

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 ($[\text{Al}_{\text{inorg}}]$). Responses in pH have become clearer at these sites as $[\text{Al}_{\text{inorg}}]$ 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

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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 [$x\text{SO}_4^{2-}$], 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. $[\text{SO}_4^{2-}]$ and nitrate ($[\text{NO}_3^-]$)), and were amongst the least acidic, with negligible, and biologically benign $[\text{Al}_{\text{inorg}}]$. Overall, sites fed by forested catchments were found to have higher $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$ and $[\text{Al}_{\text{inorg}}]$ 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 $[\text{xSO}_4^{2-}]$, 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 $[\text{Al}_{\text{inorg}}]$ at a minority of sites for the period 1988–2003. These were broadly consistent with the measured reductions in $[\text{xSO}_4^{2-}]$ 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 $[\text{SO}_4^{2-}] - 0.104 \times [\text{Cl}^-]$ (according to the ratio of Cl^- to SO_4^{2-} in sea salt); conventional indicators of chemical responses (i.e. pH, $[\text{Al}_{\text{inorg}}]$ and Gran Alkalinity); concentrations of the base cations calcium ($[\text{Ca}^{2+}]$), magnesium ($[\text{Mg}^{2+}]$), sodium ($[\text{Na}^+]$), potassium ($[\text{K}^+]$); and, $[\text{DOC}]$. 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.: $[\text{ANC}] (\mu\text{eq L}^{-1}) = [\text{Gran Alkalinity}] (\mu\text{eq L}^{-1}) + (F \times [\text{DOC}] (\text{mg L}^{-1}) - 3 \times \text{Al}_{\text{inorg}} (\mu\text{mol L}^{-1}))$. 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 $\mu\text{eq mg}^{-1} \text{C}$) 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 $[\text{Cl}^-]$ 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.

2.2. Statistical analysis

We used two statistical approaches to provide an overview of hydrochemical trends at different temporal scales. In order to determine the significance of short-term changes, convey the timing of key shifts and flows in the data, and compare patterns of change qualitatively between sites and between variables, we fitted non-linear smoothers to the hydrochemical data. We then used a simple linear model to express change over the course of the whole time series as a single statistic, enabling rates of change in these determinands to be compared quantitatively between sites and between variables. These approaches are complementary and can aid in each other's interpretation. For example, if the concentration of a solute exhibits common non-linear features across sites within a region (i.e. they are coherent) this is often indicative of a common driver, or set of drivers. Differences between sites in the overall rate of change in the determinand can then be used to inform how the pressure from the driver varies spatially.

Exploratory analysis of the hydrochemical time series suggested that trends within individual determinands were non-linear but importantly, were also non-monotonic. Neither parametric linear regression models nor non-parametric Mann–Kendall procedures are able to capture the shorter-term, local, variation in the mean in such time series. To achieve this in a manner that was consistent across sites and variables we fitted semi-parametric additive models (AMs) to the data.

AMs allow for smooth trends to be estimated from the data using penalised regression splines. The following AM was fitted to each series:

$$y_i = \beta_0 + f_1(\text{time}_i) + f_2(\text{day}_i) + \varepsilon_i, \quad \varepsilon = N(0, \sigma^2 \Lambda) \quad (1)$$

where y_i are the observed hydrochemical data, β_0 is the intercept or constant term, f_x are smooth functions of time (in days since the start of the series) and the day of the year respectively. $f_1(\text{time}_i)$ represents the trend in the response and describes how the level of the response varies through time. $f_2(\text{day}_i)$ represents the seasonal, within-year pattern in the hydrochemistry. Thus the seasonal signal and the longer-term trend are separated into two independent, additive components of the model. ε_i are the model residuals, which are assumed to be zero mean, Gaussian random variables with variance $\sigma^2 \Lambda$. Λ is a correlation matrix that describes the dependence structure of the residuals. Autocorrelation in ε_i can be taken into account by assuming a simple time series process for the residuals plus the usual assumption that the residuals are zero mean, Gaussian random variables. As the number of days between observations varies moderately, and some observations are missing, we adopted a continuous-time AR(1) process as the simple time series model.

Models were fitted in a linear mixed model (LMM) framework using the mgcv package (version 1.7-6; Wood, 2011) for the R statistical software (version 2.13-0; R Core Development team, 2011) via restricted maximum likelihood estimation (REML; Wood, 2004, 2006, 2011). Fitting within a LMM framework affords the use of a generalised likelihood ratio test (GLRT) to determine whether the model with structured residuals was a significantly better fit than a model that assumes independent residuals. The simpler independence model was retained unless the model with structured residuals provided a statistically significantly better fit.

The fitted models describe the variation in time in the mean of the probability distribution of the response. The fitted smooth functions are determined by a series of coefficients, estimates of which are computed using REML, which are subject to uncertainty. To enable fitted trends to be interpreted simply, we identified the periods along the fitted trend where the slope, the rate of change in the trend, was statistically significantly different from zero, i.e. periods where the hydrochemistry is either increasing or decreasing in a significant manner. This was achieved by

computing the first derivatives of f_1 using the method of finite differences. Fitted values of the trend (f_1) were obtained from each model for a grid of 200 equally spaced time points over the period of observation. This grid was shifted in time by a very small amount and fitted values of the trend again determined from the model. The differences between the two sets of fitted values, divided by the difference in time, yield the first derivatives of the trend. Standard errors for the first derivatives were also computed and a 95% point-wise confidence interval on the derivative determined. Where the confidence interval on the first derivatives is bounded away from zero, the trend is significantly different from zero at the 95% level. These periods are illustrated on the figures showing the fitted trends by a thicker line.

We then fitted a simple linear model to quantify the overall long term trend in key drivers (e.g. $[\text{xSO}_4^{2-}]$) and responses (e.g. [ANC], [DOC], etc.) across the network. We chose this approach over the more commonly applied Mann–Kendall procedure for a number of reasons. The first is that the linear regression model follows a similar framework to the AMs described above—in fact a standard Gaussian linear model is a special case of the formula given in Eq. (1). For consistency, therefore, we elected to stay within a similar modelling framework so that the results were comparable and each model could inform the other. The linear regression approach also allowed the inclusion of additional terms in the model, direct comparisons to be made between sites and between variables comparisons, and for rates of change to be estimated explicitly.

The factor “sample month” and the continuous time variable “sample date” were included as model predictors, representing the within-year seasonality and change over time (i.e. unit change per year), respectively. Although the linear models provide robust, unbiased estimates of the mean change over the whole time series, the non-linear variation illustrated by the additive modelling could have resulted in systematic variation in the residuals, leading to biases in the determination of statistical significance. We therefore used a bootstrapping procedure, resampling each dataset 1000 times, to determine the probability of the degree of trend occurring by chance assuming a distribution of randomised time series. The bootstrap estimates of the confidence interval around the slope parameter were estimated by sampling n observations from the data, where n is the observed sample number, whilst preserving the order in which they were sampled in the bootstrap iteration—hence reordering the data over time in a manner unbiased under the null hypothesis. Linear trends were deemed “significant” where the observed trend was in the most extreme 5% of all estimated trends obtained from the bootstrapped data. We then used the “sample date” slope coefficients, to examine quantitatively, relationships between variables or sites as follows:

- a) the relationship between the rates of change (between 1988 and 2008) in major acid anions, base cations and AB-ANC at individual sites
- b) differences in the relative rate of change in charge contribution from Gran Alkalinity, [DOC] and $[\text{Al}_{\text{inorg}}]$ (variables that together are used to compute [AB-ANC] in relation to the key driver of change—i.e. rate of change in $[\text{SO}_4^{2-}]$);
- c) the rate of change in organic acidity (determined from $F \times [\text{DOC}]$) as a proportion of change in mineral acidity contributed by $[\text{SO}_4^{2-}]$ across an acidification gradient (based on mean $[\text{Al}_{\text{inorg}}]$);
- d) evidence for differences in the rates of change in key hydrochemical variables in geographically close pairs of forested and moorland sites, (Loch Chon and Loch Tinker in the Scottish Trossachs; Loch Grannoch and Round Loch of Glenhead in Galloway southwest Scotland).

Finally, we applied quantile regression, to determine whether trends in the severity of the more acidic samples at individual sites

(that tend to occur after heavy rain or seasalt deposition events) differed significantly from the average trend. Quantile regression allows the modelling of any quantile of the data space, as opposed to the median or mean only as provided by standard regression. This was performed non-parametrically and in a manner similar to ordinary linear least squares regression to minimise the sum of squared residuals. To estimate the slope parameter β of a standard univariate linear model using quantile regression, the following function is minimised:

$$\arg \min_{\beta} \left\{ \sum_{i=1}^n (y_i - \beta x_i) \right\}$$

where $\rho_{\tau}(z) = z(\tau - I(z < 0))$ with $I(\cdot)$ representing the indicator function and τ the quantile to estimate. For example, $\tau = 0.9$ when estimating the 90th percentile. As this function is a two parameter equation (slope and intercept), it is minimised using numerical based techniques such as the Nelder–Mead optimisation method (Nelder and Mead, 1965).

As the regression coefficients were estimated non-parametrically by minimising the quantile error, no distributional assumptions were made and we were thus unable to obtain estimates of upper and lower limits for the estimated trend in the quantile in question. Confidence intervals were therefore determined using the same bootstrap-based procedure described earlier. Quantile regression was again run 1000 times on resampled data, generating a distribution of slope estimates from which the confidence interval was obtained by reading off the 2.5th and 97.5th percentiles. To determine whether extreme event acidity was changing at a different rate to median acidity levels we tested for significant differences in slopes for 90th and 50th percentiles.

3. Results

3.1. Trend assessment

3.1.1. Non-marine sulphate trends

Linear trends in $[\text{xSO}_4^{2-}]$ were consistently negative and statistically significant across the network (Table 1), with the exception of Narrator Brook in southwest England. In common with previous assessments the reduction in concentration was most pronounced (circa $-7 \mu\text{eq L}^{-1} \text{yr}^{-1}$) at sites in the south and east of the UK (e.g. the Old Lodge stream and the River Etherow) but was still detectable at Loch Coire nan Arr ($-0.46 \mu\text{eq L}^{-1} \text{yr}^{-1}$) in north west Scotland where anthropogenic sulphur deposition has historically been relatively low. The additive modelling plots (Fig. 1 and Supplementary Information) demonstrate that $[\text{xSO}_4^{2-}]$ trends were mostly not linear, but temporal patterns were strongly coherent across the network, as previously described by Davies et al. (2005) and Evans et al. (2010). According to the analysis of first derivatives, significant reductions were largely confined to the latter half of the 1990s. The non-linear temporal trends observed in surface waters were similar to those observed for deposition of xSO_4^{2-} at nearby Acid Deposition Network sites (see Curtis and Simpson, 2014), supporting earlier observations that surface water S concentrations are responsive to reductions in deposition at most sites at no more than an annual time-step (Cooper, 2005).

Uniquely for the AWMN, surface water $[\text{xSO}_4^{2-}]$ at Narrator Brook in south-west England did not show a significant long term decline. In contrast, bulk deposition loads at nearby Yarner Wood, whilst stable until 1995, showed a significant post-1995 decline (Curtis and Simpson, 2014). However, the soils at Narrator Brook, one of only two AWMN sites that were not glaciated during the last glaciation, appear to have a greater capacity for S adsorption than elsewhere in the network; older soils tend to have greater S adsorption capacity (Johnson and Henderson, 1979). This may account for

the low degree of temporal variation and lack of clear response to changes in deposition at the site.

Between 2000 and 2008 most sites showed little further significant decline in $[\text{xSO}_4^{2-}]$ despite some evidence for continuing declines in bulk deposition (Curtis and Simpson, 2014). For the majority, post-March 2003 concentrations remain between 3 and 5 times higher than those for the least deposition-impacted site in the AWMN, Loch Coire nan Arr, in the far north-west of Scotland (Tables 2a and 2b).

3.1.2. Nitrate trends

In contrast to $[\text{xSO}_4^{2-}]$, linear trend analysis of $[\text{NO}_3^-]$ resulted in a roughly even division between sites showing positive and negative trends (Table 1). There was a degree of geographical clustering with respect to trend sign; sites with larger, and statistically significant, negative trends occurring in Wales, the southern Pennines, the English Lake District and the Mourne Mountains of Northern Ireland. Conversely, three Scottish sites, showed significant slight increases.

At all sites, $[\text{NO}_3^-]$ remained considerably lower than $[\text{xSO}_4^{2-}]$ (in terms of equivalence) throughout the monitoring period, and trend slopes for this secondary acidifying anion are generally much smaller. However, it follows that these long-term changes will have either partly negated or slightly enhanced the overall rate of recovery in water acidity. The chief exception here was Scoat Tarn in the English Lake District, where $[\text{NO}_3^-]$ was relatively high initially and declined at 71% of the rate of reduction in $[\text{xSO}_4^{2-}]$. The additive modelling plots (Fig. 1 and Supplementary Information) emphasise the substantial inter-annual variability in $[\text{NO}_3^-]$ across the network, much of which is likely to be due to effects of climate on soil nitrogen processing (see Section 4.3).

3.1.3. Chloride trends

Temporal variation in $[\text{Cl}^-]$ at the Round Loch of Glenhead, (illustrated by the additive modelling plot in Fig. 1) was typical of several sites in western locations on the UK mainland, in addition to Ben-crom River in the Mourne Mountains and Old Lodge in the Ashdown Forest (see Supplementary Information). These sites showed particularly large peaks in $[\text{Cl}^-]$ concentration centred around 1990, and less pronounced peaks around the turn of the century and, most recently, during the winter and spring of 2007 and 2008. This apparent decadal periodicity is consistent with that described over ten years ago by Evans et al. (2001a) when it was linked to the influence of the North Atlantic Oscillation (Section 4.3).

3.1.4. pH/H⁺ trends

The majority of sites showed long-term increases in pH (as well as reductions in hydrogen ion concentration $[\text{H}^+]$ – derived directly from the pH data), although there was no significant pH increase in the low deposition areas of northwest Scotland and Northern Ireland, and the relatively well buffered lakes Burnmoor Tarn and Loch Tinker (Table 1). The derivative analysis suggests that the periods during which pH increased significantly were relatively short-lived at several sites (Fig. 1 and Supplementary Information). Significant increases in pH at some of the more acidic sites (including the Round Loch of Glenhead – Fig. 1) lagged behind periods of significant reduction in $[\text{xSO}_4^{2-}]$.

3.1.5. Inorganic aluminium trends

Inorganic aluminium concentrations fell substantially over the monitoring period at around one third of sites, and 13 sites showed significant downward linear trends overall (Table 1). Reductions were greatest in the more acidic sites that initially had the highest concentrations, and were most marked in Blue Lough, River Etherow, Scoat Tarn and Loch Grannoch. The derivative

Table 1
 Linear trends in solute chemistry in samples taken from AWMN lakes and streams between summer/autumn 1988–March 2008. ALK=Gran Alkalinity; COND=conductivity; sol Al=soluble aluminium; lab Al=labile (inorganic) aluminium; DOC=dissolved organic carbon; ANC=Acid Neutralising Capacity. All trends deemed significant at $p < 0.05$ (using a boot strapping procedure – see Section 2) denoted by an asterisk. All time series for Narrator Brook and the Afon Gwy start in 1991.

	SO_4^{2-} ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	xSO_4^{2-} ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	NO_3^- ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	Cl^- ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	Ca^{2+} ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	Mg^{2+} ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	pH units (yr^{-1})	H^+ ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	ALK ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)	COND ($\mu\text{Scm}^{-1} \text{ yr}^{-1}$)	Sol Al ($\mu\text{g L}^{-1} \text{ yr}^{-1}$)	Al_{inorg} ($\mu\text{g L}^{-1} \text{ yr}^{-1}$)	DOC ($\text{mg L}^{-1} \text{ yr}^{-1}$)	AB-ANC ($\mu\text{eq L}^{-1} \text{ yr}^{-1}$)
Loch Coire nan Arr	-0.76*	-0.46*	-0.05	-0.28	-0.29	-0.34	-0.007	0.01	-0.13	-0.04	0.17	0.00	0.15*	0.61
Allt a' Mharcaidh	-0.47*	-0.41*	-0.01	-0.50	-0.24*	-0.12	0.005	-0.02	0.27	-0.06	-0.05	-0.14*	0.13*	0.96*
Allt nan Coire nan Con	-1.01*	-0.87*	-0.11	-1.25	-0.50*	-0.33	0.000	0.01	-0.12	-0.10	0.32	-0.50*	0.22*	0.93*
Lochnagar	-1.19*	-1.09*	0.27*	-0.96*	-0.42*	-0.26*	0.010*	-0.10*	0.03	-0.18*	-0.74	-0.53	0.11*	0.59*
Loch Chon	-1.59*	-1.23*	0.32*	-3.36*	-0.20	-0.11	0.034*	-0.19*	1.09*	-0.31*	-1.13*	-1.23*	0.20*	2.29*
Loch Tinker	-1.49*	-1.21*	0.05	-2.65	-0.68	-0.53	0.009	-0.02	0.13	-0.33*	-0.13	-0.02	0.20*	1.11*
Round Loch Glenhead	-1.86*	-1.60*	0.24*	-2.57*	-0.40*	-0.53*	0.019*	-0.41*	0.55*	-0.51*	-1.72*	-2.65*	0.15*	1.50*
Loch Grannoch	-3.10*	-2.79*	-0.20	-2.77*	-1.11*	-0.71*	0.008*	-0.36	0.38	-0.61*	-10.60*	-11.78*	0.23*	2.73*
Dargall Lane Burn	-1.34*	-1.11*	0.17	-2.15*	-0.33*	-0.34*	0.029*	-0.14*	0.67*	-0.26*	-1.73*	-1.75*	0.09*	1.30*
Scoat Tarn	-1.00*	-0.69*	-0.49*	-2.98*	-0.74*	-0.74*	0.012*	-0.21*	0.09	-0.47*	-6.42*	-6.28*	0.09*	1.20*
Burmoor tarn	-1.59*	-1.20*	0.05	-3.70*	-1.13*	-0.71*	0.012	-0.07	1.14*	-0.50*	0.01	0.12	0.12*	1.57*
River Etherow	-7.47*	-7.08*	-0.54*	-2.82	-2.82*	-2.84*	0.020	-0.88*	2.74*	-0.86*	-2.83*	-3.50*	0.41*	4.85*
Old Lodge	-8.11*	-7.37*	0.16	-2.18	-1.60*	-1.89*	0.043*	-1.49*	2.41*	-1.09*	-8.50*	-10.52*	0.42*	5.30*
Llyn Llagi	-1.66*	-1.36*	-0.36*	-2.80*	-0.90*	-0.59*	0.036*	-0.35*	0.56*	-0.71*	-0.56	-1.18	0.09*	1.00*
Narrator Brook	0.10	0.27	0.05	-1.66*	-0.09	0.07	0.029*	-0.11*	0.94*	-0.49*	1.63*	1.30*	0.02	0.22
Llyn Cwm Mynach	-1.41*	-1.20*	0.20	-1.74	-0.95*	-0.35	0.008	-0.07	0.02	-0.56*	-0.70	-1.65	0.02	0.34
Afon Hafren	-1.23*	-1.08*	-0.19	-1.37*	-0.39*	-0.09	0.019*	-0.24	0.24	0.32	-1.63	-1.71	0.06*	0.67*
Afon Gwy	-0.88*	-0.90*	-0.24	0.23	-0.09	0.21	0.027*	-0.20*	0.36	0.05	-2.44*	-1.55*	0.04*	0.55
Beagh's Burn	-2.42*	-1.84*	-0.05	-2.14*	-0.58	-0.97*	-0.002	-0.03	0.34	-0.35*	-0.97*	-0.18	0.42*	2.35*
Bencrom River	-1.81*	-1.65*	0.45	-1.52*	0.24	-0.64*	0.034*	-0.31	1.22*	-0.20*	-4.78*	-3.49*	0.11*	2.16*
Blue Lough	-2.96*	-2.79*	-0.59*	-1.65	-1.12*	-1.10*	0.018*	-0.69*	0.93*	-0.76*	-10.19*	-11.16*	0.21*	3.04*
Coneyglen Burn	-1.27*	-1.28*	-0.01	0.43	-0.14	-0.12	-0.001	-0.04	0.02	0.09	-0.87*	-0.13	0.26*	1.32

Table 2a

Mean water chemistry data for quarterly AWMN lake samples collected prior to April 1993 (normal font) and post March 2003 (bold). Monitoring commenced at most sites in 1998 but in June 1991 at Blue Lough, and 2007 at Loch Coire Fionnaraich. Monitoring was terminated in March 2007 at Loch Coire nan Arr.

	SO ₄ ²⁻ (μeq L ⁻¹)	xSO ₄ ²⁻ (μeq L ⁻¹)	NO ₃ ⁻ (μeq L ⁻¹)	Cl ⁻ (μeq L ⁻¹)	Ca ²⁺ (μeq L ⁻¹)	Mg ²⁺ (μeq L ⁻¹)	pH	ALK (μeq L ⁻¹)	COND (μS cm ⁻¹)	Al _{inorg} (μg L ⁻¹)	DOC (mg L ⁻¹)	AB-ANC (μeq L ⁻¹)
Loch Coire nan Arr	41.14 34.61	14.73 8.70	2.80 2.41	274.34 276.86	42.44 37.43	62.85 57.17	6.28 6.14	35.50 29.86	40.75 41.64	2.85 2.64	1.50 3.69	42.66 45.39
Loch Coire Fionnaraich	27.56	5.84	1.66	213.62	28.85	45.33	5.72	14.09	33.5	2.95	4.42	35.31
Lochnagar	60.63 43.21	51.50 35.25	10.77 16.13	87.01 75.88	29.00 23.83	30.18 27.72	5.37 5.52	0.89 1.75	20.53 18.90	17.95 16.05	0.87 2.52	2.84 11.27
Loch Chon	72.14 50.57	48.68 32.35	9.88 15.80	223.75 173.73	75.59 75.77	46.89 46.93	5.39 5.94	5.00 22.85	38.42 34.50	26.32 7.55	2.71 5.70	14.84 50.23
Loch Tinker	52.95 34.43	35.88 21.80	2.03 2.29	162.88 120.37	85.83 75.87	45.85 38.17	5.97 6.18	35.26 40.25	31.00 26.35	3.26 2.50	4.15 6.88	55.51 74.06
R. L. of Glenhead	68.41 42.60	44.94 24.21	4.81 9.28	223.90 175.40	34.85 29.18	47.93 39.26	4.89 5.14	-12.11 -4.21	39.37 31.68	68.63 29.05	2.80 4.80	-7.13 13.82
Loch Grannoch	98.12 56.64	68.32 32.13	13.89 11.35	284.18 233.76	51.37 36.01	55.81 45.65	4.62 4.73	-24.58 -18.45	53.21 44.35	246.11 80.10	3.83 7.02	-34.68 4.25
Scoat Tarn	60.72 48.63	39.05 31.96	21.21 13.53	206.64 158.98	35.68 25.24	50.84 39.97	4.99 5.16	-6.75 -5.15	37.62 29.95	132.46 37.20	0.53 1.95	-19.95 -1.39
Burnmoor Tarn	81.45 62.31	56.92 43.85	5.63 5.66	233.86 176.10	95.78 82.38	67.62 58.61	6.32 6.65	46.79 68.00	44.53 37.60	2.25 3.90	1.52 3.42	54.11 82.60
Llyn Llagi	62.16 39.47	38.81 21.93	10.42 5.59	222.71 167.27	56.94 42.99	49.88 39.73	5.14 5.68	1.04 8.64	36.28 26.35	42.64 25.45	2.13 3.44	5.86 18.58
Llyn Cwm Mynach	88.14 68.91	52.17 37.31	9.59 12.11	343.12 301.42	78.97 63.77	67.97 60.83	5.21 5.26	4.58 3.89	51.94 43.96	65.29 53.00	2.51 2.57	9.18 9.54
Blue Lough	97.55 59.69	68.59 33.57	23.49 19.44	276.22 249.05	42.64 27.59	59.23 44.57	4.66 4.89	-24.67 -11.95	55.17 45.80	326.17 177.05	3.13 5.85	-46.84 -6.22

Table 2b

Mean water chemistry data for monthly AWMN stream samples collected prior to April 1993 (normal font) and post March 2003 (bold). Monitoring commenced at most sites in 1998 but in August 1990 at Coneyglen Burn, April 1991 at Afon Gwy and June 1991 at Narrator Brook. Measurements for pH, alkalinity and nitrate commenced at Old Lodge in April 1991.

	SO ₄ ²⁻ (μeq L ⁻¹)	xSO ₄ ²⁻ (μeq L ⁻¹)	NO ₃ ⁻ (μeq L ⁻¹)	Cl ⁻ (μeq L ⁻¹)	Ca ²⁺ (μeq L ⁻¹)	Mg ²⁺ (μeq L ⁻¹)	pH	ALK (μeq L ⁻¹)	COND (μS cm ⁻¹)	Al _{inorg} (μg L ⁻¹)	DOC (mg L ⁻¹)	AB-ANC (μeq L ⁻¹)
Allt a'Mharcaidh	44.40 38.23	33.02 27.81	1.50 1.39	108.58 99.37	42.33 39.87	30.00 27.59	6.19 6.31	42.26 47.91	23.53 23.29	6.32 5.12	2.01 3.82	51.57 67.36
Allt na Coire nan Con	61.94 47.46	30.03 18.59	4.91 1.84	321.94 289.35	58.86 50.20	69.98 61.88	5.58 5.58	19.40 18.86	48.72 45.56	21.70 12.42	3.20 6.37	32.53 47.40
Dargall Lane Burn	82.00 64.01	60.17 46.06	10.70 13.48	208.21 171.17	51.48 47.41	55.89 50.61	5.30 5.56	1.23 12.53	37.81 33.73	39.88 13.57	1.41 2.67	3.39 23.67
River Etherow	296.15 191.15	262.42 163.06	44.44 38.58	319.92 267.88	179.58 142.73	172.61 135.92	4.58 4.97	-8.85 39.25	84.92 71.16	80.46 24.53	4.61 9.24	7.45 77.65
Old Lodge	289.20 173.77	224.71 127.39	7.39 7.96	615.08 579.23	167.22 142.68	156.16 128.26	4.54 5.00	-34.96 -2.92	112.70 97.41	223.14 67.12	3.47 8.13	-41.74 24.20
Narrator Brook	71.48 74.58	40.93 47.80	6.10 7.03	291.46 255.44	34.54 31.93	65.28 64.52	5.63 5.99	11.57 27.49	48.37 40.68	20.27 38.32	1.38 1.65	15.90 17.93
Afon Hafren	82.69 66.96	59.40 46.57	20.45 16.27	222.10 194.42	47.98 41.59	66.45 64.24	4.99 5.26	1.12 7.00	41.54 51.73	103.45 71.83	1.79 2.55	-2.57 8.35
Afon Gwy	67.18 56.22	49.27 39.42	11.02 7.28	170.79 160.29	41.81 38.74	53.02 55.18	5.12 5.47	5.79 13.30	30.31 29.04	61.19 39.54	1.93 2.51	7.99 17.19
Beagh's Burn	73.67 42.74	38.08 16.48	3.11 2.76	351.03 323.50	103.04 98.13	112.45 101.37	5.22 5.23	43.09 51.13	60.33 56.91	12.00 8.68	9.41 15.43	86.98 125.52
Bencrom River	97.55 59.69	68.59 33.57	23.49 19.44	276.22 249.05	42.64 27.59	59.23 44.57	4.66 4.89	-24.67 -11.95	55.17 45.80	326.17 177.05	3.13 5.85	-46.84 -6.22
Coneyglen Burn	55.07 42.04	27.15 14.70	1.42 2.65	274.61 271.04	147.80 150.09	120.38 120.33	5.69 5.83	157.86 168.73	56.03 57.41	5.30 5.33	6.54 10.12	189.57 214.75

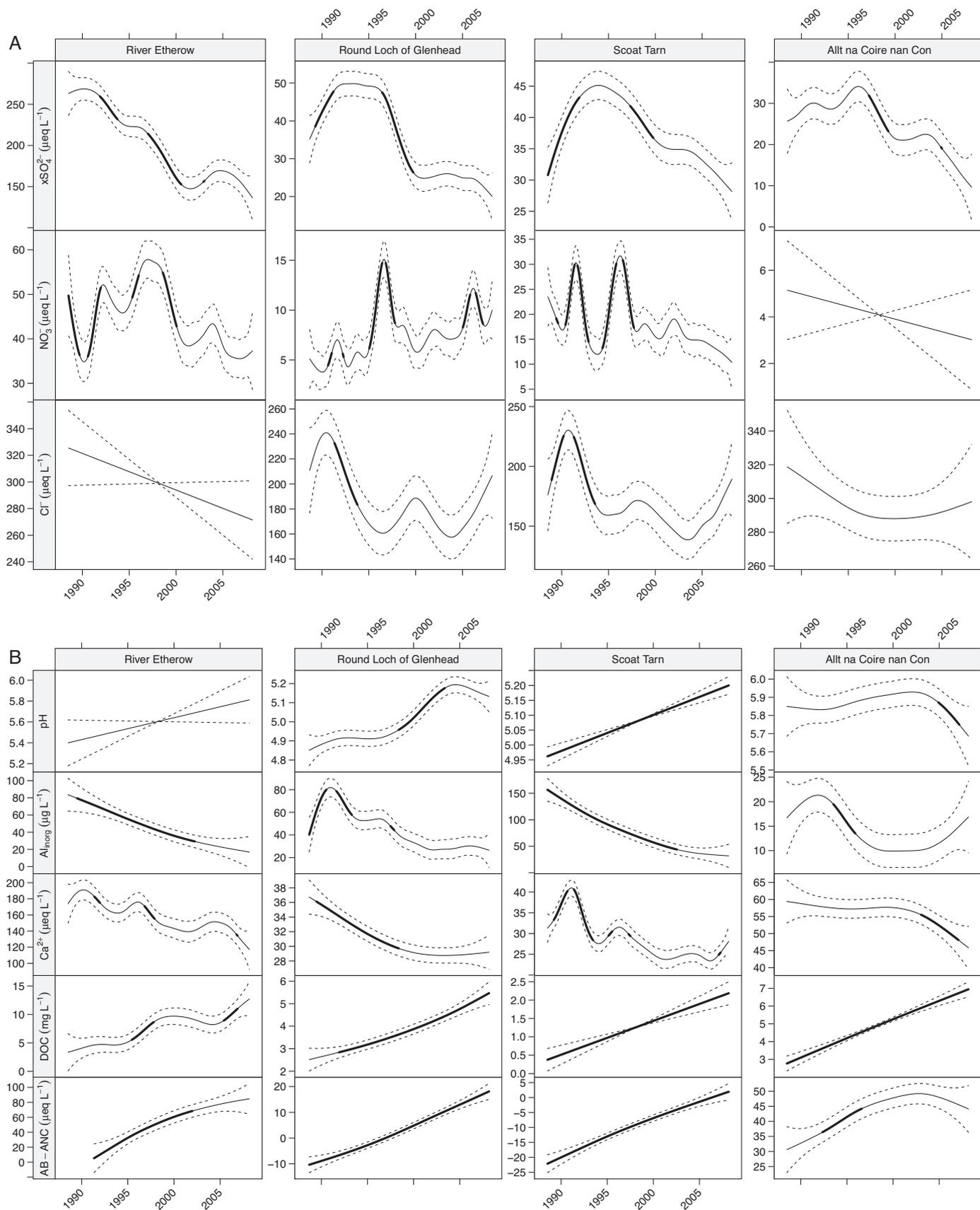


Fig. 1. Additive modelling-based fitted trends in hydrochemical concentrations in four AWMN sites, representing a sulphur deposition gradient, from the River Etherow in the southern Pennines (high deposition) to Allt na Coire nan Con in the western Scottish Highlands (low deposition), including trends in strong acid anions (A), and trends in hydrochemical variables considered to be responding to changes in acid deposition (B). Periods of significant change in the fitted trend, determined by derivative analysis, are highlighted by thickened lines. Dashed lines indicate 95% confidence limits. Comparable plots for all sites presented by region in Supplementary Information.

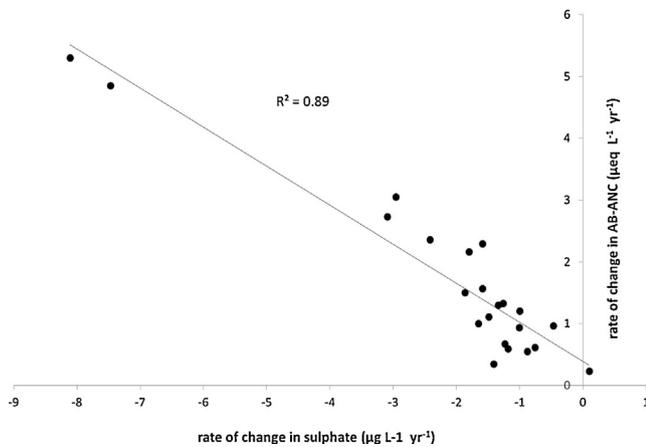


Fig. 2. Relationship between rates of change in sulphate concentration and alkalinity-based acid neutralising capacity. Data provided in Table 1.

analysis indicates that $[Al_{inorg}]$ in the River Etherow (Fig. 1) and Loch Grannoch (Supplementary Information) fell significantly throughout most of the monitoring period, contrasting with undetectable, or a relatively brief period of, significant change in pH at these sites respectively.

3.1.6. Divalent cation trends

Calcium and Mg^{2+} concentrations fell at the majority of sites. Reductions in the export of divalent cations from catchment soils are an anticipated response to falling acidic inputs, but the similarities in the derivative plots with $[Cl^-]$ trends at several of the sites with more westerly locations (Supplementary Information) emphasise the dominant influence of changes in seasalt deposition on the concentrations of these ions in surface waters in these regions.

3.1.7. Dissolved organic carbon trends

DOC concentrations increased monotonically, and largely linearly, at all sites other than Narrator Brook – the only site not to have undergone a significant long term reduction in $[xSO_4^{2-}]$ (Table 1). Derivative analysis indicates that changes with time for the majority of sites were significant throughout most of the monitoring period (Fig. 1 and Supplementary Information). These long term upward trends in [DOC] have been linked to both the reduction in anthropogenic sulphur deposition and climatically-driven reductions in seasalt deposition over the monitoring period (Evans et al., 2006; Monteith et al., 2007) (Section 4.2).

3.1.8. Acid Neutralising Capacity

In common with [DOC], [AB-ANC] increased either linearly or curvilinearly indicating a response to a similar sequence of changes in climatic and anthropogenic drivers. The shape of recovery in [AB-ANC] at Lochnagar, one of the few sites with very little seasalt influence, differs from that for the majority of sites. Here, $[xSO_4^{2-}]$ declined almost linearly, but in the first few years the reduction was balanced by an increase in $[NO_3^-]$. The net effect of these changes in drivers is that [AB-ANC] has only recently begun to increase significantly.

The overall rate of change in [AB-ANC] (as indicated by the slope of the linear models) was closely (and negatively) correlated with both the overall rate of change in $[SO_4^{2-}]$ ($R^2 = 0.89$) (Fig. 2) and $[xSO_4^{2-}]$ ($R^2 = 0.87$) across the network. This demonstrates the dominant influence of declining S deposition on the recovery of these acidified waters. However, despite the apparent close similarities in rates of change between driver and response at most sites, change in [AB-ANC] needs to be evaluated in the context of wider

hydrochemical change; i.e. the larger net decline in acid anion concentrations, i.e. $[SO_4^{2-}]$, $[NO_3^-]$ and $[Cl^-]$, and the partly balancing reductions in base cations, i.e. $[Ca^{2+}]$, $[Mg^{2+}]$, $[Na^+]$ and $[K^+]$, as illustrated in Fig. 3.

3.2. The importance of forestry for recovery

Only one forested site, Loch Grannoch, showed a statistically significant greater reduction in $[xSO_4^{2-}]$ than its moorland counterpart (Round Loch of Glenhead), although the rate was consistently larger for the forested site in each of the three pairs. Positive [AB-ANC] slopes were also consistently greater for the forested sites, but again only the Galloway pair showed a significant difference. Negative $[Al_{inorg}]$ slopes were significantly greater in the forested sites within both the Galloway and Trossachs pairs (Fig. 4).

In contrast, pH increased, and $[H^+]$, declined faster in moorland Round Loch of Glenhead than Loch Grannoch, most likely reflecting increased sensitivity of pH to declining acid deposition at higher levels of ANC (see Section 4.1). Whilst these site pairs are generally insufficiently similar to make direct comparisons of acidity status at any point in time, in all three cases, $[Al_{inorg}]$ remains higher and pH and [ANC] lower in the waters of the forested catchments on the basis of mean 2003–2008 data (Tables 2a and 2b).

3.3. Trends in the severity of acid episodes

The quantile regression analysis demonstrates that most sites undergoing long-term reductions in $[Al_{inorg}]$ and $[H^+]$ and increases in [AB-ANC] also showed statistically significant reductions in the severity of their most acidic samples, as represented by trends in 90th and 10th percentiles respectively (Table 3). Only two sites showed a significant difference ($p < 0.05$) in the rate of change in these percentiles and median (50th percentile) values with respect to $[H^+]$ and [AB-ANC]. However, the rate of decline in peak (90th percentile) $[Al_{inorg}]$ was significantly greater than declines in the 50th percentile at all of the more acidic sites, and at approximately half of AWMN sites overall, including both streams and lakes.

4. Discussion

Our analyses provide clear evidence for long-term reductions in the acidity of acidified surface waters across the UK as a direct response to the last two decades of declining atmospheric acid deposition. As such they are broadly consistent with previous international assessments of recent trends in acidified waters (e.g. Stoddard et al., 1999; Evans et al., 2001b; Skjelkvåle et al., 2005), but provide further insights into the process of chemical recovery.

4.1. Evidence for the hydrochemical impact of declining acid deposition

The additive models emphasise the temporal complexity of the hydrochemical trends. Trends in acidity have been influenced both by natural drivers, as indicated by variations in seasalt-derived $[Cl^-]$ particularly during the early years of monitoring, and substantial reductions in anthropogenic S deposition in the latter half of the 1990s. The linear models show that reductions in $[xSO_4^{2-}]$ were reciprocated by roughly proportional increases in [AB-ANC]. The largest responses in AB-ANC were seen in the sites in central and southern England where $[xSO_4^{2-}]$ reductions were most pronounced (Table 1; Fig. 2). However, the specific hydrochemical character of the changes in [AB-ANC] varied across sites, reflecting spatial variation in [DOC] and the extent to which sites had acidified.

The most acidified sites on the Network experienced large reductions in $[Al_{inorg}]$, particularly during the early years of

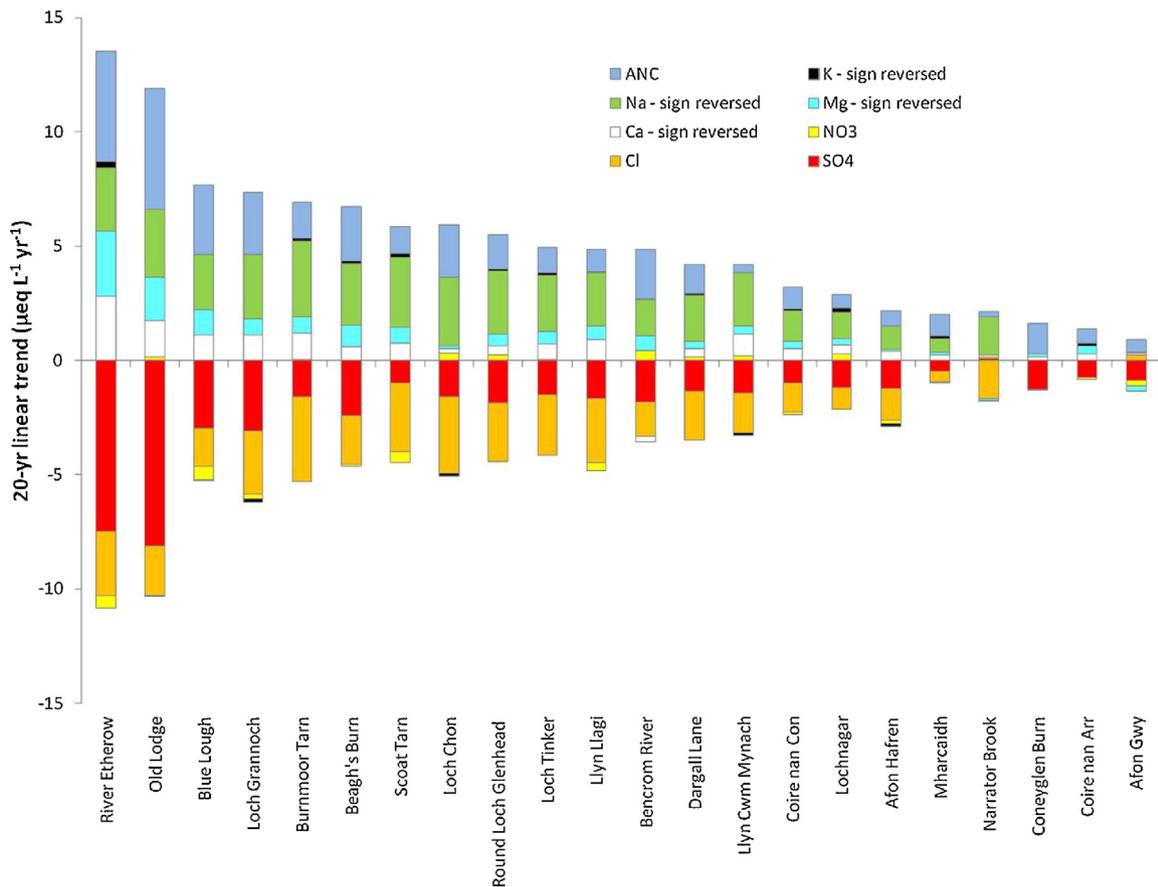


Fig. 3. Comparison of site specific trends in acid anions, base cations and acid neutralising capacity. Trends in base cations are predominantly negative but the sign is reversed to illustrate how reductions in acid anions are balanced by reductions in base cations and increases in AB-ANC. In contrast to the very tight balance between concentrations of these determinands in individual samples, the extent to which the trends balance depends on the degree to which the linear model captures trends that are comparable across determinands. For purposes of clarity, slight and non-significant trends in chloride and sodium in Loch Coire nan Arr and Coneyglen Burn have been reset to zero.

monitoring, during which changes in pH were sometimes difficult to detect. This tendency is consistent with the conceptual model of Reuss and Johnson (1986), whereby cation response to reductions in strong acid anions is initially dominated by trivalent ions,

and particularly Al^{3+} , whilst the soil remains sufficiently acidic. As $[Al]_{inorg}$ has declined at these sites, divalent cations have also decreased, as have hydrogen ion concentrations, such that pH has become increasingly responsive to further acid anion reductions.

Table 3
Comparisons of trend slopes in extreme (90th or 10th percentile) and median (50th percentile) acidity determined by quantile regression. Bold font denotes where slopes in quantiles are statistically significantly at ($p < 0.05$). Grey hatching denotes where trends in the two quantiles are significantly different from each other.

	H ⁺			Labile aluminium			AB-Acid Neutralising Capacity		
	90th percentile	50% percentile	<i>p</i>	90th percentile	50% percentile	<i>p</i>	10th percentile	50% percentile	<i>p</i>
Loch Coire nan Arr	0.0001	0.0001	0.69	-0.0002	0.0000	0.31	0.0034	0.0001	0.56
Allt a' Mharcaidh	-0.0001	0.0000	0.09	-0.0014	0.0000	0.02	0.0047	0.0027	0.56
Allt nan Coire nan Con	0.0001	0.0000	0.58	-0.0017	-0.0010	0.40	0.0011	0.0028	0.16
Lochnagar	-0.0009	-0.0002	0.17	-0.0061	-0.0002	0.11	0.0026	0.0010	0.75
Loch Chon	-0.0008	-0.0004	0.05	-0.0066	-0.0018	0.01	0.0033	0.0064	0.15
Loch Tinker	0.0000	0.0000	0.35	-0.0004	0.0000	0.61	0.0036	0.0034	0.57
Round Loch Glenhead	-0.0010	-0.0010	0.59	-0.0089	-0.0073	0.05	0.0036	0.0037	0.55
Loch Grannoch	-0.0009	-0.0008	0.6	-0.0643	-0.0232	0.01	0.0115	0.0068	0.85
Dargall Lane Burn	-0.0006	-0.0006	0.35	-0.0085	-0.0023	0.01	0.0026	0.0035	0.23
Scoat Tarn	-0.0004	-0.0007	0.92	-0.0254	-0.0130	0.01	0.0035	0.0026	0.90
Burnmoor tarn	-0.0001	0.0000	0.16	0.0000	0.0000	0.68	0.0071	0.0041	0.62
River Etherow	-0.0081	-0.0004	0.02	-0.0219	-0.0023	0.03	0.0208	0.0115	0.96
Old Lodge	-0.0053	-0.0036	0.13	-0.0396	-0.0259	0.00	0.0106	0.0129	0.00
Narrator Brook	-0.0006	-0.0002	0.00	0.0060	0.0030	0.81	-0.0001	0.0011	0.03
Llyn Llaji	-0.0016	-0.0008	0.06	-0.0043	-0.0037	0.31	0.0027	0.0030	0.44
Llyn Cwm Mynach	-0.0008	0.0001	0.23	-0.0070	0.0000	0.31	0.0012	0.0011	0.38
Afon Hafren	-0.0012	-0.0007	0.41	-0.0130	0.0007	0.02	0.0003	0.0016	0.62
Afon Gwy	-0.0017	-0.0003	0.10	-0.0076	-0.0024	0.2	0.0036	0.0001	0.97
Beagh's Burn	-0.0002	0.0001	0.24	-0.0014	0.0002	0.03	0.0037	0.0070	0.04
Bencrom River	-0.0020	-0.0012	0.17	-0.0166	-0.0101	0.17	0.0047	0.0060	0.39
Blue Lough	-0.0025	-0.0020	0.52	-0.0391	-0.0305	0.01	0.0114	0.0072	0.94
Coneyglen Burn	-0.0001	0.0000	0.46	-0.0004	0.0000	0.41	0.0077	0.0032	0.38

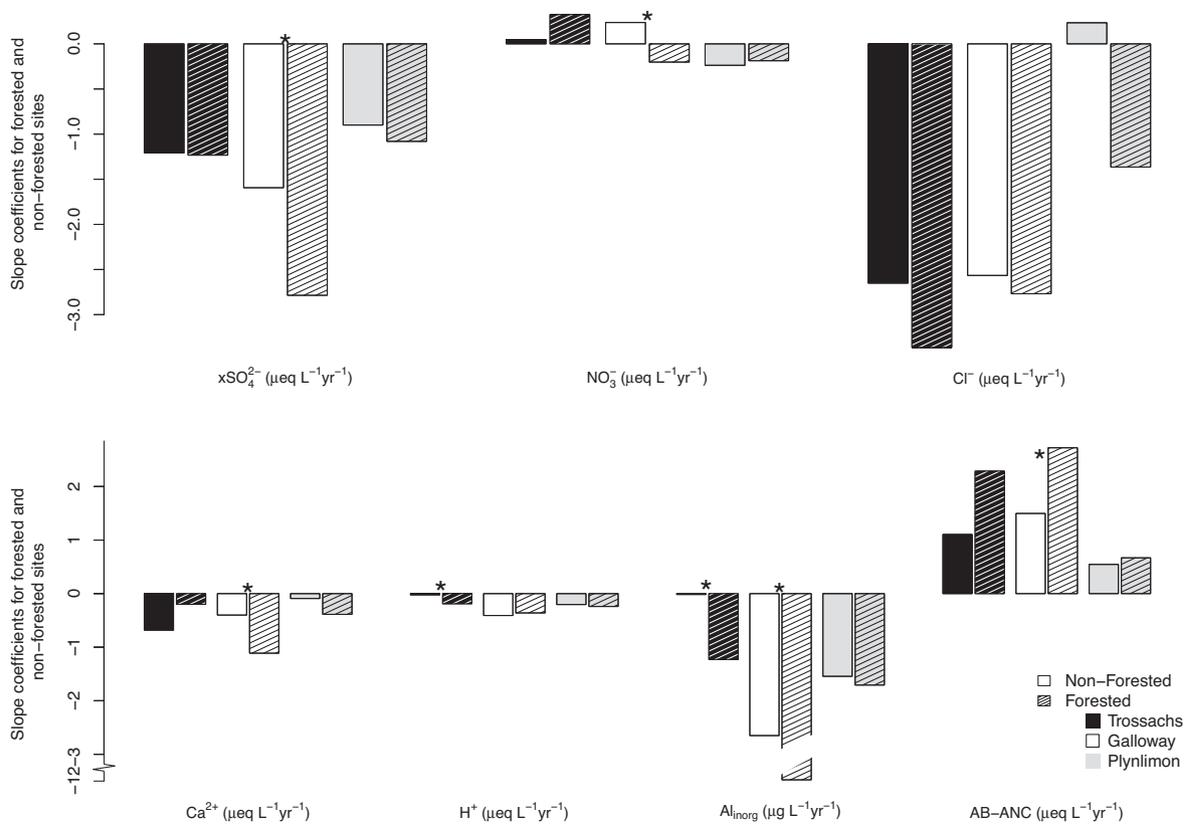


Fig. 4. Trend slopes (see Table 1) in key acidity-related variables for 3 pairs of AWMN forested/non-forested catchments. All units are $\mu\text{eq L}^{-1} \text{yr}^{-1}$ except Lab Al ($\mu\text{g L}^{-1} \text{yr}^{-1}$). Bars for forested sites are hatched. Plynlimon = Afon Gwy (moorland) vs Afon Hafren (forested); Galloway = Round Loch of Glenhead (moorland) vs Loch Grannoch (forested); Scottish Trossachs = Loch Tinker (moorland) vs Loch Chon. Asterisks denote a statistical difference in the strength of slope between sites ($p < 0.05$) determined from bootstrap based estimates sampled under the null hypothesis of no difference.

The effect is illustrated by the sigmoidal relationship between pH and [AB-ANC] in AWMN samples, that typifies the relationship between these two variables in low alkalinity surface waters (Fig. 5a and b). Fig. 5a demonstrates the increasing sensitivity of pH of individual samples from the more acidic sites as [AB-ANC] has become less negative. Fig. 5b shows the strong dependence of the pH response on [DOC], with more rapid improvements in pH occurring at sites with lower [DOC]. Whilst these hydrochemical attributes of acid sensitive waters are well known, they have rarely been demonstrated with long-term field monitoring data. As pH, together with $[\text{Al}_{\text{inorg}}]$, is considered a key variable determining the viability of acid sensitive species and communities (e.g. Petchey et al., 2004), these more acidic AWMN sites could be argued to be entering a particularly critical stage in their chemical and biological recovery.

The evidence for rapid hydrochemical responses of most catchments to reduced atmospheric inputs of S is encouraging, but by the end of the study period, $[\text{xSO}_4^{2-}]$ concentrations at most sites remained several times higher than those found at the least impacted sites such as Loch Coire nan Arr, the neighbouring Loch Coire Fionnarraich, and Coneyglen Burn (Tables 2a and 2b). Furthermore, $[\text{Al}_{\text{inorg}}]$, a key indicator of acidification status, at the more impacted AWMN sites has remained considerably higher than recorded across a wide range of acid-sensitive waters in the low sulphur deposition region of the far north of Scotland at any time over the last two decades.

Clearly, therefore, the potential remains across the more impacted regions of the UK for $[\text{xSO}_4^{2-}]$ in surface waters to fall still further. The very strong relationships we observed with [AB-ANC] imply that further decline in $[\text{xSO}_4^{2-}]$ will stimulate further reductions in $[\text{Al}_{\text{inorg}}]$ in the more acidic sites and further increases in pH more widely.

4.2. The role of dissolved organic carbon in the recovery process

An unresolved issue at the time of the last major assessment of AWMN hydrochemical data was the interpretation of a network-wide increase in [DOC] (Evans et al., 2005). Similar increases, since observed in remote surface waters in other industrialised regions of the northern hemisphere, have been ascribed variously to impacts of declining acid deposition (e.g. De Wit et al., 2007), increased N deposition (Findlay, 2005), climate change (e.g. Freeman et al., 2001; Worrall and Burt, 2004), changes in solar radiation (Hudson et al., 2003) and land-use (Yallop and Clutterbuck, 2009). Recently, analysis of AWMN data, both in isolation (e.g. Evans et al., 2006, 2008a) and in conjunction with other international time series (Monteith et al., 2007); laboratory experimental studies of soil cores removed from AWMN catchments (Clark et al., 2011); UK field experiments (Evans et al., 2012); and a range of studies of time series and experiments from Norway (De Wit et al., 2007; Haaland et al., 2010), Sweden, (Ekström et al., 2011; Erlandsson et al., 2008), Germany (Borken et al., 2011) and the USA (Driscoll et al., 2007; SanClements et al., 2012), provide clear evidence that soil organic carbon has become more soluble as a consequence of reductions in acid deposition – most likely resulting from reductions in either soil acidity, and/or, as argued for surface waters in the Czech Republic (Hruška et al., 2009), soil water ionic strength.

Fig. 6 illustrates how the three variables used to calculate AB-ANC, i.e. [Gran Alkalinity], [DOC] and $[\text{Al}_{\text{inorg}}]$, have changed relative to each other and across the network over the monitoring period. Here, change in [DOC] is expressed as change in organic acidity, on the basis of the hypothetical charge density values (Section 2.1), and the plot therefore illustrates the role of organic carbon in buffering the hydrochemical impact of falling acid deposition

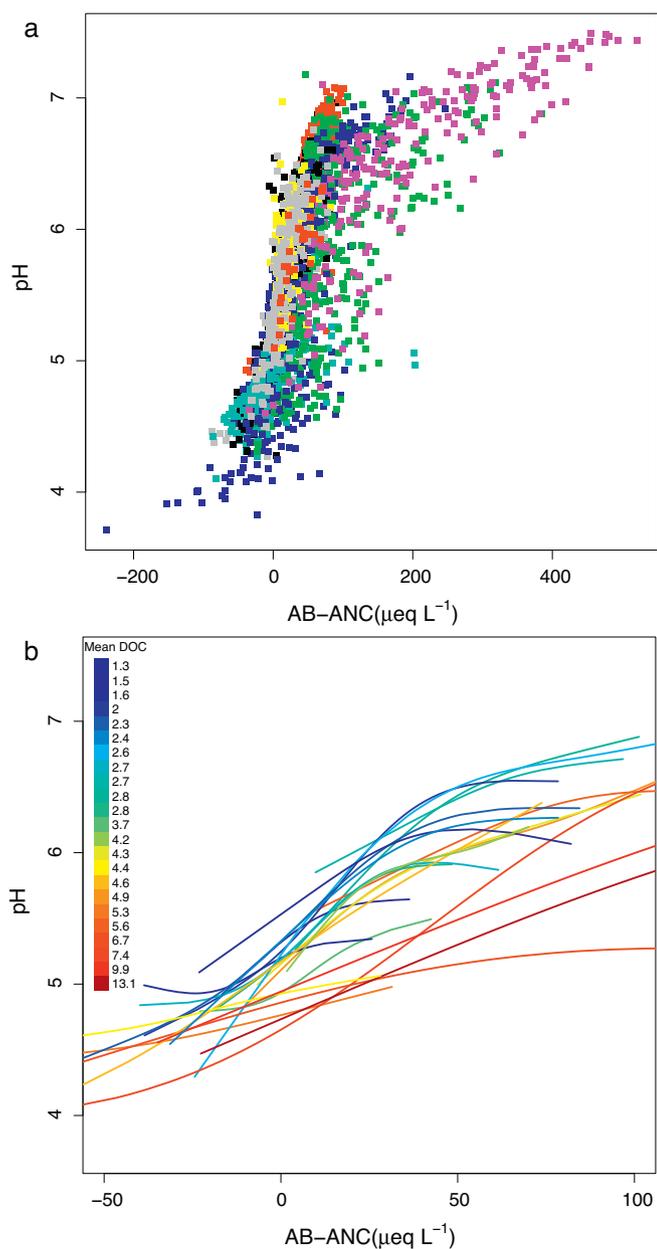


Fig. 5. (a) The relationship between pH and ANC for individual samples in the AWMN database (each site separately colour coded) and, (b) site specific pH-ANC relationships modelled by General Additive Modelling (colour coding indicates the mean DOC of the site).

across the network. The ordering of sites by the rate of change in $[xSO_4^{2-}]$ in this figure highlights both how the rise in [DOC] has tended to contribute to the increase in AB-ANC most at sites where $[xSO_4^{2-}]$ has fallen most sharply, and, conversely, how the change in [DOC] as a proportion of the total change in [AB-ANC] has been most dominant at the sites where $[xSO_4^{2-}]$ has fallen least.

The latter is attributable to the fact that the sites showing the least change in $[xSO_4^{2-}]$ have experienced the lowest levels of S deposition historically, are the least acidified and, therefore, are unlikely to elicit clear responses in either $[Al_{inorg}]$ or $[H^+]$. This is further supported by Fig. 7 that shows that the change in the charge contribution from organic acids, relative to the change in mineral acids (as represented by the change in $[SO_4^{2-}]$), is largest at the least acidified sites (i.e. those with the lowest mean $[Al_{inorg}]$). Indeed at the least impacted sites in northern Scotland (Loch Coire nan Arr and Allt na Coire nan Con) and Northern Ireland (Coneyglen Burn),

where there is no significant trend in $[NO_3^-]$ and where reductions in $[xCl^-]$ are likely to have been negligible, changes in [DOC] (when expressed in terms of charge), appear to almost completely balance changes in $[SO_4^{2-}]$.

The implication of the accumulating evidence that the process of chemical recovery in these acidified systems represents a partial replacement of strong mineral acids (provided predominantly by anthropogenic sulphur) by naturally derived weak organic acids, has reduced expectations with respect to the extent of recovery in pH (Evans et al., 2008a). However, the importance of this buffering process in determining the hydrochemical nature of recovery and hence future ecological prospects clearly varies between AWMN sites.

Observations of an approximate balancing of charges between reductions in $[SO_4^{2-}]$ and increasing organic acidity at the least impacted sites suggests both that organic matter provides a first line of defence with respect to buffering effects of anthropogenic acids, and that no other external driver need be invoked to explain long-term changes in [DOC] in these systems. Soil organic matter can therefore be argued to provide an important “ecosystem service” by protecting waters from acidification, and increasing [DOC] concentrations over the last two decades may be viewed as an integral part of the hydrochemical recovery process. This is particularly pertinent given the current investment by the UK water industry in catchment-based strategies to control DOC levels and for whom DOC is sometimes considered more of a pollutant than an element of ecosystem health.

Exceptionally large DOC concentrations recorded in the Autumn of 2006 and 2007 at several sites are not obviously linked to deposition drivers directly, but more likely reflect the impact of unusual climatic conditions on an increasingly soluble supply of soil organic carbon. The combined effects of a particularly warm and dry summer in 2006 (stimulating decomposition rates), followed by heavy rains in the days leading up to sampling in September 2006 may have contributed to concentrated pulses of DOC into these waters at the time, although work to better understand these apparent anomalies continues and further research is required.

4.3. The hydrochemical influence of climatic variability

Over the first few years of monitoring, rates of sulphur deposition were relatively stable but the majority of sites were found to exhibit strong, temporally coherent, variation in $[NO_3^-]$, $[Cl^-]$, and acidity (Monteith et al., 2000; Evans et al., 2001a, 2010). Significantly, for a network with a largely maritime distribution of sites (Shilland et al., this issue), several links were established between hydrochemical variables and the state of the North Atlantic Oscillation (NAO) in winter. The winter NAO has been shown to exert a strong influence on UK winter temperature, rainfall and storminess, and has exhibited a roughly decadal periodicity over the past century or more, in common with wider Pacific-North American teleconnections (Hurrell and Van Loon, 1997).

Colder, drier winters (characterised by a negative winter NAO Index) have been linked to higher than normal concentrations of nitrate (NO_3^-) in runoff from AWMN and other surface waters (Monteith et al., 2000; George et al., 2004). Here, the influence of soil temperatures on nitrogen cycling is thought to be the dominant process, although lower than average rainfall, and the influence of wind direction on pollutant trajectories, may also be important. Warmer, stormier winters (characterised by a particularly positive winter NAO Index), on the other hand, tend to increase the occurrence and intensity of seasalt deposition events, leading to the generation of acid episodes in acidified catchments (Evans et al., 2001a), and high rainfall, that also increases the acidity of runoff

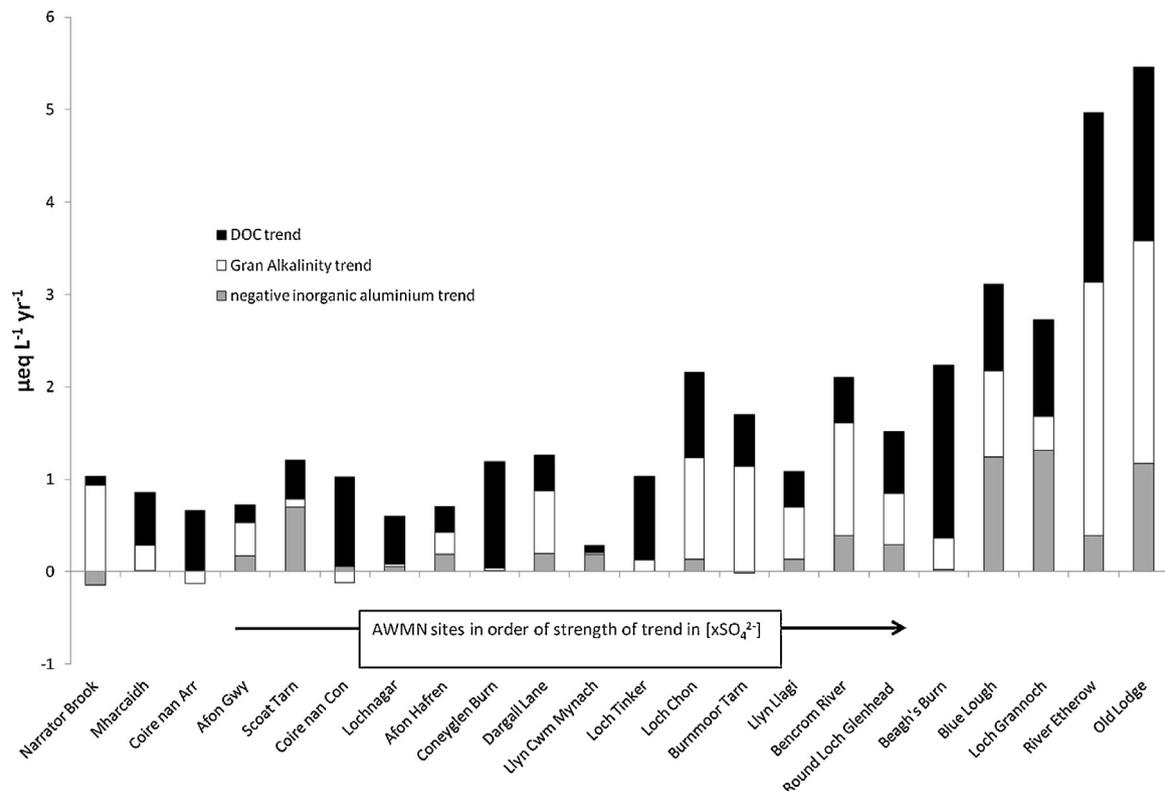


Fig. 6. Comparison of change in the estimated charge contribution from increasing dissolved organic carbon (DOC) and Gran Alkalinity and decreasing labile aluminium, variables that together are used to determine AB-ANC. Change in charge contribution from DOC and labile aluminium is determined by the equations: $F \times [\text{DOC}]$ trend ($\text{mg L}^{-1} \text{yr}^{-1}$); and, $-3 \times [\text{Lab Al}]$ trend ($\mu\text{mol L}^{-1} \text{yr}^{-1}$), respectively (see Section 2).

by reducing the influence of relatively well buffered ground water (Evans et al. (2008b)).

The current analysis demonstrates the continuing importance of climatic effects on hydrochemical signals. The absence of reductions in $[\text{NO}_3^-]$ at a national-scale is not surprising given the lack of evidence for widespread long-term reductions in N deposition (Curtis and Simpson, 2014). However, our analyses identified a geographical cluster of sites with slight downward trends in $[\text{NO}_3^-]$, i.e. in North Wales, the southern Pennines, the English Lake District and south east Northern Ireland. As these sites also tend to show the

sharpest declines in $[\text{xSO}_4^{2-}]$, this regional tendency is indicative of a response to the control of a common regional fossil fuel-based pollutant source. Recent slight reductions in the deposition of N over this region may therefore be sufficient to be contributing to recovery of surface waters from acidification. Elsewhere, the tendency for statistically significant increases in $[\text{NO}_3^-]$ in three Scottish sites, albeit small in comparison with $[\text{xSO}_4^{2-}]$ trends, appears to reflect the continuing dominant influence of climate (and most particularly winter conditions) on NO_3^- leaching in a region where N deposition trends have been, at most, very weak. This is illustrated

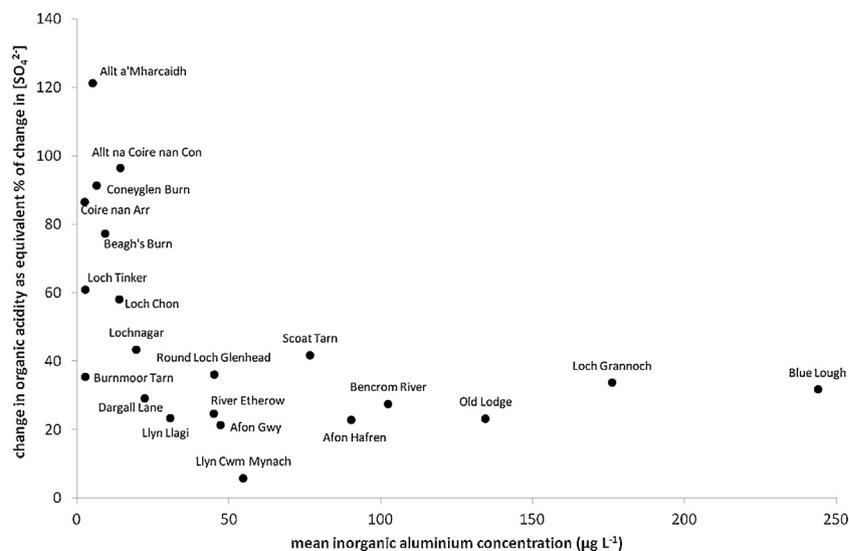


Fig. 7. Change in the modelled charge contribution from organic acids at AWMN sites as a percentage of the change in sulphate concentration, plotted against mean inorganic aluminium concentration (an indicator of acidification status).

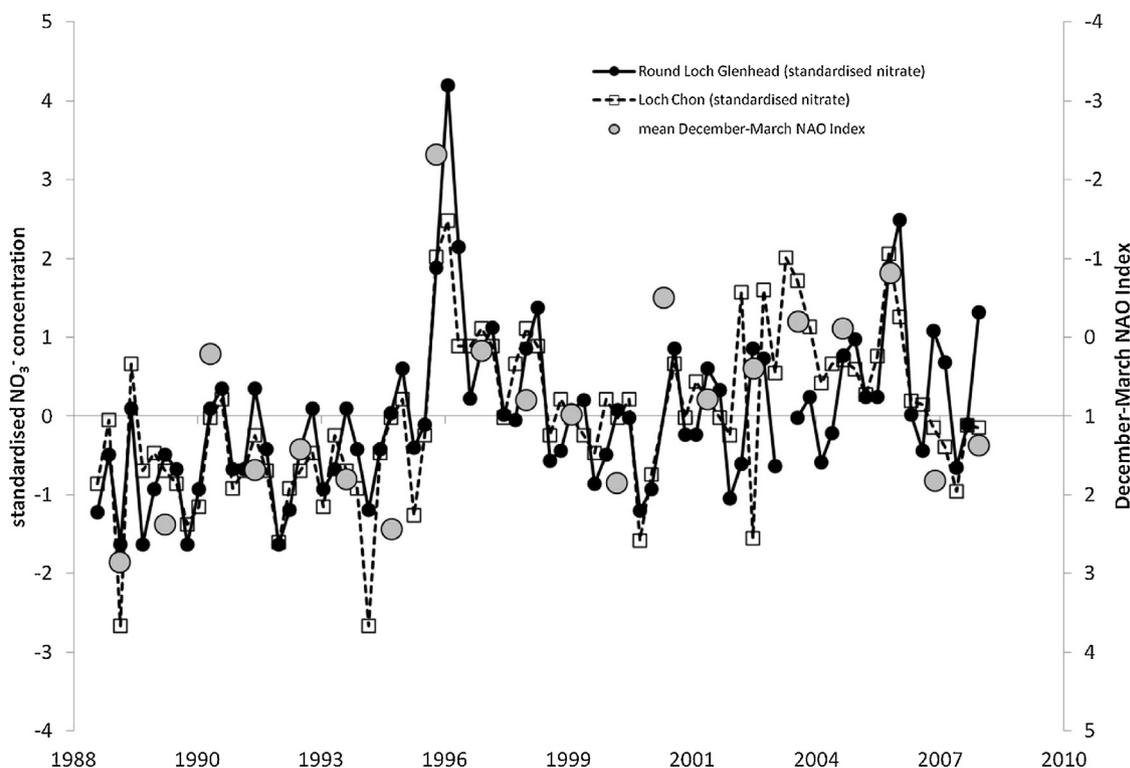


Fig. 8. Time series of standardised nitrate concentrations for two Scottish lochs showing statistically significant long-term increases in relation to inter-annual variation in the North Atlantic Oscillation Index. (December to March average). Note: NAO data presented on inverted scale. Lower NAO Index values are associated with colder, drier and more easterly-dominated winters across the UK.

by the comparison of trends in the moorland site, Round Loch of Glenhead, and the forested site, Loch Chon, and the winter NAO Index (Fig. 8)—a relationship that once held for the wider network prior to the major reduction in acid deposition in the latter half of the 1990s (Monteith et al., 2000).

Chloride in AWMN lakes and streams is derived primarily from seasalt, deposited episodically, and predominantly in areas close to the coast during winter storms. Chloride ions normally behave relatively conservatively in catchments. They are less affected by anion adsorption, biological retention and redox processes than SO_4^{2-} and NO_3^- , and are thus more mobile within soils. Chloride concentration in AWMN waters therefore provides an indication of the frequency and intensity of seasalt episodes. A recent assessment of AWMN, Acid Deposition Network and Environmental Change Network data by Evans et al. (2011) suggested that hydrochloric acid (derived from the burning of coal with a high chlorine content) made a significant contribution to total Cl^- inputs to AWMN sites, particularly those further to the south and east, in the early years of monitoring. Cessation in the burning of this fuel type, combined with the efficient removal of HCl during FGD, is therefore likely to have influenced the overall downward linear trends in $[\text{Cl}^-]$ recorded at several sites (Table 1) and to have contributed to long-term hydrochemical recovery. However the very large peaks in $[\text{Cl}^-]$ at several sites with west coast locations in the early years of monitoring occurred during some of the most stormy and westerly dominated winter conditions to have affected the UK during the last 20 years, and can only be attributed to seasalt episodes.

4.4. Evidence for the influence of coniferous forestry on hydrochemical recovery

Previous assessments of AWMN data (e.g. Monteith and Evans, 2000), and supporting palaeoecological evidence (Kreiser et al., 1990), suggested that AWMN sites with forested catchments

experienced higher acidic loads and had acidified more than nearby sites without forests. This is consistent with the long-recognised role of forest canopies as efficient sinks of atmospheric pollutants. Fowler et al., 1989, for example, estimated that within the Kielder Forest in northeast England, afforestation of moorland had increased sulphur and nitrogen inputs by 30% and 90% respectively. In theory the effect of enhanced pollutant interception on soil and water acidity could be exacerbated by the long term depletion of base cations from the catchment resulting from the harvesting and removal of timber (Sverdrup and Rosen, 1998). It has been estimated that on average, uptake of base cations by conifers at AWMN sites would account for 18% of the total base cation supply from weathering, although this rises to 27% for Sitka spruce plantations, and would be more significant still for the most acid-sensitive AWMN catchments (Evans personal communication).

The establishment of a forest, and its subsequent management, is likely to influence N cycling within the soil, and the consequent extent of N leaching to surface waters. A developing canopy might be expected to have a relatively high N demand and reduce the amount available for mineralisation and leaching as NO_3^- . Conversely, however, strong pulses in $[\text{NO}_3^-]$ are often observed after felling (Neal, 2002; Reynolds et al., 2004; Tetzlaff et al., 2007), and the complexities resulting from management are likely to account, at least in part, for substantial differences in patterns of short term variation in $[\text{NO}_3^-]$ in the forested-non-forested pairs illustrated by the additive plots provided in the Supplementary Information.

Whilst the exacerbating influence of coniferous forest plantations on acidification is beyond dispute (e.g. Miller et al., 1991; Harriman et al., 2003), there is increasing interest from land managers, charged with the development of forest–water management guidelines, in the extent to which current forestry practices may continue to influence hydrochemical recovery.

Given the importance of canopy interception in enhancing pollutant deposition it is intuitive to expect forested catchments to

have undergone more rapid reductions in the deposition of S, and hence more rapid reductions in $[xSO_4^{2-}]$ in their drainage waters. When considered as a group, rates of decline in $[xSO_4^{2-}]$, $[Al_{inorg}]$ and increases in $[AB-ANC]$ are consistently slightly more pronounced for all three forested sites, although differences between individual pairs are mostly not statistically significant. However, in the case of the Plynlimon pair of sites, that did not show any significant differences in trends, it should be noted that hydrochemical monitoring of the Afon Gwy commenced three years after monitoring began in the Afon Hafren. In a separate comparison of hydrochemical change in the upper (non-forested) reaches of the Afon Hafren with forested reaches below, Neal et al. (2010) demonstrated both that the forested reaches were receiving greater acidic loads from deposition and that they were recovering more rapidly than the non-forested sections. Despite the tentative evidence from the AWMN for more rapid recovery in forested sites, the data in Tables 2a and 2b demonstrate that there has been no systematic convergence in acid anion concentrations in relative terms. Concentrations of xSO_4^{2-} remain around 25% higher and $[NO_3^-]$ mostly remains over 50% higher in the sites with forested catchments when comparing 1988–1993 and 2003–2008 means. The chief exception here is for the Galloway pair, for which $[NO_3^-]$ in forested Loch Grannoch was only 18% higher than the moorland Round Loch of Glenhead between 2003 and 2008, compared with 65% in the earlier period, but once again short term management effects should be taken into consideration. It should also be noted that neither of the two forested sites that occur within the region where statistically significant downward trends in $[NO_3^-]$ are widely detectable (described in Section 4.3), have experienced reductions in this ion.

The more rapid increase in pH of the Round Loch of Glenhead relative to Loch Grannoch, results from the more acidified condition of the latter – recovery to date occurring predominantly through a reduction in $[Al_{inorg}]$, rather than an increase in pH. This emphasises the continued legacy of afforestation on the condition of afforested water sheds, and suggests that biological recovery of these forested systems is still likely to lag behind that in neighbouring non-forested sites.

The extent of comparable forested/non-forested pairs of sites within the AWMN alone is too limited to allow broad conclusions to be made about the role of forestry, and indeed local forestry practices, in hydrochemical recovery from acidification, and it will be necessary to incorporate other hydrochemical datasets of comparable high quality (e.g. see Malcolm et al., 2014; Neal et al., 2011) to allow a more thorough test of these observations.

4.5. Trends in hydrochemical extremes in acidity relative to average conditions

Despite long-term improvements in chemistry, the acidity of recovering acidified surface continues to vary considerably. The most acidic conditions tend to occur during periods of high rainfall (when dilute surficial run-off enriched in organic and mineral acidity dominates over more strongly buffered groundwater), and after seasalt deposition events (when marine cation deposition generates pulses of H^+ and Al^{3+} from soil exchange complexes).

It has been postulated that the recurrence of occasional acidic extremes in waters undergoing long-term hydrochemical recovery in terms of average condition may be preventing the re-establishment of acid-sensitive species (Lepori et al., 2003; Kowalik et al., 2007). However, positive trends have been shown to occur in the ANC of drainage waters recovering from acidification during both high flow and base flow conditions (e.g., Evans et al., 2008b; Tetzlaff et al., 2010; Brewer et al., 2011). Furthermore, outcomes might be expected to be catchment specific, depending, for example, on the importance of groundwater contributions to run-off

under different flow conditions, riparian soil cover, etc. (e.g. see Tetzlaff et al., 2010). If, as seems intuitive, these occasional extreme conditions are limiting biological recovery, the potential for ecological improvement will depend on the extent to which their severity is declining.

We found no evidence that acidity during more acidic periods was declining less rapidly than the trends in average acidity—as represented by the statistics in Table 1. Indeed, the 90th percentile for $[Al_{inorg}]$ in the more acidified sites has been falling significantly more rapidly than the average tendency (Table 3). This therefore supports observations relating to recovery in the AWMN macroinvertebrate data that species turnover indicative of recovery is not being prevented by occasional acidic extremes (Monteith et al., 2005). For example, one of the largest recovery responses in the macroinvertebrate fauna has been observed in the River Etherow (see Murphy et al., 2014 and Stockdale et al., 2014), despite this site exhibiting the largest fluctuations in pH and $[Al_{inorg}]$ of any site on the network. It is important to note, however, that, whilst the acidity of these episodes is falling rapidly, current day peak concentrations of $[H^+]$ and $[Al_{inorg}]$ in the more acidified streams are still substantially above those found in non-acidified acid-sensitive areas such as the far north of Scotland.

Our findings suggest that over this multi-decadal time period, routine, regularly spaced water sampling has been sufficient to quantify the rate of change in both chemical drivers and ecologically significant indicators of acidification, in a manner that is robust across measurements and across sites. More targeted, episode focussed, monitoring would no doubt have improved further our understanding of long-term change in these critical events but would have required far greater resources to support.

5. Conclusions

Our analyses of the first 20 years of AWMN data show very clear signs of chemical recovery in acidified UK surface waters, resulting primarily from large reductions in the deposition of S over the last two decades. They show that the hydrochemical nature of the response varies substantially between sites, particularly with respect to the availability of organic carbon and whether or not catchments are afforested, and that variation in climate continues to exert a significant influence on trends even at a multi-decadal scale. Concentrations of xSO_4^{2-} , NO_3^- , and Al_{inorg} remain at unnaturally high levels, whilst $[ANC]$ remains unnaturally low according to modelled hindcasts, at several sites. Furthermore, whilst surface waters in forested catchments are showing similar rates of recovery to non-forested sites, they continue to receive relatively high loads of acidic pollutants and remain considerably more acidified. Consequently, there is clear scope for further reductions in $[xSO_4^{2-}]$ that would promote further recovery in $[Al_{inorg}]$ and pH, to the benefit of these aquatic ecosystems. Large uncertainties remain over the likely future hydrochemical signatures of our upland waters, particularly with respect to future trajectories for $[NO_3^-]$ concentration, and the possible impact of future changes and increased short-term variability in climate on an increasingly soluble soil organic carbon stock.

Now over two decades in length, the AWMN hydrochemical record continues to broaden our understanding of the biogeochemical processes underpinning these systems. AWMN data are nationally unique in combining geographical coverage, quality, longevity and breadth of monitoring activity (hydrochemical and biological). They assist in refining the process-based models that allow wider spatial and temporal extrapolation, and provide a baseline against which the effects of future changes in climate and land management on hydrochemistry and ecosystem health can be assessed. The value of the latter should be more widely

recognised, particularly in the context of Water Framework Directive (WFD) surveillance monitoring. In the traditional context of atmospheric pollution, the UK AWMN, together with similar monitoring programmes in other industrialised countries, continue to provide one of the most effective means of assessing the long-term impacts of anthropogenic activity on the biogeochemistry of semi-natural systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ecolind.2012.08.013>.

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