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SID 5 Research Project Final Report

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Project identification

1. Defra Project code: CPEA17
2. Project title: Freshwater Umbrella - the effects of nitrogen deposition and climate change on freshwaters in the UK
3. Contractor organisation(s): Ensis Ltd, ECRC, University College London
4. Total Defra project costs (agreed fixed price): £ 498, 414
5. Project: start date................. 01 July 2004
   end date.................. 30 June 2007

6. It is Defra's intention to publish this form.
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Executive Summary

7. The executive summary must not exceed 2 sides in total of A4 and should be understandable to the intelligent non-scientist. It should cover the main objectives, methods and findings of the research, together with any other significant events and options for new work.

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.

Project Report to Defra

8. As a guide this report should be no longer than 20 sides of A4. This report is to provide Defra with details of the outputs of the research project for internal purposes; to meet the terms of the contract; and to allow Defra to publish details of the outputs to meet Environmental Information Regulation or Freedom of Information obligations. This short report to Defra does not preclude contractors from also seeking to publish a full, formal scientific report/paper in an appropriate scientific or other journal/publication. Indeed, Defra actively encourages such publications as part of the contract terms. The report to Defra should include:

- the scientific objectives as set out in the contract;
- the extent to which the objectives set out in the contract have been met;
- details of methods used and the results obtained, including statistical analysis (if appropriate);
- a discussion of the results and their reliability;
- the main implications of the findings;
- possible future work; and
- any action resulting from the research (e.g. IP, Knowledge Transfer).

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 δ^{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 δ^{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 δ^{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 δ^{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 δ^{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 δ^{15}N depleted NO_x deposition could therefore be a possible driver of declining lake sediment δ^{15}N, but the evidence is circumstantial and the δ^{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 δ^{15}N.

The analysis of lake surface sediment δ^{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 δ^{15}N. While there is much scatter in the relationships the study does support the hypothesis that sediment δ^{15}N may provide a proxy for total N deposition. Measurements of δ^{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 δ^{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 δ^{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 δ^{15}N suggesting that deposited N is biologically utilised in lakes and that sediment δ^{15}N may provide a historical surrogate for total N deposition.

iv) The relationship between lake sediment δ^{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 acidity of precipitation is the governing factor in observed increasing trends, since DOC solubility increases as soilwater acidity decreases. Hence future DOC leaching is related to both trends in acid deposition and climate change. With increasing summer temperatures and longer growing seasons 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 NOx 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. 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. 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.

References to published material

9. This section should be used to record links (hypertext links where possible) or references to other published material generated by, or relating to this project.

A detailed final project report (Annex 1: 222 pages) is available on the Freshwater Umbrella website www.freshwaters.org.uk and as hard copy provided to DEFRA.

Curtis, C. and Simpson, G. (Eds.) (2007) *Freshwater Umbrella – The Effects of Nitrogen Deposition and Climate Change on Freshwaters in the UK.* Report to DEFRA under Contract CPEA17, July 2007. ECRC Research Report No. 115, Environmental Change Research Centre, University College London, London, 222pp.