Trends in the hydrochemistry of acid-sensitive surface waters in the UK 1988–2008

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ABSTRACT

We conducted complementary linear and non-linear statistical modelling of the first 20 years of hydrochemical data from the 22 lakes and streams of the UK Acid Waters Monitoring Network (AWMN) in order to assess temporal patterns and rates of change in indicators of the key drivers of surface water acidification and acidity status. Over the period 1988–2008, concentrations of non-marine sulphate (i.e. of anthropogenic origin) fell in line with reductions in non-marine sulphur deposition, the principal driver of acidification. Most of the decline was confined to the latter half of the 1990s. Whilst these reductions were substantial, concentrations in recent samples from the most contaminated sites remained several times higher than those in the most remote, low-deposition regions. Nitrate (NO_3^-) concentrations also declined slightly at several sites in northern England and Wales, possibly reflecting a recent regional reduction in N deposition. Further north, NO_3^- concentrations increased slightly in some Scottish sites, reflecting a continued dominance of climatic variation on nitrogen cycling in this region. A combination of unusually high rainfall and seasalt inputs in the early years, gradual long-term reductions in hydrochloric acid deposition, and later and more substantial reductions in sulphur deposition, appeared to account for relatively linear increases in an alkalinity-based estimate of Acid Neutralising Capacity ([AB-ANC]) with time. However, variation between sites in the size of the long-term trend in [AB-ANC] was most clearly linked to the size of the long-term reduction in sulphate concentration.

The chemical characteristics of changes in [AB-ANC] across the network were dependent on rates of change in acid deposition, the extent to which sites have previously acidified, and average dissolved organic carbon concentration ([DOC]). In the most acidified waters, the response in acidity to reductions in acid deposition was dominated initially by large reductions in inorganic aluminium concentrations ([Al_{inorg}]). Responses in pH have become clearer at these sites as [Al_{inorg}] has begun to stabilise. Over the wider network, pH has been rising more rapidly in sites with lower concentrations of organic acids. A substantial proportion of the deposition-driven increase in [AB-ANC] at several sites is accounted for by increases in [DOC]. For the non-acidified but acid-sensitive waters in the far north and west, changes in [DOC] represent the only clear response to the small changes in sulphur deposition.

In the more acidified sites, a reduction in the size of occasional extreme concentrations of Al_{inorg}, that occur after periods of high rainfall or seasalt deposition events, has been more rapid than the declines in average levels, implying that at most sites the persistence of these events should not be seen as an additional barrier to ecological recovery. In a comparison of geographically paired sites with forested and moorland catchments, consistently higher levels of inorganic aluminium concentration and lower AB-ANC provided clear evidence that the former group had acidified to a greater extent. There were few significant differences in the rate at which non-marine sulphate concentration declined or AB-ANC increased and the forested sites therefore remain in a more acidified condition.

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1. Introduction

Since the onset of the industrial revolution, acidification by anthropogenic acid deposition has caused severe and widespread ecological damage to surface waters draining the UK uplands. Acidification has also affected many other geologically sensitive regions

of northern Europe and North America. Under the auspices of the United Nations Economic Commission for Europe (UNECE) convention on Long Range Transboundary Air Pollutants (LRTAP), the international community has sought to reduce effects of acid deposition on both freshwater and terrestrial environments through the implementation of a series of emission reduction protocols, (RoTAP, 2012; Shilland et al., this issue). National environmental monitoring systems designed to audit the efficacy of their implementation began to develop from the mid-1980s or later, and generally a decade or more after emissions peaked. The UK government's observation system for assessing the impact of emission reductions on the ecological health of acid-sensitive freshwaters, the UK Acid Waters Monitoring Network (AWMN) and the principal subject of this Special Issue (see Shilland et al., this issue), was established in 1988.

The primary criterion in the selection of the 22 lakes and streams for the AWMN was high acid sensitivity, as determined by low concentrations of base cations in runoff. From the outset of monitoring, however, there were wide differences between sites in water acidity, reflecting: large southeast to northwest gradients in acid deposition; greater acidic inputs in forested vs moorland sites resulting from enhanced interception by forest canopies; and, differences in geological acid-sensitivity (Monteith and Evans, 2005; Battarbee et al., 2005). Concentrations of non-marine sulphate $[xSO_4^{2-}]$, i.e. total sulphate minus an estimated marine fraction, were highest for the network in the Old Lodge stream in southeast England and the River Etherow in the southern Pennines, consistent with their locations within regions of particularly high sulphur deposition. These sites, in addition to two of the most weakly buffered sites in areas of intermediate deposition slightly further to the north and west, Blue Lough in the Mourne Mountains and Scoat Tarn in the English Lake District, also exhibited the lowest levels of pH and some of the highest concentrations of labile (i.e. inorganic) aluminium (Al_{inorg}), the latter considered to be substantially above toxicity thresholds for a range of acid-sensitive aquatic biota – including salmonids such as brown trout, and several macroinvertebrate taxa (Baker and Schofield, 1982; Warby et al., 2008; Kroglund et al., 2008; and see Malcolm et al., 2014; Stockdale et al., 2014). At the other extreme, Coneyglen Burn in the Sperrins of Northern Ireland and Loch Coire nan Arr in the northwest Scottish Highlands exhibited the lowest acid anion concentrations (i.e. $[SO_4^{2-}]$ and nitrate ($[NO_3^-]$)), and were amongst the least acidic, with negligible, and biologically benign $[Al_{inorg}]$. Overall, sites fed by forested catchments were found to have higher $[SO_4^{2-}]$, $[NO_3^-]$ and $[Al_{inorg}]$ and lower pH than nearby moorland sites (Monteith and Evans, 2000).

The first evidence from the AWMN for long-term downward trends in the main driver of acidification, i.e. declines in $[xSO_4^{2-}]$, emerged after around 15 years of monitoring. This followed a new phase of emission controls on UK plant, including the fitting of flue-gas desulphurisation (FGD) technology on some of the UK's largest power stations in the mid 1990s (Rose and Monteith, 2005). Davies et al. (2005) reported small significant increases in pH and Acid Neutralising Capacity [ANC] and reductions in $[Al_{inorg}]$ at a minority of sites for the period 1988–2003. These were broadly consistent with the measured reductions in $[xSO_4^{2-}]$ and provided the first national-scale evidence that the water chemistry of these acidified systems was in a process of recovery. More recently, widely reported increases in the concentration of dissolved organic carbon (DOC) have also been linked to the process of recovery from acidification (e.g. Stoddard et al., 2003; Evans et al., 2006; Monteith et al., 2007).

Today progress in the chemical health of acidified surface waters in the UK and internationally is increasingly well documented (e.g. Evans et al., 2001b; Davies et al., 2005; Skjelkvåle et al., 2007; Driscoll et al., 2007; Warby et al., 2008; Sucker et al., 2011) but

uncertainties remain about the character, sustainability and ecological significance of recovery. There are particular concerns over the extent to which occasional hydrochemical extremes may continue to pose a barrier to ecological recovery (Kowalik et al., 2007), and whether waters in catchments that are managed for coniferous forestry remain more at risk from the continuing effects of acidification than other land uses (Dunford et al., 2012).

To date, trends in AWMN hydrochemical data have been described mostly through linear statistics. However, as the datasets lengthen it has become pertinent to consider departures from linearity. This is necessary to determine whether recovery is being sustained or has faltered, and to allow a more detailed comparison of temporal changes between determinands and between sites. In this paper we therefore apply both linear and non-linear modelling techniques to summarise change in the hydrochemistry of AWMN lakes and streams over the first two decades of monitoring.

2. Methods

2.1. Hydrochemistry

We assessed water chemistry data for the 22 AWMN sites (see Shilland et al., this issue, for site descriptions) for the period 1988 to March 2008. The data represent quarterly samples for lakes and monthly samples for streams and include: indicators of the key drivers of acidification, i.e. concentrations of the acid anions SO_4^{2-}, NO_3^-, Cl^-, and non-marine sulphate xSO_4^{2-} – calculated in units of equivalence as $[SO_4^{2-}] - 0.104 \times [Cl^-]$ (according to the ratio of Cl^- to SO_4^{2-} in seasalt); conventional indicators of chemical responses (i.e. pH, $[Al_{inorg}]$ and Gran Alkalinity; concentrations of the base cations calcium ($[Ca^{2+}]$), magnesium ($[Mg^{2+}]$), sodium ($[Na^+]$), potassium ($[K^+]$); and, ($[DOC]$). The majority of samples have been analysed by laboratories operated either by the Centre for Ecology & Hydrology, (Wallingford, Lancaster or Bangor), or the Marine Scotland Freshwater Fisheries Laboratory, Pitlochry, using methods calibrated specifically for low ionic strength waters. All chemical analyses are performed on 0.45 μm Whatman cellulose nitrate filtered samples. Analyses follow strict protocols, ensuring intra- and inter-site comparability (Patrick et al., 1991) and have been subjected to rigorous analytical quality control comparisons (Gardner, 2008).

Acid Neutralising Capacity (ANC) was determined from an alkalinity-based ionic balance using an approach pioneered by Neal et al. (1999) and Harriman and Taylor (1999), i.e.: $[ANC] (\mu eq\,L^{-1}) = [Gran\;Alkalinity]\;(\mu eq\,L^{-1}) + (F \times [DOC]\;(mg\,L^{-1}) - 3 \times Al_{inorg}\;(\mu mol\,L^{-1})$. In this model, an assumption is made that the acid-base properties of DOC are uniform across sites, and thus that organic acid dissociation is a predictable function of pH (e.g. Hruška et al., 2003). The coefficient F represents the charge density (in $\mu eq\,mg^{-1}$ C) of DOC at the equivalence point and estimated for Scottish upland waters by Harriman and Taylor (1999) as 4.5 for samples with a pH of 4.5–5.5 and 5.0 for samples with a pH > 5.5. All Al_{inorg} at the equivalence point is assumed to be in the form Al^{3+}. The method also assumes negligible influences from other components, such as iron (Fe) and boron (B). To avoid confusion with the more commonly applied expression of ANC, i.e. the difference between the equivalent sums of base cations and acid anions, our alkalinity-based metric is denoted throughout this paper as AB-ANC. Evans et al. (2001c) argued that for sites in marine-influenced areas, where levels of $[Cl^-]$ and marine base cations can vary considerably, AB-ANC provides a more robust approximation of ANC than the conventional method, as the latter is more vulnerable to the potential compound errors of seven (or more) determinands in the calculation.