Chapter (non-refereed)

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Acid deposition in Cumbria

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Summary
Cumbria is a region receiving amounts of wet deposited acidity from the atmosphere as large as any other area of Britain, Scandinavia or Europe. This large deposit of acidity is a consequence of a combination of the very large annual precipitation and its weighted acidity, typically pH 4.4 in Cumbria.

Dry deposition also contributes substantial quantities of sulphur, nitrogen and acidity, accounting for up to half of the total annual deposition of acidity from the atmosphere.

The large chemical inputs, interesting mechanisms of deposition and unusual topography are drawing a growing number of scientists to Cumbria to help unravel the complexities of the chemical and physical aspects of acid deposition. It is probable, therefore, that Cumbria will play an important part in the next few years of acid rain research in the UK.

1 Introduction
The meaning of 'acid rain', which is a term now more familiar to the UK public than it was a decade ago, has been stretched to cover all facets of acidic air pollution. In the process, however, its meaning has become vague. To consider the components of 'acid deposition', one must separate the processes of wet deposition (acid rain in the strict sense) and dry deposition of acidic gases and particles. Precipitation (rain, snow and hail) is generally regarded as acidic if it is more acid than pH 5.6 (equivalent to 2.5 μM H^+), the acidity of pure water in equilibrium with atmospheric concentrations of CO_2. This reference point is entirely arbitrary and does not form an exact basis for gauging the influence of man on the acidity of precipitation, as there are natural processes which may be involved. Gaseous sulphur compounds (eg dimethyl sulphide, carbonyl sulphide and hydrogen sulphide) are released by natural processes (on land and at sea), and these gases are oxidized through a variety of mechanisms to sulphur dioxide, and ultimately to sulphuric acid or sulphate salts. These sulphates are eventually incorporated into cloud water and lead to acidification of precipitation. Nitric oxide may also be released from natural processes (eg denitrification) and is oxidized in the atmosphere to nitrogen dioxide and nitric acid, which may be incorporated into precipitation. The natural mechanisms by which precipitation is acidified create a range of expected acidities in rain events from about pH 4.8 to pH 6.0, with median values of about pH 5.0 (10 μM H^+) (Charlson & Rodhe 1982). Such values of rainfall acidity are observed on remote islands in the Indian Ocean (Galloway & Gaudry 1984) and are quite close to the average values observed in the north of Norway (European Monitoring Evaluation Programme 1984) and Hebridean Islands (Cape *et al.* 1984).

Natural emissions of sulphur- and nitrogen-containing gases are augmented by industrial emissions, largely as a consequence of fossil fuel combustion and smelting processes. The sulphur dioxide and oxides of nitrogen released are oxidized in the atmosphere to their respective acids and returned to the surface in precipitation, which is acidified as a consequence. In the main industrial regions of Europe and eastern North America, the acidity of precipitation events is generally in the range pH 3.0–6.0, with annual mean values between pH 4.0 and pH 4.2 (100 to 60 μM H^+), about an order of magnitude more acidic than levels of acidity resulting from natural processes.

The other major deposition pathway for atmospheric acidity is dry deposition, in which the pollutants as gases or particles are 'captured' by the surface directly. The gases SO_2 and NO_2 may be deposited on external surfaces of vegetation or absorbed within the leaves following diffusion through the stomata. The gases are then oxidized to sulphate and nitrate respectively, generating acidity on or inside leaves.

A third mechanism by which pollutants are transferred from the atmosphere to the ground is termed 'occult deposition'. In this process, the pollutants are first incorporated into cloud droplets, as in wet deposition, but are subsequently deposited when cloud droplets are intercepted by vegetation. The mechanism is of importance to sites which are enveloped in cloud for a significant proportion of time.

The particles generated from oxidation of SO_2 and NO_2 are found in the size range 0.1–1.0 μm (diameter), and, unlike the gases, are not efficiently absorbed at the ground by dry deposition. The particles are too small to have significant rates of sedimentation under the action of gravity, and are transported through the free atmosphere by turbulent diffusion. However, close to surfaces where turbulence is suppressed, gases diffuse to the surface by molecular diffusion, whereas the particles are too large to 'diffuse' at significant rates. The major removal pathway for these particulate pollutants is by wet deposition. Sulphate- and nitrate-containing aerosols form suitable cloud condensation nuclei for the production of cloud droplets, and are efficiently scavenged from the air by precipitation.

These characteristics of the chemical conversion of pollutants and wet and dry deposition pathways lead

to a systematic change from inputs dominated by dry deposition of gases close to source areas, where gas concentrations are largest, to inputs dominated by wet deposition in regions remote from sources.

In the industrial regions of central England, for example, gas concentrations of SO_2 and NO_2 considerably exceed those of particulate sulphate and nitrate, and dry deposition is the dominant removal mechanism. In contrast, the west coast of Scandinavia experiences only small concentrations of SO_2 and NO_2 similar to the concentrations of sulphate and nitrate particles, and in these areas wet deposition contributes the majority of deposited sulphate and nitrate.

2 Cumbria

Cumbria is located only 100–200 km from major sources of SO_2 and NO_x ($NO+NO_2$) in the UK, so that in appropriate meteorological conditions significant concentrations of these pollutant gases are advected over Cumbria by wind. Inputs by dry deposition are, therefore, important to the annual 'budget'.

The very high rainfall in Cumbria also makes wet deposition inputs important. In general, the concentrations of major ions (sulphate, nitrate, ammonium and hydrogen) are smaller than at east coast sites (Figure 1), but the lower concentrations are more than compensated for by larger rainfall (up to 3000 mm), so that wet deposition in Cumbria exceeds that at east coast sites by a factor of at least 2.

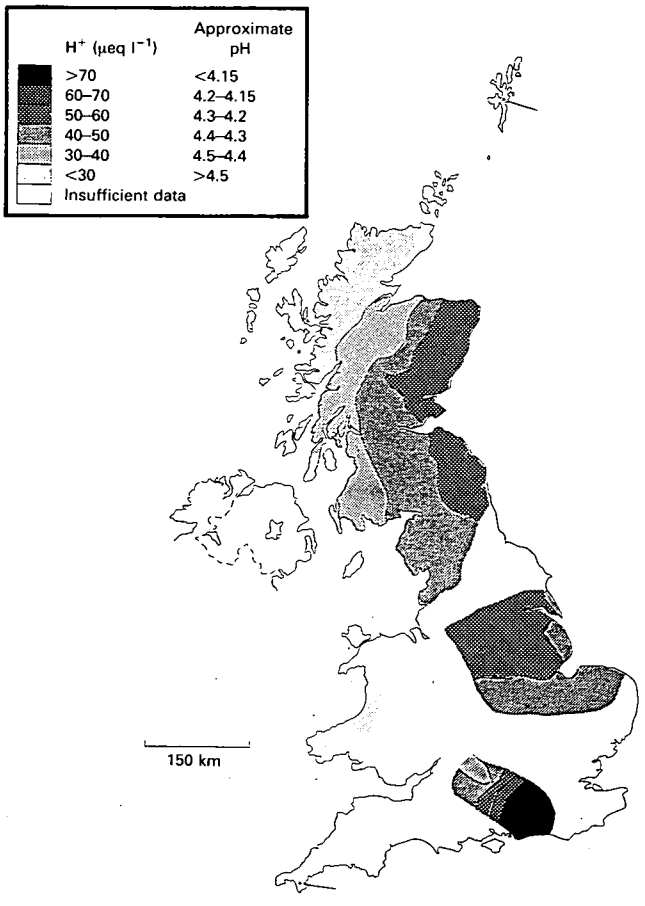

Figure 1. Rainfall weighted annual average hydrogen ion concentrations (source: Barrett et al. *1983)*

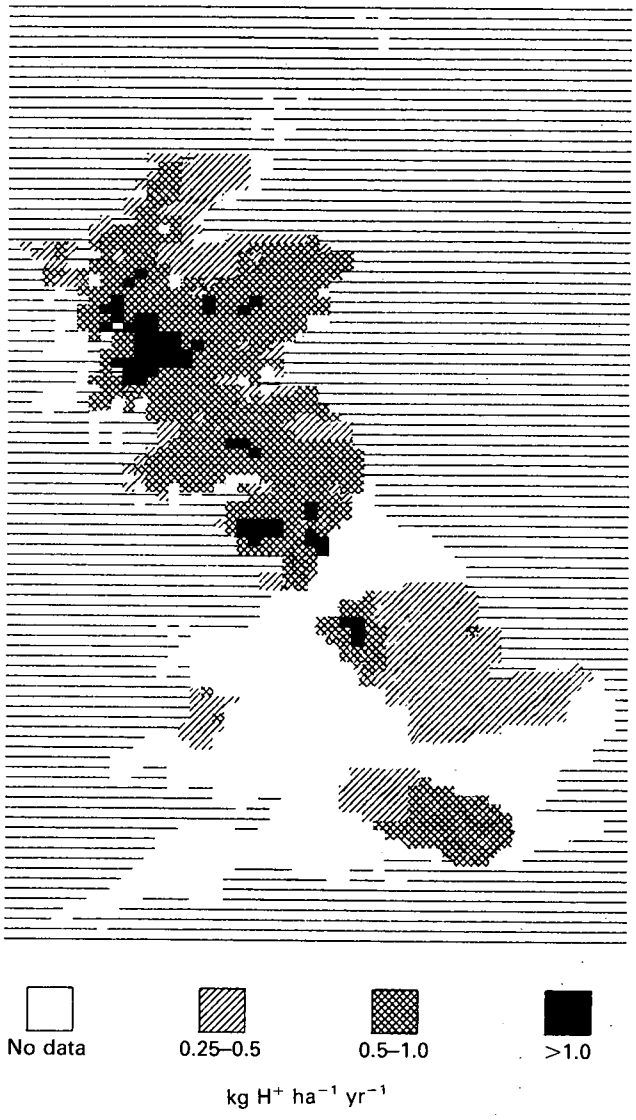

Figure 2. Wet deposited acidity in the UK

The average wet deposited acidity in Cumbria, shown in Figure 2, is as large as any other region in the UK, and is similar to the west central highlands of Scotland and the high rainfall areas of south-west Norway. The topography of Cumbria also generates considerable local variability in the distribution of wet deposition, the hills receiving the largest amounts. The proximity to source areas of pollutants (relative to Scandinavia and western Scotland) makes the dry deposition inputs larger, so that total inputs of acidity (and related ions) are larger in Cumbria than in other parts of the UK.

The geographical position of Cumbria places major source areas of air pollutants to the east and south, and clean maritime air to the west. This situation creates rainfall episodes in Cumbria with a large range of chemical composition. The acidity, for example, typically covers the range pH 4.0–7.0, or 3 orders of magnitude in hydrogen ion concentrations. Rain associated with maritime air from the North Atlantic generally has acidities of about pH 5.0, whereas rain associated with air that has passed over major source areas of air pollutants in the UK or continental Europe is typically at the pH 4.0 end of the distribution. This

variability creates an episodicity of major 'acidic rain' events such that 30% of the wet deposition occurs on just 4 or 5 out of the 250 rain days each year. The chemical variability of different rain events is similar elsewhere in Britain, but few regions experience such large variability across short distances. The coastal areas receive the lowest wet deposition, which for acidity is about 0.5 kg H^+ ha^{-1} annually, while at the hill tops 10–20 km inland wet deposition may exceed 1.5 kg H^+ ha^{-1} annually. The range of annual wet deposition of acidity within Cumbria is as great as the range throughout Britain.

3 Topographic effects

The large increase in rainfall with distance from the west coast is a consequence of the orographic enhancement of rainfall as air is lifted over the Cumbrian mountains. The larger amounts of rain may also deposit more sulphate, nitrate, acidity and other ions to the hill tops than at low altitudes, and recent studies by ITE in collaboration with the University of Manchester Institute of Science and Technology (UMIST), and with the Atomic Energy Research Establishment (Harwell), have begun investigating the chemical properties of rain- and cloud-water on Cumbrian hills. These investigations are necessary to extend our understanding of rainfall chemistry in Britain, from measurements at low altitudes, avoiding the practical problems of hill top measurements, to the processes occurring at high altitudes. In general, the concentrations of the major ionic components of rainwater (sulphate, nitrate, chloride, ammonium, sodium, magnesium and hydrogen) are much larger in cloud-water than in rain. These differences are of considerable interest as cloud occurs frequently on Cumbrian hills, and direct deposition of cloud droplets by impaction on vegetation provides a mechanism which further increases the inputs of pollutants at high altitudes.

While this research is still at an early stage, the recent measurements have generated much interest in the 'pollution climate' of hill tops, which is not readily predicted from measurements made on low ground. The ways in which an improved understanding of deposition mechanisms on hills will modify earlier 'speculative' maps of wet deposition cannot yet be quantified. However, the direction of the change is quite clear for many west coast hills, which are frequently in cloud: the wet deposition estimates (already the largest in the UK) will need to be revised upwards! The information in Figure 2 should therefore be taken as a guide to the wet deposition patterns, which in practice will be more complex and, in particular, should show the higher land in the west receiving larger amounts of wet deposition.

Estimates of dry deposition are made using different methods, as it is not easy to measure dry deposition of the gases SO_2 and NO_2. All measurements to date have been obtained in research programmes, and there are no networks of dry deposition monitoring. However, the studies to date have enabled us to gain a good understanding of the deposition mechanisms, which, in turn, has enabled estimates to be made of rates of deposition from a knowledge of the vegetation present, some of the aerodynamic properties of the vegetation, and from air concentrations of the gases.

For Cumbria, the dry deposition estimates rely on our knowledge of dry deposition rates to forests and grassland. This knowledge is based on rather few measurements, and many of the plant species present in Cumbria are 'unknown' in the dry deposition literature. So here, as with wet deposition, we have estimates, but there are important weaknesses. To improve estimates of dry deposition, measurements of the mechanism under a wider range of conditions are required, and for application to Cumbria more measurements are needed of the air concentrations of SO_2 and NO_2. The lack of such measurements has necessitated the use of numerical models (B E A Fisher, pers. comm.) to calculate gas concentrations in order that estimates of dry deposition may be obtained (Figure 3).

Figure 3. Dry deposited acidity in the UK

4 Changes with time

Data on rainfall chemistry in Cumbria include a set of observations in the 1950s (Gorham 1958) and separate measurements during the late 1970s (Fowler *et al.* 1982), but no consistent long-term detailed measurements are available for the study of trends. The growing interest in rainfall chemistry has produced a number of recent data sets for sites in or close to Cumbria. One of these sites, at Eskdalemuir in Scotland, shows a decrease in acidity during the period 1980–84 (Irwin 1986), a period during which UK SO_2 emissions also decreased. This trend has been observed at other UK and Scandinavian sites (Fowler *et al.* 1985), but it has not so far been possible to separate the relative importance of meteorological and emission factors as contributors to the trend. The year-to-year variability in meteorology makes detailed analysis of such short runs of data difficult. Climatological average rainfall amounts, for example, are generally quoted as mean annual values over a 30-year period. The considerable scientific (and political) interest in links between emissions and deposition will, however, continue to stimulate the search for the nature of such links, and in time the relative importance of changes in meteorological and emission factors on changes in deposition patterns may be quantified.

5 Conclusions

Cumbria is a region receiving amounts of wet deposited acidity from the atmosphere as large as any other area of Britain, Scandinavia or Europe. This large deposit of acidity is a consequence of a combination of the very large annual precipitation and its weighted acidity, typically pH 4.4 in Cumbria. The region shows large variations in annual inputs of wet deposited acidity, from relatively small values close to the coast (0.5 kg H^+ ha^{-1}) to very large values on the hills (1.5 kg H^+ ha^{-1}).

Dry deposition also contributes substantial quantities of sulphur, nitrogen and acidity, accounting for up to half of the total annual deposition of acidity from the atmosphere. The cloud which frequently envelops Cumbrian mountains often contains large concentrations of the major ions found in rain, and this cloud may be 'captured' by hillside vegetation, providing an additional deposition mechanism and helping to generate a unique 'pollution climate' on the tops of these hills.

6 Acknowledgements

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