

United Kingdom Acid Waters Monitoring Network

This booklet explains the problem of freshwater acidification and introduces the work of the **United Kingdom Acid Waters Monitoring Network**.

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# 1 INTRODUCTION

## Freshwater acidification

Acidic deposition (or 'acid rain', as it is often called) is one of the major threats to the ecological health of lakes and streams in many industrialised parts of the world. In the UK it has caused the acidification of freshwater systems across wide areas of the uplands over the past century. The main acidifying pollutants are the oxides of sulphur and nitrogen, chiefly derived from burning fossil fuels such as coal and oil, and ammonia, which mainly comes from intensive agriculture.

Acid water, and the high aluminium concentration often associated with it, presents a hostile environment to a range of aquatic life, from microscopic

algae, to zooplankton, larger aquatic plants, aquatic insects, fish and water birds. Acidification leads to the loss of many 'acid sensitive' species and an overall decline in biodiversity.

Acidifying pollutants can be carried over very long distances before being deposited, either directly or in rain in the form of sulphate, nitrate or ammonium. When deposited on soil, the acidic anions, sulphate and nitrate, react with soil base-cations (calcium, magnesium, potassium and sodium), forming neutral salts which are washed out into water courses. Deposited ammonium can be transformed to nitrate during nitrogen cycling

processes within the catchment.

If weathering of the underlying bedrock is too slow to maintain the soil's supply of base-cations, their availability declines. Increasingly the acid cations - hydrogen and aluminium - are leached from the soil in their place, leading to freshwater acidification. This process occurs more rapidly and more severely in catchments overlying acid sensitive geology, where base-cation generation is slow. Much of the UK uplands fall into this category, particularly western areas. See Figure 1.

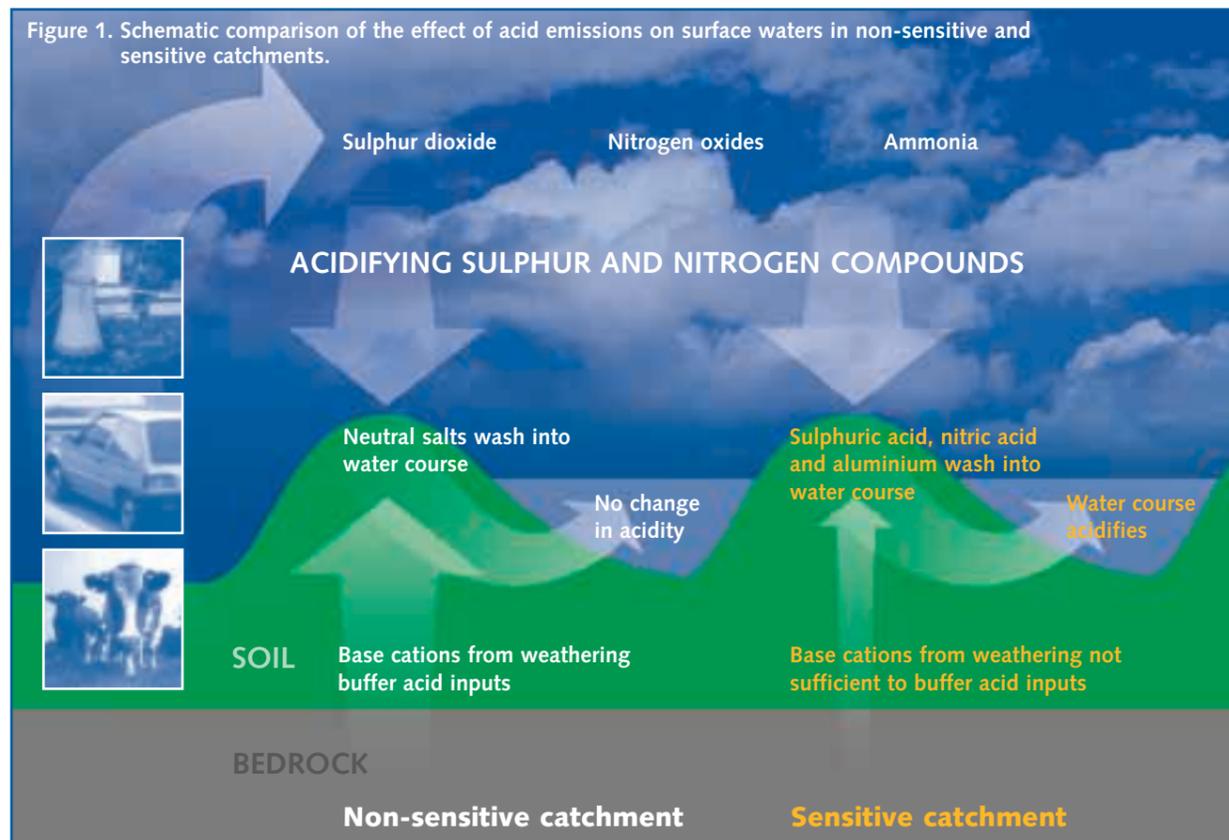
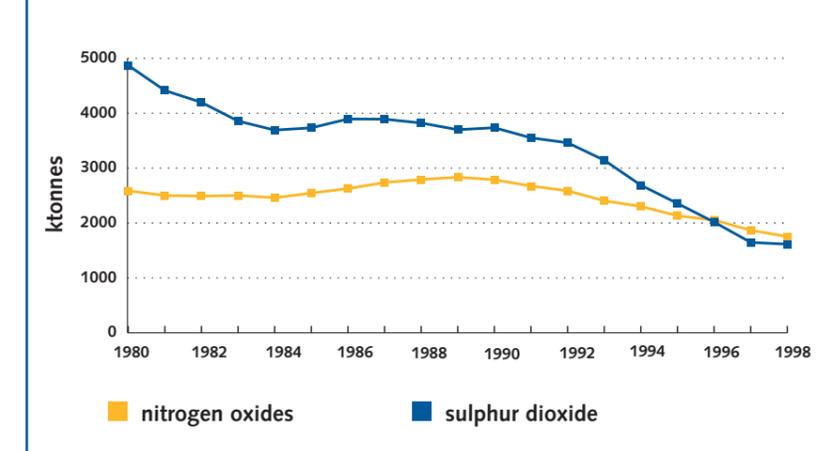
Acid deposition is not only a problem for freshwater ecosystems.

Acidification of mineral soils can adversely affect plant growth and may change the composition of plant communities. Damage to soil micro-organisms can slow down decomposition processes. In urban areas, acidic pollutants damage the surfaces of sensitive buildings, such as cathedrals built of limestone.

### The international response to acidification

The 'transboundary' nature of acidifying pollutants calls for an international response. In 1979, at the time of growing evidence of acidification in Scandinavian lakes, the UNECE (United Nations Economic Commission for Europe) set up the Convention on Long Range Transboundary Air Pollution. This was the first international agreement to tackle air pollution on a broad regional scale. Since then, the international community has agreed a range of protocols to cut emissions. The most recent is the so-called 'Multi-pollutant, Multi-effect' Protocol, signed in 1999. It set emissions targets called 'ceilings' for four pollutants - sulphur dioxide, nitrogen oxides, ammonia, and volatile organic compounds, to be met from 2010. The UK is committed to annual emissions ceilings of 625 ktonnes for sulphur dioxide, 1,181 ktonnes for nitrogen oxides and 297 ktonnes for ammonia. The European Union is currently negotiating the National Emission Ceilings Directive, in which

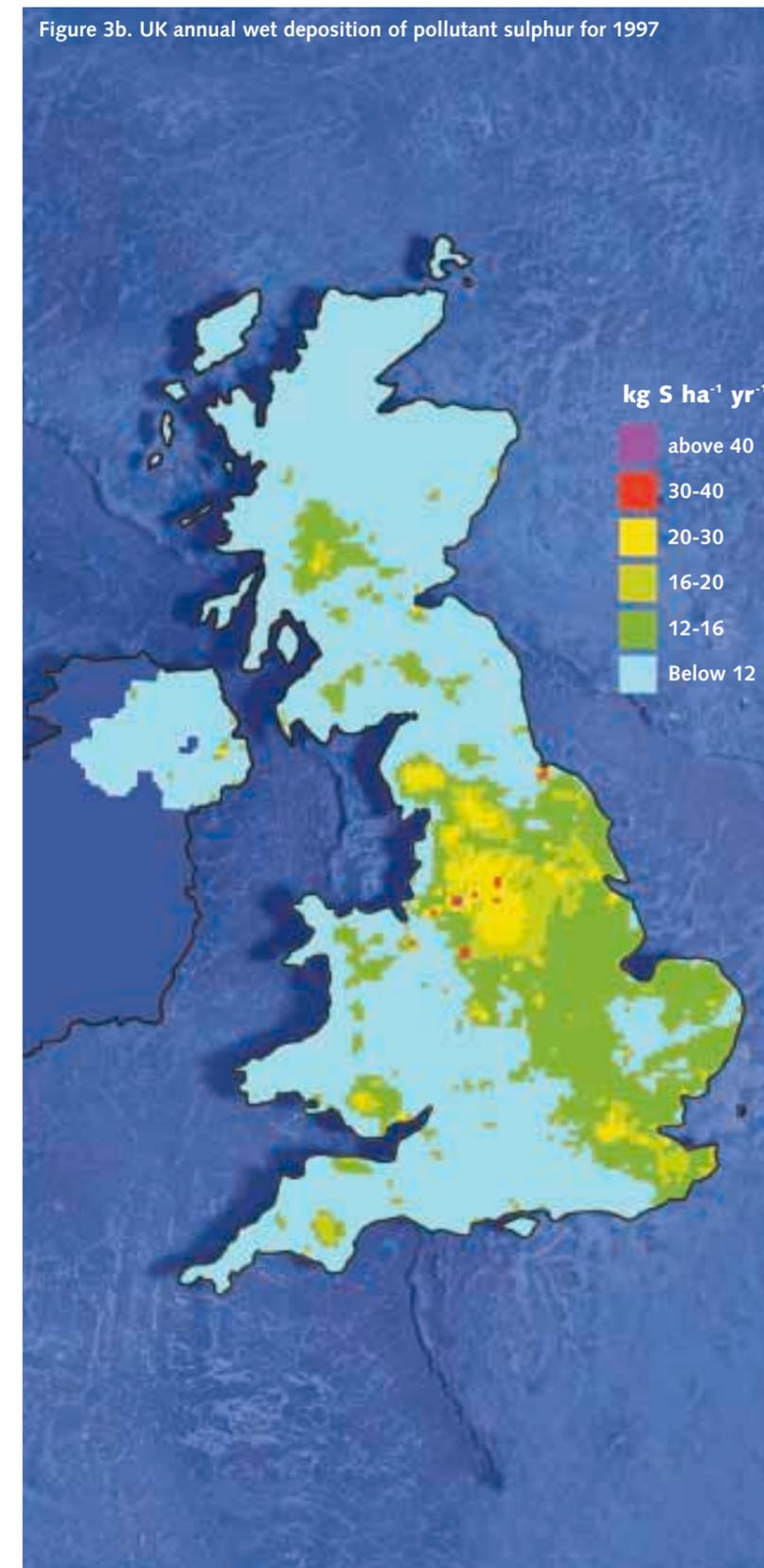
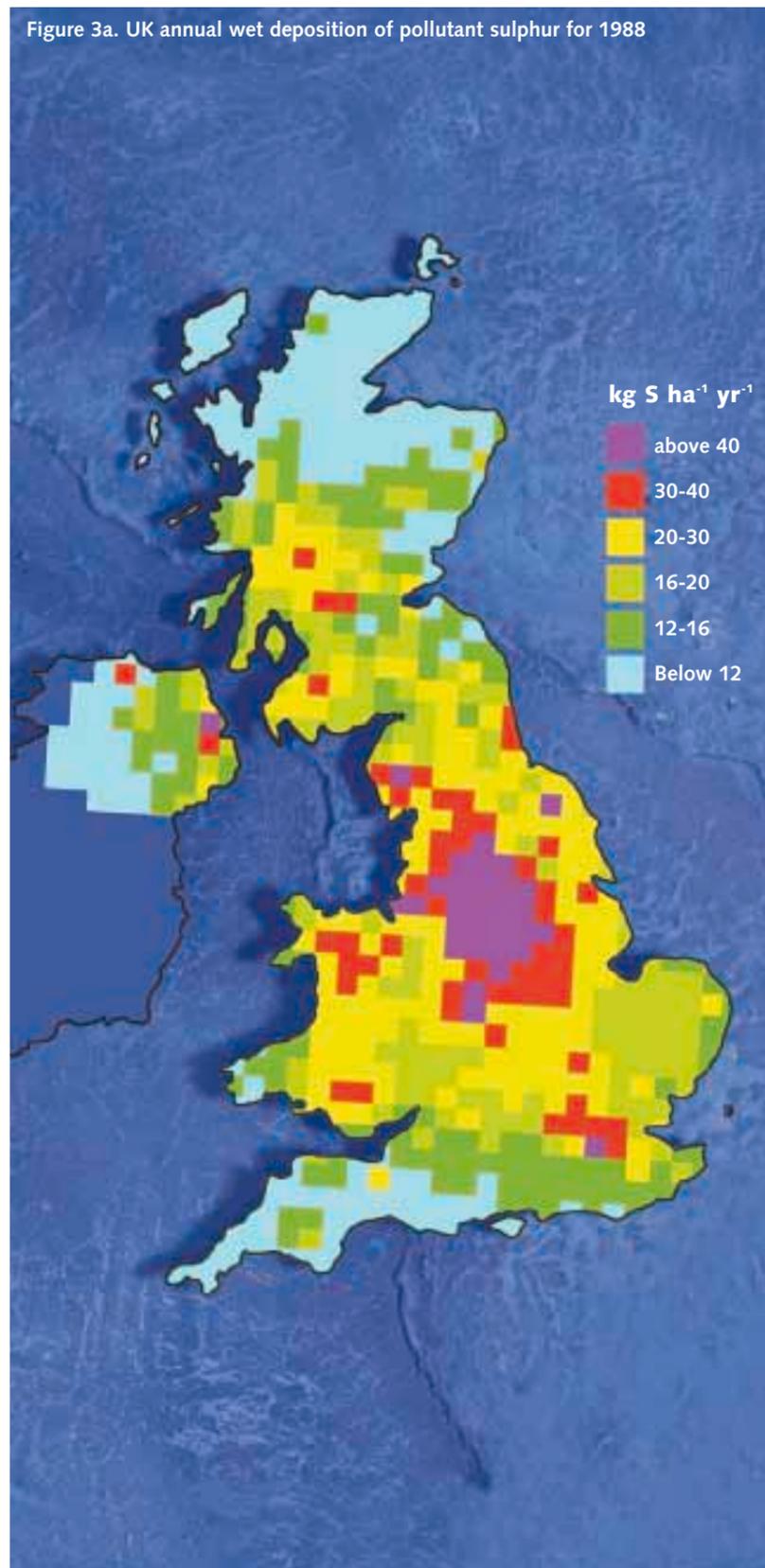
Figure 2. UK emissions of SO<sub>2</sub> and NO<sub>x</sub> from 1980 to 1998



member states will agree ceilings for the same acidifying pollutants as covered by the Protocol.

Since the implementation of sulphur controls under the UNECE's Convention on Long Range Transboundary Air Pollution, sulphur dioxide emissions have been dramatically reduced. In the UK, emissions have fallen by 75 per cent since 1980. See Figure 2. Other members of the UNECE have achieved similar cuts. Emissions of other pollutants which are likely to contribute to acidification, including nitrogen oxides and ammonia, have also declined in some countries, but at a much lower rate than sulphur.

## Changes in acid deposition in the UK



The chemistry of deposition over the UK has been monitored by the DETR funded Acid Deposition Network since 1986. For the UK as a whole, deposited levels of pollutant sulphate have declined significantly between 1988-98, but rates of decline have varied considerably between regions. The largest decreases have occurred in areas close to the major pollution sources where emissions have been most reduced - the Midlands, the Pennines and southeast England. In the more remote, high rainfall, uplands of the north and west, trends in pollutant sulphate are harder to detect. Very similar regional differences in trends have occurred in the acidity of rainfall.

## 2 THE UK ACID WATERS MONITORING NETWORK

Damaged or threatened environments need to be thoroughly monitored to assess the effects of emissions reduction policy. The United Kingdom Acid Waters Monitoring Network (UKAWMN) was established in 1988 by the then Department of the Environment, to assess the effect of emission reductions on selected acid sensitive freshwaters. Soon after, further support was provided by the Department of the Environment, Northern Ireland. We expect that, as emissions reduce and acid deposition declines, weathering should begin to replenish the soil base-cation store. This will reduce the acidity of lakes and streams. Improved chemical conditions should permit re-colonisation by acid sensitive plants and animals, providing they are not physically hindered from doing so, for example by inadequate migration routes. This process is termed 'recovery'. Its detection is a central aim of the UKAWMN.

The UKAWMN comprises 11 lakes and 11 streams. See Figure 4. The sites represent the more acid sensitive freshwaters found in the UK. Most are situated over weathering-resistant rock types, such as granites, sandstones and grits, which have been unable to neutralise pollutant acidity in recent decades. Analysis of sediment cores from these lakes (see page 9) proves that most have acidified over the past 150 years. It is likely that most UKAWMN stream sites have also acidified. The sites represent a variety of latitudes, altitudes, and amounts of acid deposition, and in some regions pairs of

forested and non-forested sites are included. This should allow the importance of these characteristics, for acidification and recovery, to be assessed. For example, managed forests may reduce the catchment soil store of base-cations, both by direct uptake during growth, and by enhancing the interception of acid pollutants, so increasing leaching rates. We are therefore interested to know whether lakes in forested catchments can recover as quickly, and to the same extent, as those in moorland areas.

Network scientists conduct a range of chemical and biological measurements at regular intervals (see below). We have recently published a report detailing results of analysis of data from 1988 to 1998 ([www.geog.ucl.ac.uk/ukawmn/](http://www.geog.ucl.ac.uk/ukawmn/)) and monitoring continues. This booklet includes a summary of the findings in the report and also incorporates the results of chemical analysis of more recent water samples to March 2000.

### Chemistry

We take water samples every month from streams and every three months from lakes. We carry out a range of measurements in the laboratory, including:

- \* **pH and alkalinity**
- \* **sulphate, nitrate and chloride**
- \* **labile aluminium (toxic forms of aluminium)**
- \* **base-cations (calcium, magnesium, potassium and sodium)**
- \* **dissolved organic carbon**



Water sampling

### Aquatic biology

UKAWMN lakes and streams contain a broad range of plant and animal groups, most of which are influenced by acidification, either directly (eg through toxic effects of high aluminium concentrations) or indirectly (eg through changes in food supply or predators). We have selected certain key groups of organisms for monitoring, which vary in their chemical sensitivity and position in the aquatic food chain. Biological sampling includes annual assessment of the following for each site.

**Epilithic diatoms** are microscopic single-celled algae that grow on submerged stones. Hundreds of species are recorded across the Network, and several tens of species can be found growing in close proximity in what are called 'communities'. Diatoms are known to be particularly sensitive to acidity. Even

Figure 4. UKAWMN site map





## 3 RESULTS

We know UKAWMN sites have been acidified by acid deposition, and that acidification has led to the loss of sensitive species and other changes in biological communities. Now emissions of sulphur are declining and this is beginning to be reflected in declining acid deposition across areas of the UK. So are the chemical and biological conditions of UKAWMN lakes and streams returning to how they were before acidification began? In short, is there evidence for the onset of recovery? We need to know:

- a) Have there been reductions in pollutant sulphate and nitrate concentrations?
- b) If yes, has this resulted in a reduction in acidity?
- c) If the answer to b) is yes, has this led to biological recovery, eg increasing numbers of brown trout or other acid sensitive species?

### a) Have there been reductions in acidic pollutant concentrations?

#### (i) Pollutant sulphate

#### What do we mean by 'pollutant sulphate'?

Terminology: sulphate is deposited both as an acidic pollutant, produced by industry, and as a neutral salt in sea-spray. Small amounts of sulphate may also reach freshwaters from geological sources, but in the case of most UKAWMN sites this contribution is negligible. We are primarily interested in sulphate from anthropogenic sources (the acidic fraction) rather than the total sulphate concentration. In seawater, sulphate and chloride occur in a constant ratio. We assume that virtually all chloride comes from sea-spray at our sites. By measuring the chloride concentration we can therefore estimate the amount of sulphate that comes from a natural source. The remaining sulphate is pollutant.

Analysis of the 1988-98 data, published in the detailed report, showed that pollutant sulphate concentrations in two UKAWMN streams had declined sharply over the decade. The two were Old Lodge in south-east England and the River Etherow in the Pennines. These streams are located in heavily affected parts of the UK, relatively close to major pollutant sources. Until recently they showed much higher pollutant sulphate concentrations than any other site in the Network. Data analysis also showed a small reduction in pollutant sulphate at Lochnagar in north-east Scotland. Elsewhere, however, there was little evidence of downward trends.

Over the 1988-98 period therefore, trends in pollutant sulphate were generally consistent with deposition trends. We saw sharp reductions at sites in regions where deposition

reductions had been strong, while there was little evidence of improvement in the most remote areas, with only small decreases in deposition. However, we were surprised that we did not detect downward trends over this period for sites at 'intermediate' distances from sources, such as those in Wales and the English Lake District.

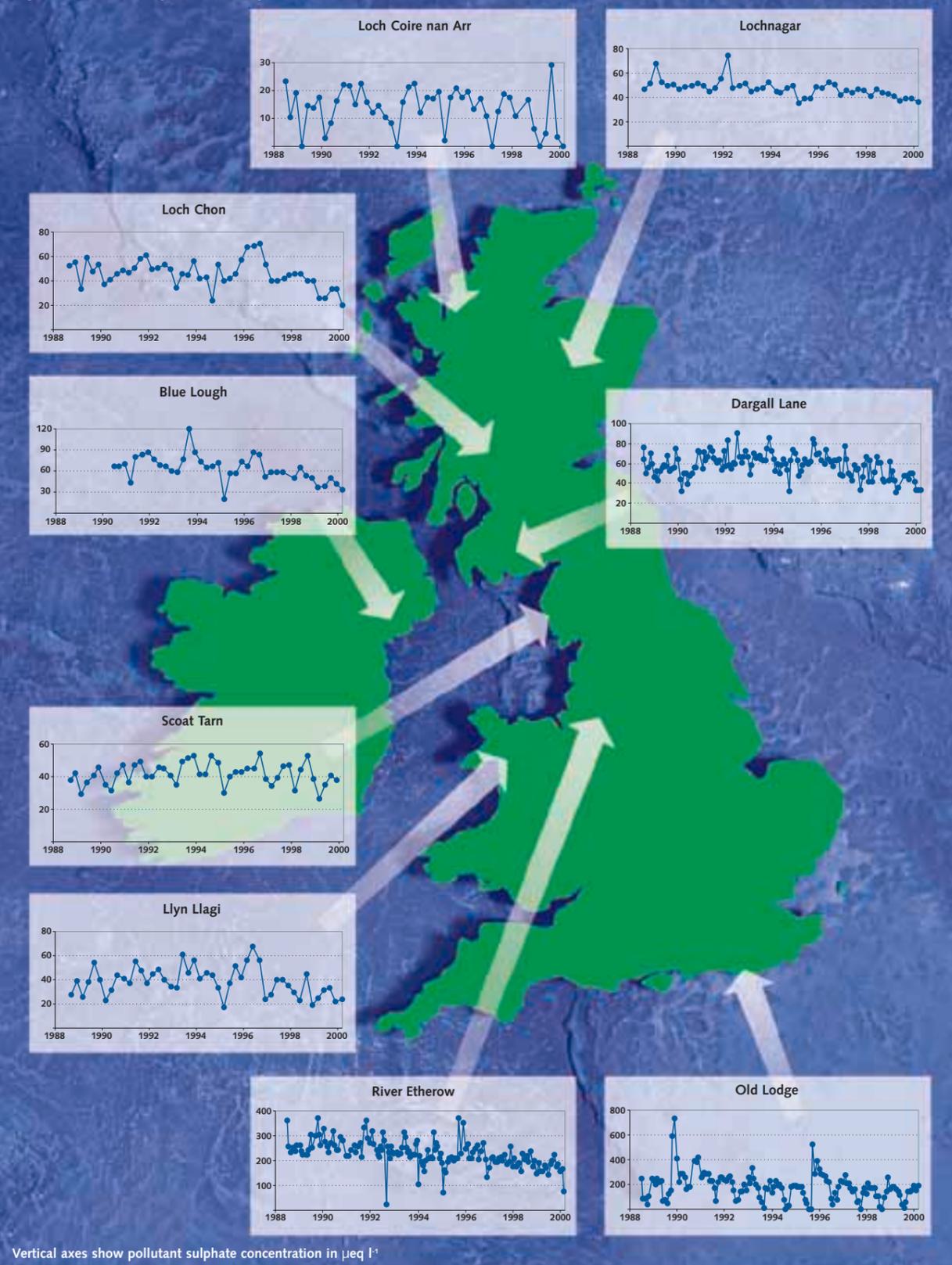
#### Why did we not observe more widespread declines in pollutant sulphate concentration between 1988 and 1998?

- There were only very slight declines in pollutant sulphur deposition in the more remote areas over the same period.
- Catchment soils in these areas may have been releasing stored sulphate, which has accumulated within them over the past 150 years.
- Climatic effects may have complicated the pollutant sulphate signal. Occasional droughts, such as the one experienced across the UK in 1995, can cause previously inert sulphur compounds, stored deep in catchment soils, to re-oxidise as sulphate. This can raise sulphate concentration temporarily once rain returns.
- The method used to estimate pollutant sulphate may be subject to short-term inaccuracies, resulting from sea-salt inputs causing additional 'noise' in the data. Although we use a fixed ratio of sulphate to chloride to estimate the marine sulphate fraction, chloride can pass more quickly into water courses than sulphate, which can be temporarily retained by catchment soils. Estimate 'errors' should cancel out over the longer term, but in cases where small real (but undetected) reductions may have occurred, we predicted that a period of more than ten years would be necessary to verify them.



Dargall Lane

Figure 5. Trends in pollutant sulphate at various UKAWMN sites (1988-2000)



#### Findings from the most recent data analysis (1998-2000): pollutant sulphate

Data from continued monitoring (to March 2000) now provides a more encouraging picture of reductions in pollutant sulphate concentration across much of the Network. Figure 5 demonstrates common changes with time at several sites. Concentrations were relatively constant from 1988-95 but have since declined substantially and are currently at the lowest levels since we began measuring. Although the strong downturn began around 1995, it has taken us a further five years to distinguish this from patterns of natural variation. Concentrations

have also continued to fall at Old Lodge and the River Etherow, although they still remain higher than at all other sites in the Network.

#### (ii) Nitrate

There is no evidence for a decline in nitrate concentration at any site. In fact nitrate concentrations appear to have increased at some sites, perhaps suggesting that their catchment soils are becoming increasingly saturated with nitrogen. This may occur if inputs of nitrogen from the atmosphere are currently exceeding the rate at which it can be taken up as a nutrient by plants and bacteria within the catchment. More generally, year-to-

year differences in nitrate concentrations at UKAWMN sites appear to be influenced by winter temperature, with the highest concentrations observed after the coldest winters.

#### Why are we concerned about nitrate?

- Pollutant nitrogen deposition now occurs at similar levels to sulphur deposition across much of the UK. Were all this nitrogen to reach surface waters (as nitrate) it would have a severe impact on freshwater acidity.
- But, nitrogen is a vital nutrient for plants and soil microorganisms. Because it is naturally scarce in upland ecosystems, much of the deposited nitrogen is retained in the catchment by the biota. As a result, relatively little acidifying nitrate currently reaches surface waters in most areas of the UK.
- The theory of nitrogen saturation suggests that this situation is not sustainable. As vegetation and soils become more nitrogen-enriched, deposition inputs may eventually exceed biological demand. These nitrogen-saturated catchments will therefore release increasing amounts of nitrate to surface waters, causing further acidification. The nitrogen saturation theory is still unproven, so nitrate data from the UKAWMN will provide an important indicator of whether we can expect more severe acidification from this source in the future.

## b) Do we see reductions in acidity where pollutant sulphate has declined?

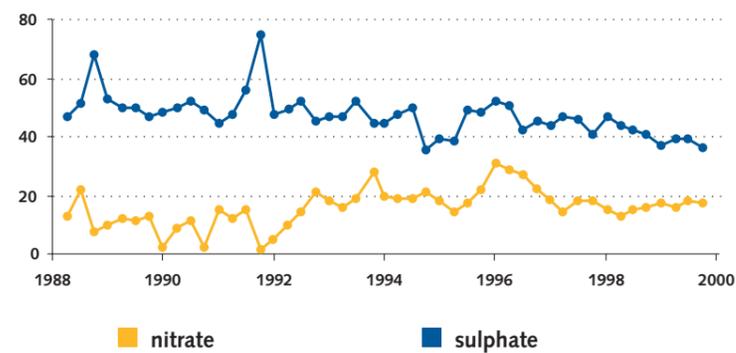
Between 1988 and 1998, Old Lodge was one of the two sites to show large reductions in pollutant sulphate. It also became slightly less acid and showed a substantial decline in aluminium concentration.

Pollutant sulphate concentration had also fallen at the River Etherow, but here we could not detect any trend in acidity. We attributed this to the large monthly variation in the chemistry of samples from the River Etherow, caused by changes in the amount of rainfall. With such noisy data, we realised that further years of monitoring would be necessary before any underlying drop in acidity could be detected.

At Lochnagar, nitrate concentrations rose faster than pollutant sulphate fell and the site had therefore become more acid. See Figure 6a and 6b. Since it was thought that the increase in nitrate was due to climatic differences between years, we did not expect this effect to persist.

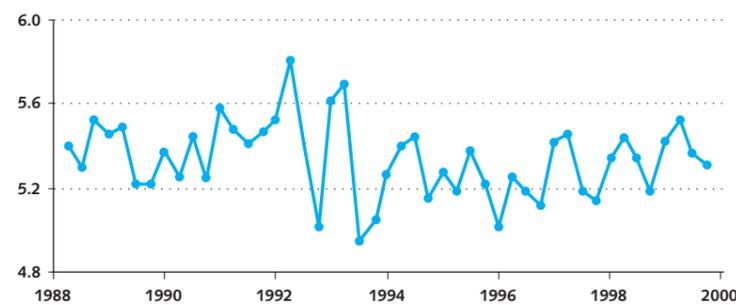
We did not expect measurable reductions in acidity at the remaining sites, given the absence of downward trends in pollutant sulphate and nitrate concentrations. However, trend tests did reveal small reductions in acidity at six of these.

Figure 6a. Trends in pollutant sulphate and nitrate at Lochnagar



Vertical axis shows concentrations in  $\mu\text{g l}^{-1}$

Figure 6b. Trend in pH at Lochnagar



There are two possible explanations.

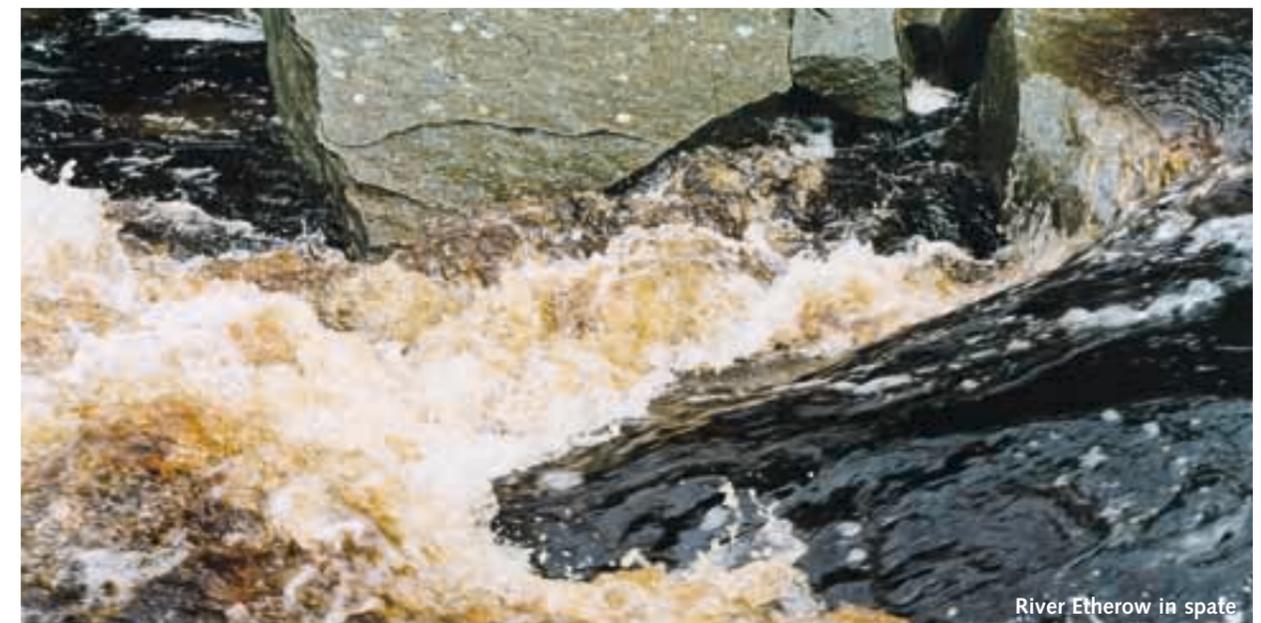
- There may have been very slight reductions in the real pollutant sulphate load at these sites, but the pollutant sulphate estimate is affected by changing sea-salt inputs. See page 11. 'Noise' may also have obscured real downward trends.
- Changes in the weather can influence freshwater chemistry. There is evidence that a general reduction in winter storms from the early 1990s to 1996 may have led to slight reductions in acidity (see below). Over the past 50 years, patterns of storminess over the UK have oscillated on an approximately 10 year cycle. The effects of weather should therefore become less important as the dataset continues to lengthen.

## How can weather influence the acidity of lakes and streams?

When rainfall is relatively light, a significant proportion percolates slowly through catchment soils and interacts with minerals in the underlying rocks. This tends to reduce the acidity of the water before it reaches the main water courses. In stormy periods, when rainfall is high, flow paths transport water rapidly through relatively acidic surface horizons of the soil, and interaction with soil minerals is minimised. At these times, water entering the watershed remains, or can become increasingly, acidic.

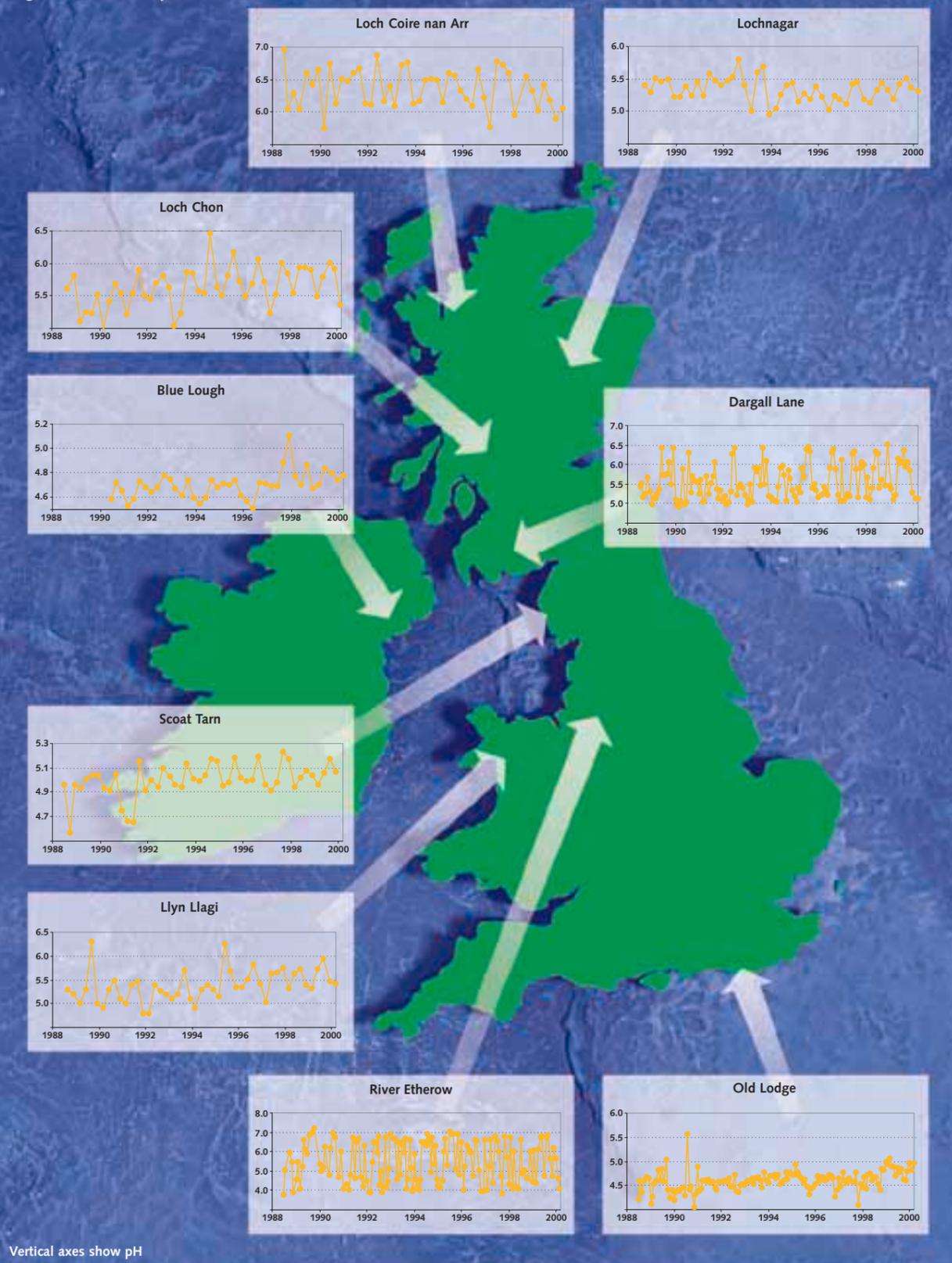
Storms also introduce sea-salts to catchments, particularly those downwind of coastal areas, via long range transport of sea spray. Although sea-salt may be considered neutral with regard to acidity, it can react with catchment soils, displacing hydrogen ions and aluminium and causing acidic pulses into water courses.

Stormy weather can therefore result in an increased number of acidic periods caused both by changes in water movement within the catchment and by the deposition of sea-salts. A gradual reduction in storminess during the early to mid-1990s may therefore have influenced trends in acidity at some sites. Over the longer term 'global warming' may further complicate our assessment of recovery since some climate modellers predict storminess in the UK to increase.



River Etherow in spate

Figure 7. Trends in pH at various UKAWMN sites (1988-2000)



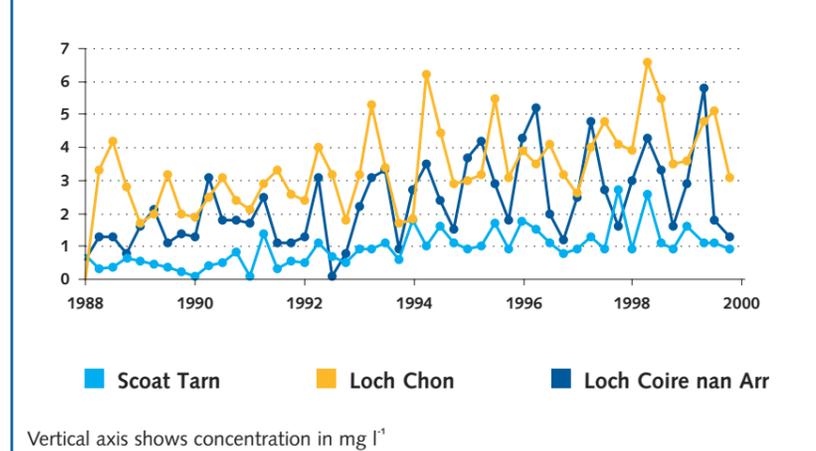
#### Findings from the most recent data analysis (1988-2000): pH

Again, analysis of the most recent data provides more encouraging evidence of improvements at several sites in the Network. See Figure 7. In contrast to the period 1988-98, links are now apparent between those sites showing reductions in pollutant sulphate and those showing declines in acidity. In total, seven of the 22 sites now show an increase in pH and six of these also show reductions in pollutant sulphate. Most of these are in areas at intermediate distances from pollutant sources, where we observed small declines in pollutant sulphate deposition between 1988 and 1998. There is still no measurable trend in acidity at the River Etherow, despite continued large reductions in pollutant sulphate concentration. It would seem that 'noise' in the pH signal, caused by variations in rainfall, may continue to mask any underlying evidence for recovery. At Lochnagar, nitrate concentrations have fallen slightly and the site is no longer acidifying.

#### Increases in dissolved organic carbon

The most strikingly consistent observation from the first 12 years of monitoring has been a gradual increase in dissolved organic carbon (DOC) concentration at all but one site in the Network. See Figure 8. Similar increases have been reported in areas of Scandinavia and North America. DOC is generated by soil

Figure 8. Trends in dissolved organic carbon (DOC) at 3 UKAWMN lakes



decomposition processes and provides the peaty coloration often seen in upland freshwaters. Its increase matters to the UKAWMN, since it provides an additional source of acidity and could therefore slow down the recovery process. However, DOC can also protect aquatic organisms from acidity, for example by binding with aluminium, and reducing its toxicity.

We do not yet understand the reasons for these increases, but they may be linked to a sequence of particularly warm summers in the 1990s. These may have stimulated soil decomposition. If so, then a continued warming trend, predicted by models of climate change, is likely to increase DOC concentration still further. It is also possible that the rise in DOC has been influenced by decreasing soil acidity resulting from decreasing acid deposition, since DOC can become more soluble as soil pH rises.

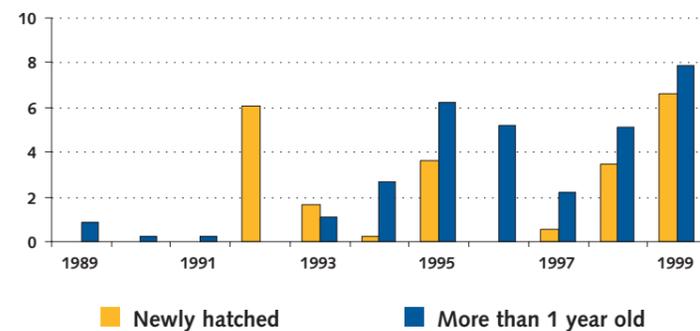
### c) Is there evidence for biological recovery?

With the relatively limited evidence of improvement in water chemistry at most UKAWMN sites, and the time lags anticipated before species are able to re-establish, it is perhaps too early to expect biological recovery. However, we have observed biological changes at Old Lodge, Llyn Llagi and Loch Chon which are consistent with measured reductions in acidity at these sites.

#### Increases in the trout population of Old Lodge

This is perhaps the most significant biological finding, since water chemistry has clearly improved at this site, seemingly as a direct response to declining deposition in south-east England. We recorded no newly hatched trout, and only very low numbers of older fish, over the first three years of monitoring. Since 1992, however, we have observed moderate numbers of trout in both age groups in most years. See Figure 9a. The apparent improvement in the trout population coincides with an increase in pH and a reduction in the concentration of labile aluminium, which is highly toxic to this species. See Figures 9b and 9c.

Figure 9a. Trends in density of newly hatched trout (less than 1 year old) and older trout at Old Lodge

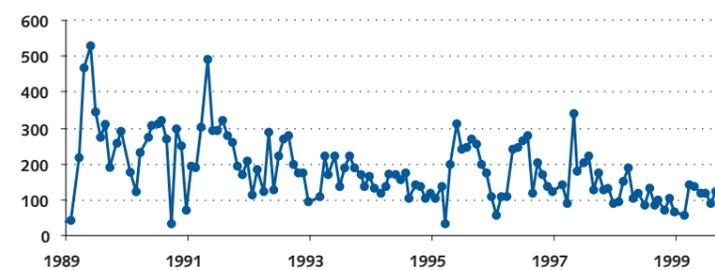


Vertical axis shows density in numbers 100 m<sup>2</sup>

Figure 9b. Trend in pH at Old Lodge



Figure 9c. Trend in labile aluminium concentration at Old Lodge



labile aluminium concentration in µg l<sup>-1</sup>



Llyn Llagi

#### Biological change in Llyn Llagi

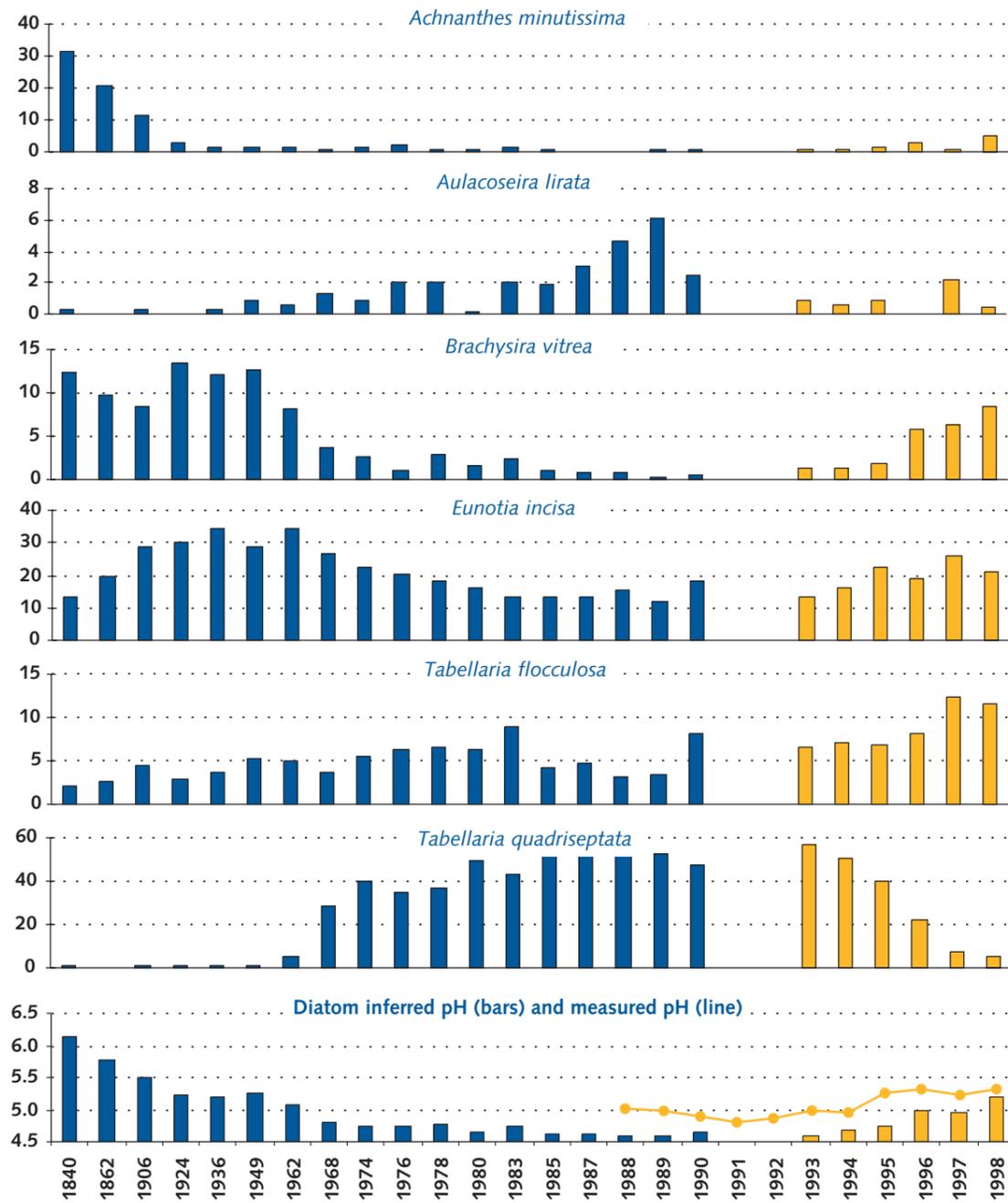
A sediment core taken from Llyn Llagi at the start of monitoring demonstrated that this site had continued to acidify until about 1990. Analysis showed that the diatom species *Tabellaria quadrisepata*, which prefers very acidic water, was rare until the 1960s, when it expanded rapidly to reach maximum abundance at the top of the core (1990 sediment). See Figure 10. When monitoring began, this species was also very abundant on submerged rocks around the lake

shoreline and in sediment trap samples. It has since declined year by year and has been replaced by species which prefer less acid conditions. By comparing sediment trap and sediment core samples we can see that *Tabellaria quadrisepata* has been replaced by species which had been abundant prior to the 1960s. To date there is little evidence for the return of the most acid sensitive species, which were common over 100 years ago.



*Tabellaria quadrisepata*

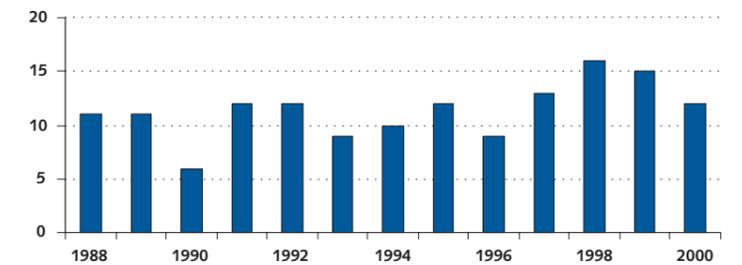
Figure 10. Changes through time in proportions of diatom species in Llyn Llagi, the pH change inferred from the diatom data and measured pH since 1988



Samples from sediment cores (blue bars) and sediment traps (yellow bars).

There is also evidence of change in the macroinvertebrate community in Llyn Llagi. See Figure 11. In the first few years of monitoring the site was dominated by stonefly species which thrive in acid conditions. More recently, samples have contained increasing proportions of acid sensitive beetles and caddisflies. There has also been an increase in the total number of species recorded, a measure of biodiversity. Generally therefore, biological recovery appears to be underway at Llyn Llagi, at least for groups at the lower end of the food chain. However, even the diatom community, which shows the clearest, improvement, still differs markedly from the community that inhabited the lake before acidification.

Figure 11. Changes in the total number of macroinvertebrate species found each spring in Llyn Llagi (1988-2000)



**Biological change in Loch Chon**

In Loch Chon, epilithic diatom and macroinvertebrate communities also show changes which indicate a reduction in acidity since the early 1990s. In addition there has been a gradual increase in the density of newly hatched trout in the loch outflow. The most recent chemical data has established a link between declining pollutant sulphate and acidity, so it is possible that we are observing the beginnings of biological recovery at this site.

## 4 SUMMARY AND CONCLUSIONS

### Biological change at other sites

We have seen changes in diatom and macroinvertebrate species at several other UKAWMN sites. However, in most cases, these are not so clearly linked to deposition driven changes in chemistry and so may not indicate real recovery. It is more likely that the majority of observed trends result from changing weather conditions. Perhaps most importantly, the reduction in the frequency and intensity of westerly storms (which cause acid episodes), since the early 1990s, may have been beneficial to some acid sensitive organisms. Additionally, some species may have benefited from a reduction in high flow events, which can physically disrupt stream habitats. Only further monitoring will allow us to disentangle the relative effects of recovery and climatic variability. We have not yet seen improvements in salmonid densities at any site other than Old Lodge and Loch Chon. No site shows improvement in aquatic macrophyte populations.



Allt a'Mharcaidh

The UKAWMN has been in continuous operation for more than 12 years. There have been substantial reductions in sulphur emissions over that time, both nationally and internationally. Two UKAWMN streams, situated relatively close to major emission sources, have experienced large reductions in pollutant sulphate concentration. At one of these, Old Lodge, a reduction in acid deposition appears to have led to a reduction in acidity and aluminium concentration. This in turn may account for a considerable improvement in its trout population.

UKAWMN sites in other acid sensitive areas have experienced more gradual reductions in sulphur deposition. They are only now beginning to show declining pollutant sulphate concentrations and acidity. In some cases it has been difficult to distinguish between emission-driven and climate-driven effects. Time lags were always expected before acid sensitive species would be able to re-establish themselves and at present clear biological evidence of recovery is limited to very few sites. However, now that widespread measurable improvements in chemistry are being

seen, it will be interesting to see how quickly and to what extent biological communities respond.

UKAWMN sample collection and analysis has been carried out by a range of organisations (see last page) working to carefully defined protocols. This has ensured a consistently high quality of data over the last 12 years. The data sets are only now of sufficient length for us to begin to answer the questions that the Network was designed to address. However, as the time series continue to develop, their value as a scientific resource continues to increase.

UKAWMN data are now routinely used to test environmental models. These allow policy makers to predict water chemistry response to various emissions scenarios at the national and international scale. We also contribute data to wider freshwater monitoring networks, including the UK Environmental Change Network (ECN) and the UNECE's International Cooperative Programme on the Assessment and Monitoring of Acidification of Rivers and Lakes. Meanwhile, the data are shedding new light on upland water processes, and particularly links between climate,

surface water chemistry and biology, that were perhaps not foreseen and may never have been revealed in short-term experiments. The Network therefore continues to further our understanding of acidified upland freshwaters and remains well placed to assess their recovery response to emission reductions into the future.

## Participating organisations

### Project coordination:

ENSIS / Environmental Change  
Research Centre at University College  
London (ENSIS – ECRC)

### Chemistry database management:

Centre for Ecology and Hydrology  
(CEH), Wallingford

### Biology database management:

ENSIS – ECRC

### Central chemistry analyses:

CEH, Wallingford

### Local chemistry analyses:

Freshwater Fisheries Laboratory,  
Pitlochry, Perthshire.  
Environment Agency, Llanelli

### Chemistry AQC:

Water Research Centre,  
Medmenham

### Macroinvertebrate analyses:

School of Biological Sciences, Queen  
Mary and Westfield College (QMW)

### Macrophyte analyses:

ENSIS – ECRC, UCL

### Epilithic diatom analyses:

ENSIS – ECRC, UCL

### Fishery coordination:

CEH, Dorset

### Fish analyses:

Freshwater Fisheries Laboratory,  
Pitlochry, Perthshire.  
CEH, Windermere  
School of Biological Sciences, QMW  
Poly Enterprises Ltd., Plymouth  
Environment Agency, Llanelli &  
Caernarvon  
Department of Agriculture, Northern  
Ireland

### Sediment trap analyses:

ENSIS – ECRC, UCL

## Photographs

E.Shilland, N.Rose and D.Monteith

## Where to find further information

More information on the UKAWMN  
and a downloadable version of the  
1988-1999 year report can be found  
at the web address:  
[www.geog.ucl.ac.uk/ukawmn/](http://www.geog.ucl.ac.uk/ukawmn/)  
Further information on DETR air  
quality research is available at:  
[www.aeat.co.uk/netcen/airqual/home.html](http://www.aeat.co.uk/netcen/airqual/home.html)

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