



**UK ACID WATERS
MONITORING NETWORK:
*10 Year Report***

**Analysis and Interpretation of Results
April 1988 - March 1998**

■ Edited by:

D.T. MONTEITH & C.D. EVANS

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■ Cover photograph: The acid sensitive aquatic moss *Hygrohypnum ochraceum* carpeting a fast flowing stretch of the Allt a'Mharcaidh, northeast Scotland.

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Executive Summary

- 1) This report provides an interpretation of data collated by the United Kingdom Acid Waters Monitoring Network (UKAWMN) over the ten year period April 1988 - March 1998. It also draws on data from the UK Acid Deposition Network which has been operating since 1986.
- 2) Between 1986 and 1997 sulphur emissions from the UK declined by approximately 57% while those from the rest of UNECE Europe declined by 45%. UK emissions of oxides of nitrogen (NO_x) declined by approximately 14%.
- 3) Over the same period non-marine sulphur deposition (i.e. of anthropogenic origin) in the UK declined by approximately 52%, but the majority of the decline was dry deposition (61%). Wet deposition reduced by 42%.
- 4) Rates of decline in sulphur deposition are geographically skewed. In areas close to emissions sources, i.e. central and southeast England, large reductions have occurred in the flux of wet and dry sulphur deposition and in the sulphur concentration of precipitation. Smaller but significant declines have occurred at intermediate distances from sources. Although there have been reductions in sulphur deposition in the acid sensitive, high rainfall, west coast areas, these are much smaller than the reductions in sulphur emissions. Indeed at many of the high rainfall deposition monitoring sites trends in sulphur deposition are not statistically significant.
- 5) Small but significant increases in concentrations and deposition fluxes of nitrate (NO_3) are evident at west coast and remote monitoring stations.
- 6) It is the aim of this report to investigate to what extent emissions reductions have influenced the surface water chemistry and biology of acid sensitive freshwaters throughout the UK. The UKAWMN consists of eleven lakes and eleven streams which have been monitored chemically and biologically over the last decade. Historical reconstructions, based on sediment cores, have demonstrated that at least nine of the lakes have become more acid over the last 150 years as a result of acid pollutant deposition. It is likely that most streams are also in an acidified state.
- 7) Over the period of analysis covered by this report (1988-1998) large declines in non-marine sulphate (xSO_4) concentrations have been recorded at UKAWMN sites in the 'close-to-source' regions, i.e. at Old Lodge (southeast England) and the River Etherow (Pennines). A smaller, but still significant, decline has occurred at Lochnagar (northeast Scotland). Nineteen of the twenty-two UKAWMN sites have shown no significant trend in xSO_4 concentration.
- 8) There is a clear spatial relationship between nitrogen deposition and NO_3 concentration in UKAWMN freshwaters. NO_3 concentrations in the most remote sites range from low to below detection limits. In these relatively low pollution environments nitrogen can limit terrestrial primary productivity, in which case virtually all nitrogen inputs are expected to be retained by catchment soils. Enhanced nitrogen inputs can result in catchment saturation and nitrogen leaching into surface waters. Since the latter is likely to be accompanied by hydrogen ions in sensitive catchments, the phenomena of nitrogen saturation presents a serious threat to acid sensitive waters. Positive linear trends have been identified at four sites which may reflect increasing saturation of their catchment soils. NO_3 concentrations at Lochnagar appear to have undergone a step-change increase which reflects a transition from a seasonal pattern to year-round leaching.
- 9) NO_3 concentrations have shown considerable inter-annual variability which appears to relate to climatic differences between years. Variation in NO_3 concentration can be linked to winter values for the North Atlantic Oscillation Index (NAOI), a synoptic scale variable which represents inter-annual variability in the relative dominance of westerly versus north-easterly weather conditions over the UK. At most sites NO_3 leaching has been highest after the coldest (most negative NAOI) winters.
- 10) Upward trends in pH, and/or alkalinity, have been identified at seven sites. This is surprising since there is no indication of downward trends in acid anion concentrations at the same sites. Due to the absence of this link, and for other reasons explored in this report, it is too early to categorically attribute these trends to long term chemical recovery from acidification. At the three sites with declining xSO_4 concentrations, NO_3 has increased, resulting in little overall change in total acidity. At Old Lodge and the River Etherow, base cation (i.e. calcium,

magnesium, potassium and sodium) concentrations have decreased. These increases in acidifying NO_3 and/or reductions in acid-neutralising base cations appear so far to have offset any positive influence of xSO_4 decreases, where observed, on surface water acidity. At Lochnagar, the decline in xSO_4 has been smaller than the increase in NO_3 , and this site has continued to acidify.

- 11) Concentrations of chloride (derived mainly from sea-salt inputs during winter) at UKAWMN sites with westerly locations have shown cyclical variation over the monitoring period and this is highly correlated between sites. Chloride concentration variability can be linked to inter-annual variations in winter storminess, which influences levels of sea-salt deposition, and, once again, to the winter NAOI.
- 12) At the same west coast sites, cyclical variation is also apparent in the concentrations of non-marine base-cations and, in some cases, hydrogen ion and labile (biologically available) aluminium. Variation in these ions appears to be driven by their displacement from catchment soil ion-exchange sites by marine cations deposited in sea-salt. Inter-annual variation in pH and alkalinity may also have been influenced by variations in rainfall, which determines the proportional contributions of relatively alkaline base-flow and more acidic surface run-off. Trends in pH and alkalinity, where identified, may therefore primarily reflect a response to a decline in winter storminess, from the early 1990s to the end of the interpretative period, rather than a decline in acid deposition. The relative roles of these two effects will only become clear with further monitoring.
- 13) SO_4 occurs both as an acidic pollutant and, naturally, in neutral salts in sea-water and sea-spray. Analysis suggests that SO_4 storage by catchment soils may be enhanced following periods of high sea-salt inputs. Conversely, when sea-salt inputs are low and total SO_4 concentration in soil water declines, stored SO_4 may be released. Chloride on the other hand behaves conservatively, passing more rapidly into the drainage network. Since a fixed $\text{SO}_4:\text{Cl}$ ratio (based on sea-water constitution) is used to estimate the proportion of total SO_4 which is derived from marine and non-marine sources, errors are likely to occur in the estimate, depending on the prevailing sea-salt regime. Non-marine SO_4 concentrations may therefore be underestimated during periods of high sea-salt inputs and overestimated when inputs are low. This effect may have masked the small reductions in actual non-marine SO_4 concentrations expected at some sites at intermediate distance from source areas.
- 14) Longer term datasets (from the early to mid-1980s to the present), available for streams in north Wales, Galloway and the Trossachs, and a loch in Galloway, demonstrate clear declines in xSO_4 and corresponding increases in pH. These underlie variations due to climate oscillations described above and provide the strongest evidence that slow chemical recovery from acidification is underway in some areas of the UK.
- 15) Significant increases have occurred in Dissolved Organic Carbon (DOC) concentrations at nineteen of the twenty-two sites in the Network. This is potentially of great importance to the Network, since an increase in organic acids could reduce, or even negate, reductions in acidity expected from declining mineral acid inputs. The remarkable spatial consistency suggests a general pattern of rising DOC levels in UK upland freshwaters. It is currently unclear whether these increases have been matched by an increase in water colour, and the molecular form of the DOC which has increased is not known. Mechanisms for the increase are also unclear at this stage, although the most probable hypothesis is considered to be increased microbial decomposition of soil organic matter resulting from increasing summer temperatures. UK summer temperatures over the last decade have been significantly higher than the long-term (i.e. last 30 year) mean. Under a scenario of rising global temperatures, therefore, DOC may be expected to increase further. In lakes, a rise in water colour could have the detrimental effect of reducing the depth of penetration of photosynthetically active radiation, required for plant growth. On the other hand, increasing colour would also provide aquatic

organisms with additional protection from exposure to UV-B radiation which is increasing in mid-latitudes. DOC has also been shown to reduce fish mortality under acidic conditions by both reducing the concentration of toxic labile aluminium (by complexing with it) and by reducing the toxicity of the remaining fraction.

- 16) The identification of climatically driven cyclicity in estimated xSO_4 , NO_3 , acidity and other important measures of surface water quality has major implications for detection of recovery-related trends, applicable both to the UKAWMN and to other monitoring programmes. Cyclical variations have the potential either to mask underlying anthropogenically driven trends, or to generate apparent trends as a result of natural processes. Since these variations appear to operate at approximately decadal timescales, there is clearly a need to monitor over longer time periods in order to fully characterise the impact of anthropogenic factors on surface water quality.
- 17) Spatial biological comparisons of multi-species datasets, i.e. epilithic diatoms (unicellular siliceous algae which grow attached to rocks), macroinvertebrates (non-microscopic aquatic invertebrates), and aquatic macrophytes (larger aquatic plants) demonstrate a generally positive relationship between the number of species found and pH. Trout densities show a roughly exponential decline with increasing labile aluminum concentration, and healthy populations are mostly restricted to sites with a positive ten-year mean Acid Neutralising Capacity (ANC, calculated as the difference between the sum of concentrations of base-cations and acid anions).
- 18) Multi-species biological datasets have been subject to linear time trend analysis to test for uni-directional change in species composition over the monitoring period. Where detected, changes may be indicative of biological responses to changing acidity status (i.e. 'recovery' or further acidification).
- 19) Linear trends in aquatic macrophyte assemblages were identified at five sites. These reflect reductions in overall cover rather than a turnover of species, and

probably result from physical disturbance rather than chemical change.

- 20) Linear trends have been detected in epilithic diatom species assemblages at nine sites and five of these are indicative of an amelioration in acidity (i.e. recovery) while one is indicative of further acidification. Trends at three sites indicative of amelioration are consistent with linear trends in acidity established from analysis of water chemistry. Linear change at other sites may also be indicative of biological recovery, although as there is no evidence for sustained year-round chemical improvement at many of these, it would seem that other factors, most notably climatic, may be involved. Generally, temporal variation in acidity in lakes is reflected by variation in epilithic diatom species composition. This suggests that for lakes, chemical recovery should lead to rapid recovery of this important group of primary producers. At stream sites, inter-annual variation can be closely linked to variations in the summer rainfall regime, suggesting that flow-governed acidity at this time of year may be the primary factor in influencing the species assemblage. Trends indicative of recovery are therefore likely to take much longer to identify for streams than for lakes.
- 21) Linear trends have been detected in macroinvertebrate assemblages at eleven sites, but trends at only three are indicative of an amelioration in acidity, and only two of these are consistent with linear changes identified in water chemistry. Linear trends at most of the eleven sites, mainly lakes, can be linked to the declining influence of winter storm activity over the monitoring period. A particularly high proportion of variance between years in the assemblage can be explained by the January NAOI, for those sites where the January NAOI is well correlated with Cl concentration and winter rainfall. This suggests that variation in the macroinvertebrate assemblage may be primarily driven by inter-annual variation in the severity and/or duration of acid episodes resulting from the effects of sea-salt deposition and cation dilution. If this is the case, macroinvertebrate communities may be expected to show long term, but punctuated (i.e. non-linear) recovery as the intensity of the most acid events gradually declines with decreasing deposition. However, other

climate-related physical effects, such as water level oscillation, cannot be ruled out as driving factors at this stage.

22) Llyn Llagi, in north Wales, and Loch Chon, in the Scottish Trossachs, are the only sites which show trends indicative of improved conditions in both epilithic diatoms and macroinvertebrates, and concomitant reductions in acidity according to water chemistry. For Llyn Llagi, a comparison of the diatom assemblage of sediment trap samples (collected since 1991) and samples from a sediment core (taken in 1990) demonstrates that recent changes in the diatom assemblage of newly deposited lake sediment are approximately the reverse of those which occurred during the latter stages of acidification. This provides powerful evidence that biological recovery, at least at the lowest trophic level, is underway at this site. Similar changes in sediment assemblages which are indicative of recovery have occurred in Loch Chon. However here it is possible that these may at least in part reflect a response to a reduction in the influence of climatically enhanced acidity over the monitoring period.

23) Few linear trends are evident in trout density or condition factor. The mobility of fish, relative to other biological groups monitored, adds to overall sample variability and for most sites it is likely that several more years of monitoring are required to allow the possible identification of trends. However, there has been a significant increase in the density of trout at Old Lodge in southwest England. This is mirrored by a decline in labile aluminium concentration and suggests that recent improvements in water chemistry may have allowed the upstream migration of fish from better buffered waters downstream. Since the decline in labile aluminium appears to be partly influenced by reductions in marine ion deposition, it is unclear to what extent this apparent 'recovery' will be sustained in the short-term.

24) The analysis of the 10 year dataset has highlighted several important issues and uncertainties:

a) Chemical and biological 'recovery' is very slight at this stage, but is predicted and needs to be identified and quantified, if,

when, and where it occurs.

b) Problems have been identified in the estimation of the temporal variation in SO_4 from non-marine sources and this could account for the absence of evidence for declining xSO_4 at some sites. Further work on data from sites with co-located deposition monitoring stations may begin to address this problem.

c) Where detected, declining acid anion trends have not been accompanied by detectable amelioration in acidity to date. The period of time required for the onset of a measurable recovery response in buffering cations is as yet unclear.

d) Deposition of NO_3 may be increasing slowly in more remote areas, while continued accumulation of anthropogenically derived nitrogen may eventually lead to nitrogen breakthrough and hence further biological damage at some sites.

e) Widespread increases in DOC may be hampering chemical recovery, but the cause and effects are currently poorly understood.

f) Inter-annual variability in water chemistry and biology is considerable, relative to expected rates of recovery. A significant proportion of this variability can be explained by climatic influences. Continued monitoring should allow the quantification of climatic effects and therefore more sensitive detection of potentially underlying trends.

25) UKAWMN data are becoming increasingly valuable in the testing and calibration of acidity prediction models such as MAGIC (Cosby *et al.*, 1985) and FAB (Posch *et al.*, 1997).

26) Data from UKAWMN sites are becoming increasingly important to wider monitoring networks, including the Environmental Change Network (ECN) and the UNECE ICP (International Cooperative Programme on the Assessment and Monitoring of Acidification of Rivers and Lakes).

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Alan Jenkins

The processes that link the emission of acidifying pollutants to the atmosphere, their transport and deposition and the subsequent acidification of soils and freshwaters are largely understood and well documented (e.g. Reuss & Johnson, 1986). The major pollutants of concern include oxides of sulphur and nitrogen derived from the burning of fossil fuels and ammonia derived largely from agricultural sources. These acidifying pollutants undergo chemical reaction in the atmosphere, are carried by the air over large distances from their sources and deposited as gases, aerosols and dissolved in rain water. Acidification of soils begins immediately as base cations are stripped from the ion-exchange complex and base saturation decreases. If the rate of supply of base cations from primary weathering in the catchment is less than the incoming flux of strong acid anions, the base cation store in the soil becomes depleted and hydrogen ions and aluminium species will accompany acid anions into the surface water, promoting acidification. The impact on biota results both from the toxicity of high hydrogen ion concentration and from the increased toxicity of aluminium at lower pH, and is manifest in decreases or loss of populations at all trophic levels.

The first legislation aimed at reducing S emissions was signed under the auspices of the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution in 1985 (the First Sulphur Protocol). The signatory countries committed themselves to a 30% reduction in S emission relative to 1980 levels by 1993. The UK did not ratify this protocol but still achieved the required emission reductions. In 1994 a Second Sulphur Protocol was signed under which the UK agreed to a c. 80% reduction in emissions, again relative to 1980, by 2010. The UK emissions are currently on track to meet this target. In addition there have been various EU Directives binding member states to similar targets. For nitrogen, the first UNECE protocol was signed in 1988 and committed to a stabilisation of the emission of oxidised nitrogen compounds at 1987 levels by 1994. In 1999, a further protocol incorporating

multi-effects and multi-pollutants (sulphur, nitrogen, ozone and volatile organic compounds) was signed to introduce yet further reductions in emissions of acidifying pollutants.

The impact of the measures adopted to reduce acidic emissions should be reflected in long term trends in water chemistry and biology at acid-impacted sites. Identification of trends in long term data, however, is often complicated by changes in sampling frequency, analytical techniques and laboratories. The UK Acid Waters Monitoring Network (UKAWMN) was established in 1988 to provide a consistent water data record for chemistry and biology, across a range of acid-impacted sites, with which to assess the impact of reducing emissions of acidifying pollutants. The interpretation of trends at each site is underpinned by complimentary information from the UK Acid Deposition Monitoring Network and this allows the link between emission reductions and atmospheric deposition to be evaluated. It is unlikely that emission reductions will translate into uniform deposition reductions across the whole of the country.

This report presents the results of analysis of the first ten years of UKAWMN data. Analysis of ten year trends at UKAWMN sites in Chapters 4,5 and 7, is augmented by a brief analysis of a few longer term, high quality chemistry datasets in Chapter 6. These Chapters are preceded by an overview of recent analysis of data from the UK Acid Deposition Monitoring Network (Chapter 2) which sets the recent acid deposition regime in spatial and temporal contexts.

Analysis has focussed on the identification and quantification of time trends in chemical and biological data which may point to improvements (i.e. recovery), stable conditions or further deterioration. The link between chemical and biological recovery is likely to be non-linear and significant time lags are expected, particularly for those organisms at the higher end of the food chain. Generally therefore, trends in chemistry and biology have been analysed in isolation and results have been integrated qualitatively. In addition,

attention has been paid to the nature and causes of inter-annual variability in UKAWMN data, a significant proportion of which can be linked to variations in climate. Given the relatively large inter-annual variation observed in most datasets relative to changes with time, it is vital that these sources of 'noise' are better understood, so that underlying recovery trends may be more readily detected in future.