maxima could therefore be raised.

Currently there is little evidence for this and Evans *et al.* (2006) demonstrated that DOC trends in the UK were occurring at all levels of flow and this could therefore not explain long term trends. They concluded that while short term variation in flow would undoubtedly influence variability, it had not exerted a dominant control of DOC trends in the UK over the past two decades.

Conclusions

The dissolved organic carbon concentration of UK upland surface waters is dependent on many processes influenced by climate, and particularly by the effects of temperature and soil moisture on NPP, decomposition rates, and by the effect of the intensity of precipitation which governs flow paths. It had been proposed that several of these factors have influenced the large increase in DOC concentrations in UK waters and elsewhere over the last 20 years.

Increasingly however, evidence points to a governing role of precipitation chemistry on DOC concentration, and in recent decades the dominant effect on this has been anthropogenic sulphur deposition. Providing acid anion fluxes to catchments continue to fall, SOM solubility should continue to rise, thus increasing the importance of climatic factors on concentrations into the future.

On balance it would seem that as solubility increases, synergistic effects of increased NPP and decomposition rates under a scenario of increasing summer temperatures and longer growth seasons should increase mean annual DOC fluxes and concentrations further. Added to this, increased hydrological variability, and particularly wetter winter conditions and increased seasalt events will increase seasonal variability, with higher DOC maxima (cf. NO_3^- leaching described in previous section).

These potential effects of future climate change have major consequences for aquatic ecosystems, through changes to the light and heat environment, the extent of transport and (where DOC is lost in lakes through photo-oxidation) delivery of toxic metals and organic compounds and effects on acidity. Furthermore, future changes to water quality will have major implications for future water treatment costs.

Ultimately though, scientific understanding is insufficient for scenarios to be predicted with any certainty. It is vital, therefore that monitoring of these upland systems is continued and that, increasingly, in situ and laboratory experiments are encouraged, ideally using sites and soils in monitored catchments, so that the interactions between anthropogenic deposition and climate change effects on DOC can be modelled with greater confidence.

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SECTION 3: IMPACTS OF CLIMATE CHANGE ON TRACE METALS AND PERSISTENT ORGANIC POLLUTANTS IN UPLAND FRESHWATERS

Neil Rose

Executive summary

- Based on the Aarhus Heavy Metal, the Stockholm Convention, and Persistent Organic Pollutant (POP) Protocols, the Water Framework Directive lists of hazardous and priority hazardous substances and other legislation and guidelines, the main trace metals of concern are mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu) and zinc (Zn) while the main POPs include PAHs, PCBs, PCDD/Fs, organochlorine pesticides, brominated compounds and organometallic compounds such as tributyltin (TBT). The POP priority hazardous substances include anthracene, pentabromodiphenylether, chloroalkanes, endosulfan, HCB, HCBD, HCH, nonylphenol, pentachlorobenzene, PAHs and TBT. Annual average and maximum allowable concentration Environmental Quality Standards (EQS) for inland surface waters have been proposed for these but data for UK upland waters are very limited.

- Predictions for how climate changes will impact emissions from industrial processes are rare except for electricity generation. It is predicted that despite the projected increase in electricity demand to 2020, UK coal consumption will continue to fall which could result in a decline in metals and POPs emissions. However, the UK will need to replace c. 30% of the current generating capacity (coal, nuclear) by 2025 and how this is undertaken will have a major impact on UK emissions. For Hg and volatile POPs the broader (possibly hemispherical) geographical scale needs to be considered. It is predicted that metal emissions in Europe will continue to decline and although coal consumption in developing countries could increase rapidly, the introduction of control technologies does not necessarily imply a similar increase in emissions. As a result, projected industrial metal emissions could either increase or decrease.

- The potential for the increase in invasive species, in vector-borne disease, crop pests and the possibility of reduced efficacy of herbicides as a result of climate change may lead to increased usage of pesticides in the UK and further afield. Long-range transport and increased atmospheric residence times will provide the means for POPs to be transferred to the UK uplands. Increased usage of upland areas for agriculture could also result in elevated inputs of trace metals, from fertilisers, to waterbodies in these areas.

- Warmer air temperatures will allow greater volatilisation of POPs and Hg and longer atmospheric life-times. The potential for greater distribution will therefore increase as will the movement of these pollutants to areas that are colder by virtue of their latitude or altitude. However, it is the retention of these compounds in upland waters that is critical. Warmer water temperatures will reduce retention and possibly lead to re-emission to the atmosphere from

pollutant 'stores'. Changing wind patterns could alter distribution patterns and pollutant source areas.

- Climate change is predicted to alter the distribution and seasonality of precipitation (drier summers, wetter winters) and dramatically reduce snowfall, while there is also potential to increase cloudiness in upland areas. Wet deposition and scavenging by snow and fog are efficient atmospheric removal processes for metals and POPs and so these changes will alter pollutant inputs to upland waters. However, projections of precipitation and cloudiness remain uncertain.

- There is a vast store of previously deposited pollutants in catchment soils and lake sediments. Climate change may be a key factor in the re-mobilisation of these contaminants to upland waters. Climate-enhanced catchment soil erosion and leaching from catchment soils may elevate pollutant inputs to upland waters from this store. Warmer and wetter conditions could increase mercury methylation while longer ice-free periods could increase algal scavenging of contaminants from the water column and into the food-web.

- Many physico-chemical and biological factors influence the toxicity of trace metals and POPs to aquatic biota including pH, water hardness, dissolved oxygen content, water temperature, suspended solids content, DOC concentrations, metabolic rate, diet, generation rate, etc. Climate change will influence all these factors though the direction (improvement or deterioration) and scale of impact and interactions may vary from site to site.

- In conclusion, there is considerable potential for climate change to impact on the emission, transport, deposition, re-mobilisation, re-emission and toxicity of trace metals and POPs in UK upland waters. While many predictions and scenarios, especially with regard to projected air temperatures, appear to give reasonable agreement (to direction if not to scale), there is still considerable uncertainty as regards future changes to precipitation, cloudiness, wind speeds and the magnitude and frequency of extreme events.

- Uncertainties relating to how climate effects will impact upon trace metals and POPs in upland ecosystems are compounded by a lack of basic information on these substances (especially Hg and POPs) in UK upland waters. The baseline against which we may measure the future effects of trace metals and POPs in upland ecosystems is largely missing and unless this significant gap in knowledge is filled as a matter of some urgency, it will not be possible to assess future changes at these sensitive sites.

- There is an urgent need to establish a monitoring programme to undertake empirical measurements at a wide range of upland waterbodies, in all areas of the UK over an extended period of time. Such knowledge will allow a better understanding of the key processes and drivers affecting the levels of toxic substances in upland aquatic food-webs. These data are also required to improve models for future prediction. Without such basic background knowledge, even the most robust models will lack 'ground-truth' and may offer only poor projections of future impacts.

Introduction

Background and current relevance

The potential for climate change to impact on freshwaters in the UK has been recognised for a number of years. In 1988, the Department of the Environment contracted the various Natural Environment Research Council (NERC) institutes to assess the likely direct and indirect impacts of a doubling of CO_2 by 2050. George (1988) wrote the report on climatic impacts on freshwater ecosystems and, apart from considering the more direct impacts of air and water temperature increases, also highlighted possible impacts on lake thermodynamics, water chemistry, microbiological processes such as decomposition, as well as impacts on lake eutrophication, algal blooms and the distribution of aquatic biota as a result of changes to water flow and temperature. However, the impact of climate change on pollutants in freshwaters was treated only cursorily in this report, with possible changes to pollutant transport, toxicity and microbial degradation of organic pollutants being briefly considered.

In a follow-up report, Whitehead and Jenkins (1989) further considered the impact of climate change on water quality. With respect to pollutants, they highlighted the potential effect of changing rainfall (i.e. reduced dilution in low-flow periods particularly for industrial and domestic waste and urban run-off) and for the uplands an increased pollutant load resulting from elevated rainfall and cloud cover enhancing 'wash out' from the atmosphere. Further, they suggested that elevated temperatures could increase the levels of agricultural pests and hence an elevated use of pesticides and fungicides.

In the two decades since these reports there have been a number of developments which make an updated review both necessary and timely. First, awareness and concern from both government and public to the impacts of climate change on all areas of the natural and human environment have escalated considerably, particularly in the last few years. Second, there has been significant shift in pollutant status. Not only have there been large (even dramatic) declines in emissions and deposition of pollutants in the UK and across Europe (e.g. Baker, 2001), but new compounds and groups of compounds have become more important in the environment and have been found to fulfil the persistent organic pollutant (POP) 'PBT' criteria of persistence, bioaccumulation and toxicity (e.g. brominated and fluorinated organic compounds). Third, new knowledge on the long-range transport of POPs and trace metals on intercontinental, hemispheric and global scales has shown how biota, even in remote areas, can bioaccumulate toxic compounds to high levels (Rognerud *et al.*, 2002; Vives *et al.*, 2005). This has led to renewed concern regarding the impacts of these pollutants to ecosystems (e.g. effects on the growth, development, reproduction and endocrine systems of freshwater biota) and to human health mainly through the consumption of fish and subsequent transgenerational effects caused by the transfer of toxic burden to both unborn and newborn children. Fourth, research has shown that the changing climate may lead to the remobilisation of pollutants deposited over the industrial period allowing previously 'stored' contaminants back into the environment and thereby increasing their availability to freshwater biota despite emission and deposition reductions. Fifth, the implementation of the EU Water Framework Directive in 2000 has changed the legislative framework for freshwater quality across

Europe and now drives UK freshwater policy. In particular (for this current study), the setting of guideline values and proposed environmental quality standards for a range of "priority substances", and its sub-set of "priority hazardous substances", has pushed trace metals and persistent organic pollutants (POPs) back up the freshwater agenda.

The EU Water Framework Directive (WFD) (2000/60/EC) has been called "the most substantial piece of EC water legislation to date" (DEFRA website, 2007a) and establishes an integrated approach to the protection, improvement and sustainable use of Europe's rivers, lakes, estuaries, coastal waters and groundwater. It requires these waters to reach "good status" by 2015 by setting environmental objectives including ecological targets for surface waters. The WFD requires that biological, hydromorphological and chemical elements of water quality should be based on the degree to which present day conditions deviate from those expected in the absence of significant anthropogenic influence, termed reference conditions. The four categories of 'Good', 'Moderate', 'Poor' and 'Bad' status are then defined according to the degree of deviation from the reference state. This also allows an assessment to be made of how much further improvement is required in order to raise the status of the waterbody of concern. Article 10 of the Water Framework Directive (WFD) sets out an approach involving the use of environmental quality standards (EQS). Communication 'COM(2006) 398 final' (2006) from the Commission of the European Communities states *"On the basis of information concerning the toxicity, persistence and bioaccumulation potential of a substance, together with information on what happens to the chemical in the environment, it is possible to determine threshold concentrations to protect people, flora and fauna. When EQS are established for water, or sediments, or plant / animal tissues they provide a benchmark for ensuring the ecological integrity of aquatic ecosystems or the protection of human health when using water"*

However, for trace metals and POPs the WFD takes one further very important legislative step. For the first time, not only must steps be taken to improve the status of waters as defined by EQS, but the Directive specifically states that for certain key pollutants existing levels of contamination should not increase. The proposed Directive 'COM(2006) 397 final' states that for mercury (Hg) hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) *"it is not possible to ensure protection against indirect effects and secondary poisoning by mere EQS for surface water on Community level. Therefore in those cases, EQS for biota should be set up. In order to allow Member States flexibility depending on their monitoring strategy they should be able either to monitor those EQS and check compliance with them in biota, or convert them into EQS for surface water. Furthermore, it is for Member States to set up EQS for sediment or biota where it is necessary and appropriate to complement the EQS set up at the Community level. Moreover, as sediment and biota remain important matrices for monitoring certain substances by Member States in order to assess long term impacts of anthropogenic activity and trends the Member States should ensure that existing levels of contamination in biota and sediments will not increase"*.

This final statement is of particular relevance to this current study, for one of the main potential impacts of climate change on trace metals and POPs in upland freshwaters is the re-mobilisation of previously deposited pollutants from storage back into waterbodies where they can become available for biological uptake (see below). There is evidence that climate is now a key factor in the release of stored pollutants from catchments into surface waters (e.g. Blais *et al.*, 2001; Rose *et al.*, 2004) and hence climate could confound both emissions reductions policies (where these relate to protection of upland waters from deposition) and impact on the strategy for WFD compliance.

Species of concern

While regulatory bodies at the national and international level have been, and remain, concerned with the presence and effects of trace metals and POPs in the environment and have produced lists of those chemical species (elements, compounds) which are considered the greatest hazard to ecosystem and human health, the WFD establishes a new regime for prevention and control of chemical pollution of surface and ground waters. In the WFD, a limited number of chemical pollutants have been identified as being of particular concern in surface waters due to their widespread use and high concentrations in rivers, lakes and coastal waters. These are defined as "priority substances". There are 33 of them and they were first agreed as substances (or groups of substances) for regulation in 2001. A sub-set of these are defined as "priority hazardous substances" and more stringent environmental objectives apply to these due to their persistence, bioaccumulation and toxicity. Both the list of priority substances and that of the priority hazardous substances include trace metals and POPs.

Trace metals

Lead (Pb) and nickel (Ni) are included on the WFD list of priority substances while cadmium (Cd) and Hg are included on the list of priority hazardous substances. Environmental Quality Standards (EQS) for inland surface waters (rivers and lakes) have been proposed to protect against (i) short-term, direct and acute toxic effects and (ii) long term chronic effects. The former EQS is based on a maximum allowable concentration while the latter uses an annual average (although the Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE) also indicates that acute exposure can have long term consequences) (COM(2006) 397 final). The EQS for these metals are shown in Table 4.4. For these trace metals compliance allows Member States to take background levels and bioavailability into account. However, it should be noted that it is considered likely that the EQS for Ni and Pb will need to be amended in the light of forthcoming risk assessments.

Air quality legislation for trace metals also pertains to water quality, especially in upland waters, by virtue of long-range atmospheric transport. The 1998 Aarhus Protocol on Heavy metals under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) entered into force on 29th December 2003 and targets Cd, Pb and Hg. The Protocol aims to cut emissions to the atmosphere of these metals from industrial sources (e.g. iron and steel, non-ferrous metal industries), combustion processes (power generation, road transport) and waste incineration to below their 1990 level or below a level from an alternative year between 1985 and 1995. These three metals were also considered the three "priority" heavy metals for human health and the environment in a review of the Protocol considering emissions, depositions, critical loads and exceedances (Hettelingh *et al.*, 2006) although critical loads and exceedances of other metals, Cr, Ni, Cu, Zn, As and Se were also considered.

Table 4.4: Environmental Quality Standards (EQS) proposed for heavy metal priority substances in inland surface waters (Source: COM(2006) 397 final)

Trace metal	Annual average ($\mu g\ l^{-1}$)	Maximum allowable concentration ($\mu g\ l^{-1}$)
Cadmium (and its compounds)*	≤0.08 (<40 mg $CaCO_3\ l^{-1}$)	≤0.45 (<40 mg $CaCO_3\ l^{-1}$)
	0.08 (40 - <50 mg $CaCO_3\ l^{-1}$)	0.45 (40 - <50 mg $CaCO_3\ l^{-1}$)
	0.09 (50 - <100 mg $CaCO_3\ l^{-1}$)	0.6 (50 - <100 mg $CaCO_3\ l^{-1}$)
	0.15 (100 - <200 mg $CaCO_3\ l^{-1}$)	0.9 (100 - <200 mg $CaCO_3\ l^{-1}$)
	0.25 (≥200 mg $CaCO_3\ l^{-1}$)	1.5 (≥200 mg $CaCO_3\ l^{-1}$)
Lead (and its compounds)	7.2	not applicable **
Mercury (and its compounds)	0.05	0.07
Nickel (and its compounds)	20	not applicable **

* EQS is dependent on water hardness defined in five categories.
** where maximum allowable concentrations are 'not applicable' the annual average EQS is considered protective against short-term pollution peaks since they are significantly lower than the values derived on the basis of acute toxicity.

Two EU Air Quality Daughter Directives also relate to setting limit values for trace metals in ambient air. The first Daughter Directive (1999/30/EC) sets a limit value for Pb which was transposed into UK law in the Air Quality Limit Values Regulations 2001 as an annual limit value of 0.5 $\mu g\ m^{-3}$. Similarly, the Fourth Air Quality Daughter Directive (transposed as The Air Quality Standards Regulations 2007) sets limit values for As, Cd, Ni and the polycyclic aromatic hydrocarbon (PAH) benzo(a)pyrene, but only sets a requirement to monitor for Hg in ambient air, setting no limit value (DEFRA, 2006). Target values for As, Cd, Ni and benzo(a)pyrene relate to the total content of these pollutants in the PM_{10} fraction averaged over one calendar year and are 6 ng m^{-3}, 5 ng m^{-3}, 20 ng m^{-3} and 1 ng m^{-3} respectively. These values are due to be attained by the end of 2012.

The EU scientific co-operation (SCOOP) 3.2.11 (2004) on dietary exposure to the population of the EU Member States focussed on As, Cd, Pb and Hg and provided occurrence, intake and Provisional Tolerable Weekly Intake (PTWI) data for these trace elements including for freshwater fish. For Hg in particular intake via fish consumption is a major pathway for humans as it is present almost exclusively as methylmercury. Current PTWI (set by the Joint FAO/WHO Expert Committee on Food Additives (JEFCA)) for methylmercury is 1.6 $\mu g\ kg^{-1}$ body weight which corresponds to 0.112 mg $week^{-1}$ for a person weighing 70 kg. Fish also represent a significant source of As for human intake. Other EU Council Directives pertaining to metals in waters are included in Table 2.

In summary, the main trace metals of concern are Hg, Cd, Pb, Cu, Ni and Zn. The non-metals As and Se are also often considered alongside these. Hg in particular is of special concern and is often treated separately to the other trace metals. Due to its volatility, it has a long atmospheric lifetime of c. 1 year (e.g. Hylander & Goodsite, 2006) and is thus able to travel very long-distances prior to deposition and is therefore included in hemispherical transport models (e.g. Travnikov, 2005). Hg is currently not included in models for upland waters (CHUM-AM, WHAM) (Tipping *et al.*, 2007a;

b) and there is a severe lack of data for this element for UK surface waters. In these respects Hg is very similar to persistent organic pollutants (POPs).

Table 4.5: Selected EU Council Directives pertaining to metals in waters.
(Elements in parentheses are often included with trace metals in literature and legislation, but are non-metals).

Directive		Metals
78/659/EEC	Freshwater Fisheries	Cu, Zn
75/440/EEC	Surface Waters Abstracted for Human Supply	Cu, Zn, Cd, Cr, Pb, Hg, Ba, (As), (Se), Mn,
76/464/EEC	Dangerous substances	Hg, Cd, (As)
80/68/EEC	Discharges to Groundwater	Hg, Cd
96/61/EC	Integrated Pollution Prevention and Control	"Metals and their compounds"

<u>Persistent organic pollutants (POPs)</u>

While the number of trace metals of concern is relatively small, there is a vast array of organic compounds which fulfil the persistence, bioaccumulation and toxicity criteria for POPs. Therefore, it is often more appropriate to consider POPs in terms of classes of compounds (e.g. PAHs, PCBs, PCDD/Fs, PBDEs), where each class may contain some hundreds of chemicals related by virtue of their structure and effects. Furthermore, many chemicals are developed each year for which there is limited testing of environmental impact and the effects of many of these are only predicted from the known impacts of compounds to which they are structurally related.

On a cautionary note, many studies report concentrations and fluxes of these pollutant classes in terms of their sum (e.g. ΣPCB) and the specific isomers and congeners comprising these 'sums' may vary from study to study making comparison difficult. While there are often a 'usual' suite of compounds analysed (e.g. the seven PCB isomers 28, 52, 101, 118, 138, 153, 180; Grimalt *et al.*, 2004) it is important to know in each case which set of compounds are being summed to generate the total. Similarly, summed values may also include derivatives (e.g. ΣDDT may also include DDE and DDD).

While new organic chemicals are produced each year, others may also be banned and their production and / or usage greatly reduced or ceased. In these cases, although new emissions to the environment are limited, the persistence of the compounds already released to, and stored within, environmental media (including biota) mean that the compound, or class of compounds, may continue to be an environmental issue for decades or possibly centuries (see Section 5 below) . These are often termed 'legacy' POPs to differentiate them from those in 'current-use'.

The 1998 Aarhus Protocol on POPs under the UNECE CLRTAP bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene) while others are scheduled for elimination at a later stage (DDT, heptachlor, hexachlorobenzene and PCBs). The Protocol also severely restricts the use of DDT, HCH (including lindane: γ-HCH) and PCBs and furthermore obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their levels in 1990 or, as with the Heavy Metals Protocol, an alternative year between 1985 and 1995. These compounds of concern listed under the Aarhus POPs Protocol are thus similar to the initial twelve also targeted for elimination under the Stockholm Convention, (i.e. aldrin, chlordane, DDT, dieldrin, dioxins, endrin, furans, heptachlor, HCB, mirex, PCBs and toxaphene), a global treaty aimed at reducing and eventually eliminating POPs (http://www.pops.int/.). The UK National Implementation plan for the Stockholm Convention was published in April 2007 (http://www.defra.gov.uk/environment/chemicals/pdf/pop-nationalplan.pdf).

The priority substances and priority hazardous substances listed under the Water Framework Directive also include a range of POPs including PAHs, organochlorine pesticides, brominated compounds and organometallic compounds such as tributyltin. The priority hazardous substances include anthracene, pentabromodiphenylether, chloroalkanes, endosulfan, HCB, HCBD, HCH, nonylphenol, pentachlorobenzene, PAHs and TBT and hence annual average and maximum allowable concentration EQS for inland surface waters have been proposed for these as shown in Table 4.6. Proposed EQS for other (non-priority substances) pollutants are given in Table 4.7. The POPs of concern thus include both legacy and current-use chemicals.

Table 4.6: Environmental Quality Standards (EQS) for proposed for selected POPs priority substances in inland surface waters (Source: COM(2006) 397 final)

Compound	Annual average ($\mu g\ l^{-1}$)	Maximum allowable concentration ($\mu g\ l^{-1}$)
Anthracene	0.1	0.4
Pentabromodiphenylether	0.0005	not applicable **
Endosulfan	0.005	0.01
Fluoranthene	0.1	1.0
Hexachlorobenzene (HCB)	0.01	0.05
Hexachlorobutadiene (HCBD)	0.1	0.6
Hexachlorocyclohexane (HCH)	0.02	0.04
Naphthalene	2.4	not applicable **
Pentachlorobenzene	0.007	not applicable **
Benzo(a)pyrene	0.05	0.1
Tributyltin compounds	0.0002	0.0015

** where maximum allowable concentrations are 'not applicable' the annual average EQS is considered protective against short-term pollution peaks since they are significantly lower than the values derived on the basis of acute toxicity.

While the list of trace metals of concern remains largely the same, given the continual addition of new organic compounds to the environment there is a need to regularly review and update those compounds included within the legislation. A good example of this are the fluorinated organic compounds PFAS (Perfluorinated Alkyl Substances), used to provide protective coatings to textiles and paper. These are now known to fulfil the PBT criteria and one, PFOS (perfluorooctyl sulphonate) is of particular concern (Norwegian Pollution Control Authority, 2005). Following a DEFRA funded report (Footitt *et al.*, 2004) on risk reduction strategy for PFOS a revision of Council Directive 76/69/EEC is currently under consultation regarding restrictions on the marketing and use of this compound (DEFRA 2007b).

Table 4.7: Environmental Quality Standards (EQS) for proposed for selected other POPs (non-priority substances) in inland surface waters (Source: COM(2006) 397 final)

Compound	Annual average (µg l^{-1})	Maximum allowable concentration (µg l^{-1})
DDT (total) *	0.025	not applicable **
Aldrin		not applicable **
Dieldrin	Σ = 0.01	not applicable **
Endrin		not applicable **

* For full list of isomers comprising total DDT see COM(2006) 397 final
** where maximum allowable concentrations are 'not applicable' the annual average EQS is considered protective against short-term pollution peaks since they are significantly lower than the values derived on the basis of acute toxicity.

Climate impacts on emissions of trace metals and persistent organic pollutants

Although the scope of this study focuses on the impact of climate change to freshwaters in the UK uplands, there is good evidence for the long-range transport of contamination to these areas from sources in Europe and beyond. For example, Rose *et al.* (2007) describe the evidence for sources of contamination derived from Scotland, the rest of the UK, Europe and other continents to Lochnagar, a remote mountain loch to the south-east of the Cairngorm Mountains. Dispersion modelling (e.g. HARM, EMEP) shows the scale of deposition of acidifying substances to the loch from industrial sources in Scotland (particularly the area around the Firth of Forth), power stations in Wales, Northern Ireland and England (particularly the Midlands) and, while this represents the vast majority of acidifying deposition, there is also evidence to suggest transported contaminants from other European countries, including Germany, France and Spain. Given the source of this contamination, it is likely that these are also major source areas for other atmospherically deposited pollutants (especially trace metals) to this remote loch. Palaeolimnological (lake sediment) studies at Lochnagar also provide evidence for a range of contaminant source areas including a record of ^{137}Cs from the Chernobyl nuclear reactor accident in Ukraine in 1986, toxaphene from Eastern Europe and the United States (Rose *et al.*, 2004) and ^{241}Am and ^{137}Cs from global weapons testing. There is, therefore, a need to consider how climate change will affect emissions and transport of contaminants at larger geographic scales. It is now known that the atmospheric lifetime of elemental Hg (Hg^0) is in the order of one year allowing it to be transported, on average, three times around the world prior to deposition (Hylander & Goodsite, 2006). At these scales, emissions to the atmosphere need to be considered on at least the hemispheric level (e.g. Travnikov, 2005).

Industrial emissions

Industrial processes, and especially the electricity generation industry via fossil-fuel combustion, are the major source of many trace metals and POPs (especially PAHs) to the atmosphere and it is therefore important to consider how climate change may affect emissions from these sources. While it is difficult to predict how climate change may affect some industrial processes resulting in pollutant emissions there has been, of necessity, some consideration as to future trends in electricity generation and the role that fossil-fuel combustion may play within it. In particular, the future role of coal combustion is of great importance for many trace metal emissions, especially Hg as this is responsible for up to 66% of global Hg emissions (Pacyna *et al.*, 2006).

Within the UK, the Department of Trade and Industry's (DTI) Energy Review (2006a) projects that electricity generation will increase to 2020 although the fraction generated by coal and oil should decline to be replaced by natural gas and renewable sources, especially biofuels and wind generation. Both of the DTI's central scenarios for primary energy demand, the first "favourable to gas" and the second "favourable to coal" also predict a decrease in coal consumption by 2020 (DTI, 2006b). These suggest a decline from 1990 levels of 66.9 Mtoe (Million tonnes oil equivalent) to 23.3 Mtoe and 33.1 Mtoe, respectively and UK coal production is set to decline steadily especially after 2010 (DTI, 2004). However, while the UK's current electricity generation is produced from diverse sources, a number of both coal and nuclear power stations are approaching the end of their lives and will need to be replaced. Around 8 GW of currently installed coal capacity must close by 2015 (about a third of the current coal total) and more than 10 GW of the UK's nuclear power stations must close by 2023 (DTI, 2006a). In total, the UK is likely to need about 25 GW of new electricity generation capacity by 2025 which is more than 30% of current capacity. Furthermore, climate change may also influence current electricity generation, albeit in a minor way. A reduction in summer rainfall, particularly in upland areas may reduce the generating potential of some hydroelectric schemes and this shortfall would need to be replaced by other, possibly conventional fossil-fuel, means. Therefore, while future trends in trace metal and POPs emissions in the UK are very uncertain (NEGTAP, 2001) the strategy for replacing the current installed electricity generation capacity over the next few decades, for supplying the foreseen additional energy demand (see also Section 2.3 below) and to cover potential climate-induced shortfall in hydroelectric generation will go a long way to deciding future trends in the UK's emissions of trace metals and POPs (particularly polycyclic aromatic hydrocarbons) to the atmosphere.

On the European scale, Hettelingh *et al.* (2006) have projected heavy metal emissions for 2010 and 2020 based on two policy scenarios: CLE (base line scenario with current legislation and current (April 2005) ratification of the Heavy Metal Protocol) and FI (base line scenario with current legislation and full implementation of the Heavy Metal Protocol). The emissions of selected metals for UNECE Europe under these scenarios are given in Table 4.8. An additional scenario FIAM (full implementation with additional measures) reduces the projected 2020 values, shown in Table 4.8, further still. These scenarios would appear to suggest that trace metal emissions in Europe will continue to decline over the next 10-15 years, although there are no projections beyond this and very little research has been done in this area (Pacyna *et al.*, 2006). A more detailed discussion of these scenarios and further implications of a revision to the Heavy Metal Protocol are given in Hettelingh *et al.* (2006) but it should be highlighted that even after implementation of the Protocol industrial processes including fossil-fuel combustion for heat and power production, cement production, the iron and steel industry; industrial and residential combustion and road transport remain the most important source sectors for metal emissions to the atmosphere. One area with a greater predictive uncertainty is that of waste incineration (Lindqvist, 1995; Pacyna *et al.*, 2006). The scale of this process and the content of the sorted or unsorted waste to be incinerated are difficult to project into the future but could remain a significant source of both trace metals and POPs.

Table 4.8: Emissions of selected metals (tonnes/yr) in UNECE Europe for 2010 and 2020 under the CLE and FI scenarios compared with emissions for 1990 and 2000 (from Hettelingh *et al.*, 2006).

	Cd	Hg	Pb	Cu	Ni	Zn
1990	650	501	41879	6078	11930	27659
2000	377	344	15021	2846	4144	19503
2010 CLE	327	328	7317	2642	3750	18025
2020 CLE	323	326	7650	2772	3426	19006
2020 FI	217	316	5761	2126	2622	13766

Beyond Europe, and considering the long-range transport implications for metal and POPs deposition to upland UK lakes, global electricity consumption is predicted to more than double over the next few decades from 14780 billion kWh to more than 30000 billion kWh (Energy Information Administration (EIA), 2006). The capacity for generating this additional electricity is also predicted to increase in all sectors, so coal and oil usage for electricity generation is predicted to increase over the same period. However, these changes are quite regional so whereas coal consumption in the 30 member countries of the OECD (Organisation for Economic Co-operation and Development) increase only slightly, a much larger increase is observed in non-OECD countries especially in Asia (EIA, 2006). In China alone, coal consumption is predicted to increase by more than three times in both electricity generation and other industrial sectors over this period. Similarly the installed electricity generation capacity for India is expected to increase from 120 GW in 2002 to c. 350 GW by 2090 of which a major proportion will be generated by coal such that coal's share of the electricity generation market in 2090 will be close to double India's current total installed electricity capacity (International Energy Agency (IEA), 2006).

However, it should be stressed that increased coal consumption does not necessarily imply increased metal and POPs emissions to the atmosphere. In many locations, emissions control equipment including particulate removal techniques such as electrostatic precipitators (ESPs) and fabric filters (FFs) are now commonly employed in major electric power plants and central heating plants especially where these are new installations. Further, the application of flue-gas desulphurisation (FGD) or wet scrubbing techniques to remove acidifying species also has a major impact on other pollutant emissions especially more volatile ones such as some POPs and Hg (Pacyna *et al.*, 2006). Emission control measures for these pollutants also impact on the emissions of others (e.g. greenhouse gases), either positively or negatively (EEA, 2004) while air quality targets may also require measures (e.g. end-of-pipe, energy conservation, fuel substitution, change in production level, etc.) leading to reductions or increases in the emissions of metals and POPs. Therefore, while the increased global energy demand will almost certainly include an increase in the consumption of fossil-fuels this does not necessarily translate into increased metal and POPs emissions. Pacyna *et al.*'s (2006) prediction for global Hg emissions for 2020 reflect this with an estimate of a cautious ± 20%. Hence, this prediction does not even give a greater probability to an increase or a decrease in global Hg emissions and uncertainty as to the implications of this for UK upland waters are equally uncertain.

Agricultural applications and land-use

The impact of climate change on agricultural practices in the UK will depend upon the balance between elevated CO_2 and temperature and water availability. These will influence current and projected changes to land-use while there may also be opportunities for the development of new crops or the development of 'new' areas. The UK Climate Change Impacts Review Group (UK CCIRG) in their first report (1991) suggested that predicted climatic changes may lead to greater agricultural use of "currently unproductive upland moor and heath" in the UK although this would require "considerable inputs of lime and fertiliser". Such an act could obviously have a major impact on upland waters with catchments in these areas and would lead to increased sediment loads and eutrophication. The input of trace metals to affected waterbodies would also likely increase as run-off from fertiliser application would include additional trace metals such as Cu and Zn. On a large scale this may seem a little far-fetched, but if climate change alters agricultural practices, efficiencies and yields both in the UK and abroad, then there may be considerable pressure to use upland areas in these ways.

The UK CCIRG also predicted that warmer temperatures, especially in winter, could enhance the spread of diseases as mild conditions allow greater growth and spread of pathogens. Furthermore, the possibility of continual growth through the winter may allow a "green bridge" on which diseases could thrive through to spring-sown crops. Warmer temperatures and changes in precipitation may also allow invasive species to move to areas where they have been previously climatically-limited and while this may allow the development of new crops, this may also include undesirable species (both those associated with new crops and other opportunistic species) which will need to be controlled both to reduce the impact on agricultural yield but also to lessen the impact on native wild species. Patterson *et al.* (1999) provide a good summary of the potential effects of climate change on agricultural pests. Briefly, they suggest that the effects could include:

- Physiological and biochemical changes in host crop plants in response to rising CO_2 affecting the feeding patterns of insect pests;
- Potential for shifts in pest life-cycle and behaviour (e.g. distribution, degree of infestation, dispersal, mortality etc.);
- Reduction of pest generation times allowing more rapid population increases;
- Accelerated poleward migration (and by inference altitudinal movement). For example, it is predicted that a 3 °C increase in temperature by 2025 - 2070 could shift the northern limit of the European corn borer (*Ostrinia nubilalis*) northwards by 1220 km (Porter *et al.*, 1991);
- Reduced predictability of disease outbreaks due to changing and more unstable weather conditions;
- Changes to temperature, precipitation, wind, soil moisture and atmospheric humidity will influence the application and effectiveness of herbicides;
- Changes in temperature and moisture availability will affect the uptake and metabolism of herbicides by crops and target weeds;
- Environmental instability reducing the effectiveness of pesticides on target pests and / or more injury to non-target organisms.

With these possible consequences for agriculture and the possibility that "more effective vectors (different species of mosquito)" of human diseases may arrive in the

UK as a result of climate change (Department of Health, 2007), there is potential for elevated pesticide usage both in the UK and abroad. It has already been established that pesticides need neither be produced nor used in the UK in order to impact on UK upland waters and that these substances can travel long-distances prior to deposition at these sites. Rose *et al.* (2001) used the sediment record of Lochnagar to show the temporal trends in deposition of toxaphene, a pesticide widely used as an insecticide (particularly in the US cotton-growing industry) following the ban on DDT in the 1970s and also used as a piscicide (Stern *et al.*, 1996). Toxaphene was never produced nor used in the UK, but the concentrations in the sediments of Lochnagar approached levels seen in the US Great Lakes which are known to have been affected by both riverine inputs and atmospheric deposition. Two peaks in the sediment profile were observed at Lochnagar, the earlier one showed good agreement with the US source curve and was thought to reflect global patterns, while the later peak was thought to be due to transport from source areas in eastern and southern Europe. Unfortunately there have been no other comparative studies in the UK with which to compare these data. It is therefore unknown whether the concentrations observed in Lochnagar are typical, high or low for UK upland lakes. In addition to toxaphene, the sediment record of Lochnagar has also shown temporal trends in atmospheric deposition of other pesticides including the 'legacy' chlorinated pesticides DDT, dieldrin, aldrin, chlordane and HCH as well as the 'current-use' pesticides endosulfan and lindane (Muir and Rose, 2007).

The control of invasive species and diseases by chemical means does not, therefore, have to occur in the UK for their impacts to be felt in UK upland waters. The effects of climate change on agricultural practices are likely to impact much more strongly in southern Europe than in the UK and the increased use of pesticides in these lower latitude areas could result in elevated transport to colder, higher latitude (and altitude) waterbodies (see below). In addition, and given the possibility for long-range transport from beyond Europe, the usage of these chemicals in countries where their application is less strictly controlled could also impact upon inputs to the UK uplands via atmospheric transport and deposition. By contrast, the elevated use of fertilisers in lowland areas of the UK, or in other areas of Europe or beyond in response to climate-induced reduction in agricultural yield, is unlikely to lead to increased metal inputs to upland lakes although the general level of trace metals in the environment may be increased by this process.

Finally, one further climate-induced land-use change that may lead to enhanced emissions of trace metals and POPs is the possibility of increased wildfire prevalence. With the likelihood of longer and more frequent droughts in summer across Europe there is the potential for an increased incidence of both natural (Maracchi *et al.*, 2005; Kelly *et al.*, 2006) and human-caused (Wotton *et al.*, 2003) forest- (and other natural biomass) fires. Such events could result in the emission of PAHs (Keshtkar & Ashbaugh, 2006) and Hg (Turetsky *et al.*, 2006) to the atmosphere, the latter suggested as a result of Hg release from organic-rich soils. This being the case, then there is also the potential for similar emissions of PCDD/Fs by this mechanism if fires were to occur in coastal areas (cf. Meharg & Killham, 2003). Kelly *et al.* (2006) also showed an increase in Hg in fishes both in lakes where burning had occurred in the catchment and a studied mountain lake in the region. It is suggested that there is an initial pulse of both total and methylmercury to streams and lakes following a fire, but that increased productivity as a result of nutrients from the ash restructures the food chain such that Hg levels in fishes are also elevated over the longer term. The increase in nutrients from deposited ash is also thought to enhance methylation of deposited Hg (as a result of fire-related Hg volatilisation) and that already present in the burned and unburned catchments.

Domestic applications

The enhanced emissions of trace metals and POPs from domestic applications as a result of climate change is mainly indirect from changes in demand for electricity. Most domestic electricity demand is currently for heating, lighting, hot water, cooking and entertainment. Future changes to this demand as a result of climate change is likely to be limited although it could be foreseen that warmer temperatures and increased residential energy efficiency measures may result in a reduction in future electricity demand. For example, the DTI (2006b) project that by 2020 97% of UK homes will have central heating of which 78% will be gas-fired. The reduction in demand for heating resulting from a warming climate may be offset to some degree by the need for additional domestic cooling. Indeed, in the USA domestic electricity demand for air conditioning is projected to exceed that for heating (Hadley *et al.*, 2006) but this is in part due to the inefficiency of the electric cooling units and the use of other fuel sources (i.e. gas or oil rather than electricity) for residential heating. It also raises the rather interesting problem of whether impacts on human health are greater as a result of heat stress or from the increased levels air pollutants resulting from the increased electricity demand for air-conditioning (Bernard *et al.*, 2001).

While not directly linked to climate change, emissions from road vehicles are a significant source of both trace metals (e.g. Cu, Zn, Ni, Cd, Pb) (e.g. Linton *et al.*, 1980; Janssen *et al.*, 1997; Westerlund & Johansson, 2002) and PAHs (Baek *et al.*, 1992; Lowenthal *et al.*, 1994; Pengchai *et al.*, 2004) and for trace metals at least are expected to remain so even after implementation of the Heavy Metal Protocol (Hettelingh *et al.*, 2006). The UK National Road Traffic Forecasts (1997) predict traffic growth of 34% for all vehicles by 2031 (compared with 2006) (DETR, 1997) although this growth is considerably higher for light and articulated heavy goods vehicles (HGVs) than for cars, rigid HGVs and passenger service vehicles. However, despite recent and predicted increases in vehicle numbers, progressively tighter vehicle emission standards have led to significant reductions in air pollutant emissions from this sector since 1990 (DETR, 1999). Furthermore, the UK Air Quality Strategy predicts that emissions from vehicle exhausts will continue to decline to 2010 where they level off to the limit of the predictions in 2025. Obviously, these predictions are subject not only to further emissions legislation but also progress in fuel and vehicle technology. Although emissions from exhausts are therefore expected to be at a low level in the next few decades, other vehicular sources of metals are not subject to the same legislative control and hence can contribute to environmental metal levels. Westerlund and Johansson (2002) show emission factors for a range of metals from wear of brake linings and, with increased numbers of vehicles on UK roads, there is potential for elevated particulate metals emissions from this source.

As outlined above, there is considerable potential for new and increased numbers of pests affecting agricultural productivity as a result of climate change and this may lead to elevated pesticide usage. While not on the same scale, there is also the potential for the same factors to lead to increased usage of chemical pest control in gardens. This could lead to evaporative loss and transport from source areas to the UK uplands.

Changes in trace metal and POPs transport as a result of climate change

One of the most direct and measurable consequences of elevated atmospheric CO_2 concentrations is the increase in air temperature. While there are regional and seasonal variations to the extent of this warming, it will be a phenomenon that will be experienced to a greater or lesser extent across the globe. This increased energy in the atmosphere will have its own climatic effects but it will also affect the distribution and transport of pollutants emitted to the atmosphere. Persistent organic pollutants vary markedly in their properties even within a contaminant class (see, for example, Table 1 in Muir & Rose, 2007) and hence they will be differentially affected by changes in air temperature. The volatilisation of compounds is a temperature dependent process and therefore in a warmer atmosphere those compounds which volatilise readily (e.g. Hg and some POPs) will have longer atmospheric residence times and be able to travel greater distances prior to deposition. However, atmospheric transport is often not direct but involves a number of transfer processes. These can include removal from the atmosphere by exchange with surfaces (e.g. soil, vegetation, water) or by partitioning into rain and snow or onto particles which can then themselves be removed by precipitation (Macdonald *et al.*, 2003) (See also Section 4). Such removal may, however, only be temporary as re-volatilisation of the chemical from the surface back to the atmosphere can occur once appropriate conditions allow (i.e. increased temperature on a daily or seasonal basis). Transport from sources for these volatile contaminants can therefore occur in a series of exchanges or 'hops' and hence this transport is known as the "grasshopper" effect (e.g. Gouin *et al.*, 2004). Furthermore, and as a consequence of this continuous exchange between atmosphere and surface, the more volatile, lighter species (for POPs often the less chlorinated compounds) preferentially volatilise and are transported on and so a fractionation occurs in a "global chromatographic" process (Macdonald *et al.*, 2003). A warmer atmosphere may therefore alter this process by allowing a longer atmospheric lifetime (e.g. Dalla Valle *et al.*, 2007) between 'hops' but also by permitting less volatile compounds to travel to cooler locations than they had previously been able to. Long-range transport is already known to be a significant process for contaminant distribution on the hemispherical and even inter-hemispherical scale. Travnikov (2005) shows that while 61% of Hg deposited in Europe is from European sources, 23% of the remainder is derived from other northern hemisphere continents (Asia 15%; North America 5%; Africa 3%) while sources in the southern hemisphere contribute 4%. Therefore any process that enhances atmospheric lifetime of contaminants therefore provides the means for greater intercontinental transport which may be of particular concern where industrial development is currently, and projected to, increase rapidly.

The "grasshopper" movement of POPs and Hg is an important mechanism by which these pollutants can move from lower to higher latitudes, but this transport to cooler locations and resulting fractionation also occurs on an altitudinal basis. Hence, altitudinal gradients have been seen to occur in the waters, sediments and biota for various classes of POP in European mountain lakes (e.g. Grimalt *et al.*, 2001; Fernández *et al.*, 1999; 2000; Vives *et al.*, 2004a; b). However, while the movement to higher altitudes by this process is important, probably the most critical factor is the retention of these compounds in the water and their absorption to organic matter and these processes are also temperature dependant. In upland lakes, because of the lower water temperature, less volatile POPs (or 'semi-volatile' compounds) are preferentially absorbed in water and selectively trapped in sediments and fish. Thus, higher altitude lakes are preferentially enriched in less-volatile compounds over more volatile ones. Hence, while mobility within the atmosphere may increase as a result of increasing air temperatures, in upland lakes there will also be less absorption of semi-volatile compounds and possibly even some release of them (cf. Gouin *et al.*, 2004). As a consequence we may expect a shift in the altitudinal (or latitudinal) gradients of POPs accumulation although the predicted temperature increases are unlikely to affect the least-volatile compounds in any significant way.

Increases in air temperature and the related increases in water and soil temperatures will therefore result in the re-emission of volatile pollutants back to the atmosphere. While this process occurs already, an increase in water and soil temperatures will mean an increased frequency for the more volatile compounds (shorter 'rests' between hops) and may permit the re-emission of some less volatile compounds, which had been effectively bound, for the first time. This will have two consequences. First, the atmospheric concentrations of these contaminants may increase (to be transported northwards or upwards). The UK uplands are not sufficiently high to observe an altitudinal gradient (J. Grimalt pers. comm.) and so this re-emission could result in reduced contamination to UK upland lakes, as once re-emitted they will only be deposited again in areas that are cooler than exist within the UK. Secondly, this would be beneficial to the source water body or soil as concentrations are lowered and availability to biota reduced (Macdonald *et al.*, 2003). However, on a broader geographical consideration, this process would delay recovery at the sites where re-emitted pollutants are ultimately deposited and retained (Gouin *et al.*, 2004).

For metals other than Hg and for the least volatile POPs these processes are less important. However, for those metals and POPs which are bound to particulates changing wind patterns as a result of climate change may be more significant though these are poorly predicted by Global Climate Models (GCMs) (Patterson *et al.*, 1999). Such changes could alter contaminant source areas, distribution, transport and deposition of airborne pollutants but currently to an unknown extent. Hence these may be either beneficial or deleterious for the UK uplands. In background areas (i.e. those not directly impacted from sources) Hg deposition is reasonably evenly distributed over the northern hemisphere and so changes to wind patterns would probably have little impact. Climate changes of this nature may also transport particulate bound trace metals and POPs from previous storage in soils especially in arid regions where predicted warmer and drier conditions may lead to increased wind-blown dust transport (e.g. Prospero & Lamb, 2003).

Changes in trace metal and POPs deposition as a result of climate change

Airborne pollutants transported to upland areas of the UK may be removed by both dry and wet deposition. Wet deposition includes all forms of precipitation: rainfall, snowfall and occult deposition through orographic cloud (Fowler *et al.*, 1988; Krupa, 2002). Any impact that climate change may make to enhance or reduce wet deposition will therefore alter the inputs of pollutants to upland water bodies by these mechanisms.

Wet deposition by rainfall has been shown to be an important process for the removal of trace metals both in dissolved form in rainwater and by washout of particulate bound metals (e.g. Struck *et al.*, 1996; Rocher *et al.*, 2004). Different elements have been seen to exhibit different scavenging properties (Simamura *et al.*, 2006). Mainly natural elements (e.g. Na, Mg, Ca, Sr) are efficiently scavenged while some anthropogenic elements, including Zn, Cu, Se and Sb were scavenged with 'intermediate' efficiency. Sn was found to be less efficiently scavenged. Rainfall is also found to be important for removal of POPs from the atmosphere (Macdonald *et al.*, 2003), including PAHs (Halsall *et al.*, 2001; Rocher *et al.*, 2004; Sahu *et al.*, 2004), PCBs and PCDDs (e.g. Simcik, 2004).

Although future predictions for rainfall are thought to be less certain than those for air temperature, especially on a regional basis, the UKCIP climate change scenario data for the 50 km grid squares in which UK Acid Waters Monitoring Network (AWMN) sites are located (see Task 4.1 Introduction) provide predictions for change in precipitation as a percentage compared with a baseline of MORECS 1961-1990 mean monthly values. These data suggest that for all scenarios (low, medium and high) for all projected periods (2020; 2050; 2080) winter precipitation increases, but decreases for all other seasons. In all cases the annual values of precipitation decline. Given the concomitant increase in air temperatures under all scenarios for all seasons, the increase in winter precipitation implies an increase in winter rain rather than snowfall in upland areas (see below) and hence the removal of pollutants from the atmosphere by rain may become more important in future winters. Furthermore, Rocher *et al.* (2004) found that removal by rain was dependent on rainfall amount rather than rain event characteristics (e.g. intensity, duration). Therefore, it is likely to be changes in total rainfall (leading to higher pollutant fluxes) that affect inputs via this mechanism rather than any increase in the frequency of intense rain events. By inference, dry deposition of pollutants will become more important in the other seasons and especially in summer periods when rainfall reduction is predicted to be at its greatest in all target years and under all scenarios. Dry deposition is thought to be the chief removal process for PAHs in summer (Halsall *et al.*, 2001) and therefore the predicted climate changes may also enhance this process. The direct consequences of changes in precipitation patterns will also affect the transport and impacts of toxic substances. Elevated winter precipitation will increase flushing of toxic substances while reduced summer rainfall will reduce dilution (Wilby *et al.*, 2006).

The scavenging of pollutants from the atmosphere by snow is thought to be more efficient than that of rain (e.g. Carlson *et al.*, 2004). Many studies have considered the role of snow in the deposition of POPs including PAHs (Franz & Eisenreich, 1998; Wania *et al.*, 1999; Brun *et al.*, 2004), PCBs (Franz & Eisenreich, 1998; Wania *et al.*, 1999; Garbarino *et al.*, 2002) and a number of pesticides and related compounds including endosulfan, HCHs, DDE and DDD (Carlson *et al.*, 2004). Studies also show snow scavenging of metals (e.g. Garbarino *et al.*, 2002) and winter peaks in methylmercury in deposition at Lochnagar (Rose, unpublished data) may be linked to snowfall. Predicted increases in winter temperatures under all scenarios suggest the prevalence of snowfall will be reduced in all target years and hence removal by this process would be expected to be reduced. Kettle and Thompson (2007) predict that for Lochnagar there will be no snow in March-April-May by 2020 and that by the 2080s there will be a decrease in the annual snowfall average of between 50% - 100% from the 1961-1990 average value.

The role of occult deposition through the interception of orographic cloud in uplands is less studied, but an area of increasing research. It has been shown that pollutant deposition by this process, over and above that of inputs by bulk deposition, can significantly enhance inputs of acidic species (Fowler *et al.*, 1988; 1991), trace metals (Herckes *et al.*, 2002; Norton *et al.*, 1997) and anthropogenic particulates including fly-ash (Crossley, 1988; Rose & Yang, 2007). Increased cloudiness would be an expected consequence of higher global temperatures and it has been suggested that cloudiness has increased over Europe by 6% over 80 years (Henderson-Sellers, 1986). However, despite this expectation, future predictions for cloudiness are very uncertain and so it is unknown whether this process will increase pollutant inputs to upland areas in the future.

The uncertainties related to modelled projections for metal depositions are also high for trace metals and so it is difficult to compare trends. Hettelingh *et al.* (2006) suggest that modelled concentrations (in precipitation) and depositions of Cd, Pb, Cu, Zn and Se are significantly lower than measured data. Therefore depositions in 2020 in some regions of Europe could be up to twice those of 2000 as a result of the way in which emission data for the two years were obtained. Future exceedances of metal critical loads could therefore be higher than anticipated. While further work is required to improve models and emission data, this highlights the need for empirical data.

Legacy contaminants. Trace metal and POPs remobilisation as a result of climate change

The industrial emission of trace metals is generally thought to have begun in the 18th century (Farmer *et al.*, 1999; Tipping *et al.*, 2007b) while the history of POPs emissions is shorter, on the scale of decades. Many organochlorine compounds were first synthesised and used on an industrial scale from the early to mid decades of the 20th century while PBDEs are more recent only having been produced and used in the last 20 years. The legacy of this widespread and intensive industrial activity is a vast store of previously deposited pollutants in lake sediments, catchment soils and, to a lesser extent, in biota. While upland lake sediments can store a significant amount of deposited pollutants (Yang *et al.*, 2002; Rose & Yang, 2007), catchments of waterbodies are generally much larger than the waterbodies themselves and therefore it is in catchment soils where the majority of previously deposited contaminants are stored. With dramatic declines in atmospheric emissions of trace metals and some POPs over recent decades (e.g. Baker, 2001) the remobilisation of these stored pollutants have already become an important source of contamination to upland waters (e.g. Yang *et al.*, 2002). Any climate change induced enhancement of this remobilisation from either lake sediments or catchment soils could result in a lack of response to emissions reductions and even lead to an increase in pollutant inputs to upland waters in the future. This may enhance the availability of pollutants to aquatic flora and fauna (Rose *et al.*, 2004).

Remobilisation from catchment soils: Soil erosion

Erosion of contaminated levels of catchment soils is one process that may transfer catchment-stored metals and POPs to upland waterbodies. Scottish land cover data (MLURI, 1993) show 24% of the land classified as peatlands exhibited significant signs of erosion, an area estimated to be c. 12000 km^2 (Helliwell *et al.*, 2007). The stability of these areas under a changing climate is of concern, not least because of the potential for significant losses of carbon from these upland areas and erosion rates can be high (5 cm yr^{-1}; Tallis, 1998) either as a result of surface or within-peat flow. Within-peat flows eventually form the gully systems characteristic of eroded peat.

Possible causes of peat erosion include catchment vegetation change and the removal of peat during high intensity rain events (Helliwell *et al.*, 2007) a cause of concern given climate projections (Hulme *et al.*, 2002) and a process already thought to contribute to the release of industrially-derived Pb from peat soils in the Pennines (Rothwell *et al.*, 2005). Gully erosion causes a drying of the peat within 1-2 m of the gully and this can lead to lowered vegetation diversity, vegetation cover and reduced bank stability (Tallis, 1997; Anderson & Yalden, 1981). In circumstances where the peat surface becomes exposed to wind, peat degradation may also accelerate erosion. There is currently debate regarding the possibility of drier summer conditions leading to lowered water tables, thereby increasing the susceptibility of peat to erosion (Yeo, 1997; Helliwell *et al.*, 2007). Eroding gullies at many sites in upland UK are deep and hence the eroding material entering the waterbodies can be expected to include a substantial amount of uncontaminated (pre-industrial) peat material as well as contaminants stored in the upper levels. However, while this may not elevate the concentration of contaminants entering the waterbodies the pollutant flux will increase as will, consequently, the potential for contaminants entering the food-chain via detrital feeders. The EU funded research project Euro-limpacs (Integrated Project to Evaluate the Impacts of Global Change on European Freshwater Ecosystems; EU project 505540) (http://www.eurolimpacs.ucl.ac.uk/) is currently assessing the role of soil erosion in the transfer of metals from catchment soil storage to upland waters in Scotland as a result of climate change and is due to report on this by early 2009.

Remobilisation from catchment soils: Leaching

At many upland waterbodies across the UK, Europe and North America levels of dissolved organic carbon (DOC) have been seen to increase in recent decades (Monteith *et al.*, submitted). A number of hypotheses for this observation have been proposed including:

- Peat erosion (see above);
- Changes in hydrology, i.e. a decrease in discharge raising concentrations (Tranvik & Jansson, 2002);
- Reductions in sulphur deposition ;
- Decomposition of organic matter by biodegrading hydrolase enzymes (enzyme latch mechanism) would result in increased DOC release following periods of drought (Freeman *et al.*, 2001);
- Higher temperatures enhancing microbial activity leading to decomposition of peat and production of DOC (Worrall *et al.*, 2003);

- Rising temperatures increasing the abundance of enchytraeid worms *(Oligochaeta)* which in turn influence microbial decomposition of organic matter by litter fragmentation and soil aeration (Cole *et al.*, 2002).

Metals are known to have a strong affinity for DOC and hence elevated concentrations of DOC entering upland waters from catchments might result in enhanced metal inputs. Certainly positive correlations for both Hg and methylmercury with DOC have been observed in high altitude lakes in the United States (Krabbenhoft *et al.*, 2002) and models have suggested that climate enhanced future increases in organic carbon will be important for element leaching (Holmberg *et al.*, 2006). POPs are also known to have a strong affinity for DOC (Gao *et al.*, 1998; Winch *et al.*, 2002) and this mechanism would therefore also be applicable for catchment stored organic contaminants.

However, the increase in DOC input does not necessarily imply increased toxicity to aquatic biota or even increased bioavailability. As DOC binds strongly to metals and POPs bioavailability may be reduced as a result of DOC concentration increases. The influence of climate change on DOC in upland waters is considered in detail in Section 2 above. The EU funded research project Euro-limpacs is currently assessing the role of DOC leaching from catchments in the transfer of metals from soils to upland waters in Scotland as a result of climate change and is due to report on this by early 2009.

Leaching of metals from catchment soils will also be affected by acidification and so climate-induced changes to acid status will also affect this process (Tipping *et al.*, 2003). Apart from the possibility of organic acid inputs possibly being a confounding factor to the recovery of upland waters from acidification (Monteith *et al.*, 2007), the increased role of nitrogen dynamics in upland catchments will play an important role in the acidification of catchment soils and hence on metal loss to upland waters. The influence of climate on nitrogen is discussed further in Section 1 above.

Changes to mercury methylation

Apart from the enhanced released from storage of pollutants as a result of climatic processes, there is also the potential for changes in pollutant availability and toxicity. As described above, the increasing levels of DOC observed in many upland waters may influence the availability of metals and POPs through the absorption of these substances to organic matter. However, climate will also affect the processes that drive the methylation of Hg and so will be critically important in the bioavailability of this compound to aquatic biota.

Predicted climate changes will affect Hg methylation in two main ways, through changes in precipitation and temperature. The effects of increased precipitation have been studied as part of the EU funded research project Euro-limpacs (Munthe, 2006) at an experimental catchment at Gårdsjon in Sweden. Precipitation in the forested catchment was increased to 2-3 times natural throughfall levels and led to changes in the hydrological pathways in soil and to enhanced leaching of both total mercury and methylmercury. The increased precipitation resulted in the formation of anaerobic conditions in the soil which favours methylmercury production. The experiment which ran for five months led to an increase in methylmercury in run-off from c. 0.1

ng l^{-1} prior to the increase in irrigation, to 1.0 ng l^{-1} after 3.5 months and individual measured values of >5 ng l^{-1}. Concurrent increases in DOC concentration were also observed in the catchment run-off. Following the conclusion of the increased irrigation period, methylmercury levels declined but remained above the pre-experimental concentrations for some months. Increases in total Hg in the run-off during the irrigation experiment were found to be proportional to the increased precipitation but the methylmercury flux was significantly larger indicating factors other than hydrology are also influencing production.

The methylation of Hg stored in sediments and catchment soils is a microbial process and as such is temperature dependent. An increase in air temperature and resulting increases in soil and water temperatures may therefore enhance the methylation process. While drier summers (see Task 4.1 Introduction) may reduce Hg methylation an increase in winter rainfall and an increase in winter temperatures would be expected to enhance the methylation process and elevated leaching of methylmercury from soils to surface waters. Hence, predicted climate changes could lead to a greater re-emission of catchment stored Hg in a biologically available and toxic form although this may be ameliorated by concomitant increases in DOC.

Ice cover

Elevated winter air temperatures will reduce ice formation and lead to longer ice-free periods on upland lakes (e.g. Marsh & Lesack, 1996). While there is considerable anecdotal evidence for reductions in catchment snow and lake ice cover for UK upland lakes over recent decades (e.g. Thompson *et al.*, 2007) it has been suggested that due to their altitude range and maritime climate they are unusually sensitive to even small increases in temperature. For example, Scottish lochs with elevations of just below 1000 m can be expected to witness reductions in the duration of their lake ice-cover of c. 61 days for a 1.5 °C warming (Kettle & Thompson, 2007). Many may become, in effect, ice-free under the scenarios expected for the UK uplands by the end of the century.

Longer ice-free periods will have many subsequent impacts on upland lakes. Evaporation will increase, as will water mixing leading to deeper thermoclines, greater sediment resuspension from littoral areas and sediment focussing, while ice scour will be reduced resulting in increased macrophyte growth. In terms of trace metals and POPs deposition, longer ice-free periods will increase the extent to which lakes can interact directly with the atmosphere and this will alter air-water contaminant exchange fluxes (Macdonald *et al.*, 2003). Furthermore, the reduced ice-cover will allow a longer growing period for both macrophytes and algae, as long as nutrients remain available, and hence autochthonous sedimentation may be expected to increase as well as possible sources of allochthonous material from, for example, catchment soil erosion (see above). Given nutrient availability, algae will also be able to scavenge pollutants from the water column over a longer period thereby introducing them to the aquatic food chain directly or, upon death when they become part of the sediment, via detrital feeders. However, whether this introduction of elevated levels of pollutants to the aquatic food chain proves deleterious to the aquatic food-web, or beneficial by reducing concentrations in the water column, remains uncertain.

Changes in the effects of trace metals and POPs to biota as a result of climate change

Many factors influence the availability and toxicity of trace metals and POPs to aquatic organisms (Rippey *et al.*, 2007). These include both physico-chemical and biological factors. It is likely that climate change will influence these factors in both direct and indirect ways and the synergism or antagonism of these factors and climate's effect upon them will influence toxicity of trace metals and POPs in many and various ways that can neither be well predicted nor generalised across a large number of upland waterbodies. A good example of this is pH which has a strong influence on the toxicity of trace metals to aquatic organisms. Here, climate influences may both aid (warmer winters resulting in a decline in winter nitrate concentrations) or confound (increased precipitation elevating surface flow of S and N; increased DOC) recovery from acidification (Rose *et al.*, 2004; Monteith *et al.*, 2007) and it is the balance between these processes, and climate's effect upon them, that will affect availability of metals and POPs to aquatic biota and their toxicity possibly at a site-specific level. These and other factors are briefly outlined in Table 4.9.

Conclusions and Priorities for Research

There is considerable potential for climate change to impact on the emission, transport, deposition, re-mobilisation, re-emission and toxicity of trace metals and POPs in UK upland waters. While many predictions and scenarios, especially with regard to projected air temperatures, appear to give reasonable agreement (to direction if not to scale), there is still considerable uncertainty as regards future changes to precipitation, cloudiness, wind speeds and the magnitude and frequency of extreme events. Furthermore, model predictions on coarse scales (e.g. 50km x 50km grids) provide little information on the enhanced (or reduced) impacts that may occur in upland areas, e.g. the role that climate change may play in exacerbation or amelioration of lapse rates and orographic enhancement etc. The indirect effects of these processes, their interactions and synergies only raise the level of uncertainty for projected impacts still further.

Predictions of how climate change effects will impact upon trace metals and POPs in these ecosystems are therefore similarly uncertain and are compounded by the lack of basic information on these substances (especially Hg and POPs) in UK upland waters. Therefore, while we may speculate on the role that climate change may play on, for example, Hg toxicity to aquatic organisms in any number of target years, uncertainties are so high that currently even the direction of that change is highly debatable. Indeed, the baseline against which we may measure the future effects of trace metals and POPs in upland ecosystems (whether as a result of climate change or not) is largely missing and unless this significant gap in knowledge is filled as a matter of some urgency, it will not be possible to assess how present and future policy decisions will affect these sensitive sites.

Table 4.9: Selected physical, chemical and biological factors affecting toxicity of trace metals and POPs to aquatic organisms and possible impacts of climate change upon them.

Factor influencing toxicity	Climate change influence?
Physical Factors	
pH	pH influences free ion (M^{2+}) availability. Climate change could reduce winter nitrate; increase weathering rates; increase input of S and N from surface flows; elevate organic acid concentrations.
Water Hardness	Increased water temperatures would reduce $CaCO_3$ solubility. $CaCO_3$ forms insoluble carbonates and reduces metal availability by adsorption. Generally, metals are more toxic to fish in low $CaCO_3$ waters.
Oxygen content	Increased water temperatures would reduce dissolved oxygen (DO) content. DO effects oxidation state of metals thereby influencing bioavailability. Reduced DO has physiological effects on aquatic organisms adding to stress.
Temperature	Water temperature affects solubilities of elements and compounds and rates of chemical reactions. Increased water temperatures will increase methylation of Hg; reduce the retention of volatile POPs (and Hg); reduce 'cold stress' to organisms within upland waters. Degradation of POPs will be enhanced. Respiration will also be increased thereby elevating toxicity (cf. Khan *et al.*, 2006)
Suspended solids	Prolonged summer drought and / or increased rainfall events could elevate catchment soil erosion. Warmer water temperatures could enhance autochthonous production. Suspended solids retain contaminants which once bound are less 'available' to biota. Dissolved ions (e.g. M^{2+}) are more biologically available so adsorption reduces toxicity.
DOC	See Section 2 for climate effects on DOC. DOC retains contaminants which once bound are less 'available' to biota. Dissolved ions (e.g. M^{2+}) are more biologically available so complexation reduces toxicity.
Salinity	Not a big problem for upland waters, but in seepage lakes increased air temperatures would increase evaporation. Increased salinity reduces dissolved metal concentrations.
Ultraviolet radiation	Photoactivation of some substances (e.g. PAHs) can occur through increased levels of UV exposure and raise toxicity by several orders of magnitude (Landrum *et al.*, 1984; cited from Wilby *et al.*, 2006).
Biological Factors	
Life stage	Warmer temperatures could increase reproductive rates and hence generation times. Some species are more susceptible to toxic substances at early life-stages and this period could be reduced. Contaminant content can also be dependent on age.
Metabolism	Increased water temperatures would increase energy demands and therefore metabolic rate. This will raise toxicity. Depletion of body 'solvents' (e.g. lipids) by metabolism increases pollutant concentrations (Macdonald *et al.*, 2003).
Diet	Climate will affect trophic structure, food-chain lengths and efficiency of fat (and adsorbed metals and POPs) transfer through food-webs and hence biomagnification.
Sessility	Lakes and rivers receiving contaminants from biological vectors (e.g. fish migrations) will be affected by changes in magnitude of migration and distribution patterns as a result of climate change.
Cold adaptation	Thermal stress to cold adapted species in addition to contaminant stress may enhance toxic effects.

Therefore, there is an urgent need for a monitoring programme to be established to undertake empirical measurements and monitoring at a wide range of upland waterbodies, in all areas of the UK over an extended period of time, in order to better understand the key processes and drivers affecting the levels of toxic substances in upland aquatic food-webs. Upland waters are the ideal medium for a toxic substances network for two main reasons. First, the sites are not impacted by direct sources of contamination, thereby providing a good indication of deposition from the atmosphere. Second, upland water bodies tend to be cooler and so there is less re-emission of the more volatile POPs (and Hg) to the atmosphere and hence retention of these contaminants is higher than in equivalent lowland waters. The dynamics of retaining the pollutants within the water body are important (see Page 192) and hence, although climate change will increase the temperatures of all water bodies upland waters will remain cooler than lowland ones and so will continue to retain relatively higher levels of POPs and Hg and remain more susceptible to elevated levels of these contaminants. Knowledge from such a network would allow the key processes to be better understood and these can then be used to improve models for future prediction. Without such basic background empirical measurements even the most robust models will lack any 'ground-truth' and may offer only poor projections of future impacts. It is interesting to note that there have been similar calls for the establishment of a monitoring programme since the first reports of climate impacts on UK water quality (e.g. Whitehead & Jenkins, 1989; Wilby *et al.*, 2006).

Apart from a better understanding of the key processes, improved models for better prediction and establishing a robust empirical base-line against which to measure any future change, there are also policy initiatives that would appear to require these basic data and the establishment of a monitoring programme for toxic substances in UK waters. 'COM(2006) 398 final' (2006) from the Commission of the European Communities states, "*On the basis of information concerning the toxicity, persistence and bioaccumulation potential of a substance, together with information on what happens to the chemical in the environment, it is possible to determine threshold concentrations to protect people, flora and fauna. When EQS are established for water, or sediments, or plant / animal tissues they provide a benchmark for ensuring the ecological integrity of aquatic ecosystems or the protection of human health when using water.....If control measures or EQS are to be effective they must be combined with an effective system of monitoring to ensure that measures are carried out and that EQS values are respected.*" Furthermore, Article 2 of the proposed Directive 'COM(2006) 397 final' states "*Member states shall ensure, on the basis of monitoring of water status carried out in accordance with Article 8 of Directive 2000/60/EC that concentrations of substances listed in Parts A (Priority substances) and B (other pollutants) of Annex I do not increase in sediment and biota.....Member states shall ensure that the concentration of methylmercury in prey tissue (wet weight) of fish, molluscs, crustaceans and other biota of 20 $\mu g\ kg^{-1}$ ($ng\ g^{-1}$) is not exceeded.*"

Once such a monitoring programme for trace metals and POPs in UK upland waters is established it will be possible to gauge the impact of future climate change on these pollutants to these important and sensitive ecosystems.

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