Article (refereed) - postprint

Evans, Chris D.; Chadwick, Tom; Norris, David; Rowe, Edwin C.; Heaton, Tim H.E.; Brown, Philip; Battarbee, Richard W. 2014. **Persistent surface water acidification in an organic soil-dominated upland region subject to high atmospheric deposition: the North York Moors, UK**.

Persistent surface water acidification in an organic soil-dominated upland region subject to high atmospheric deposition: The North York Moors, UK

Chris D. Evans[a], Tom Chadwick[b], David Norris[a], Edwin C. Rowe[a], Tim H.E. Heaton[c], Philip Brown[d], and Rick Battarbee[e]

[a] Centre for Ecology and Hydrology, Bangor, LL57 2UW, UK (Corresponding author: cev@ceh.ac.uk).
[b] 4 Station Road, Castleton, Whitby, YO21 2EG, UK
[c] NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, NG12 5GG, UK.
[d] Philip Brown, The School House, Castleton, YO21 2DA
[e] Environmental Change Research Centre, University College London, Gower St., London WC1E 6BT, UK.

Abstract

The North York Moors National Park, in Northeast England, is one of the few upland areas of the United Kingdom located immediately downwind of major sulphur and nitrogen emission sources. Despite this, few studies of air pollution impacts have been undertaken, and there is no formal long-term upland water quality monitoring site. We examined the condition of surface waters in the National Park based on 1) a unique 20 year stream pH record from three locations; and 2) a snapshot survey of 51 surface waters draining moorland and conifer plantations. Interpretation was supported by sulphur isotope analysis of a subset of water samples, and a diatom survey of one of the monitoring streams. Long-term pH data for a stream draining the peat plateau demonstrate extreme, year-round acidification, with recovery only evident in the last few years. Lower-elevation sites are less acidic, but show similar temporal trends, and are characterised by frequent and severe acid episodes. The snapshot survey confirmed that acidification of the moorland area is widespread, to a degree observed in few other areas globally; out of 37 moorland streams sampled, 32 had an acid neutralising capacity (ANC) below -50 μeq l^{-1}. Sulphate was found to be (by far) the dominant cause of acidification, and sulphur isotope analysis confirmed that this derives primarily from atmospheric deposition. Nitrate concentrations remain low, indicating that the organic moorland soils continue to retain most incoming nitrogen. It appears that conifer planting has exacerbated acidification, leading to five-fold higher nitrate and threefold higher aluminium concentrations compared to the moorland sites. Available biological data suggest that waters in the region have been impoverished by acidification. We speculate that the slow recovery of surface waters in the North York Moors is due to the release of a legacy of stored sulphur from the peats, released during droughts. We conclude that: 1) acidification is far from being a solved problem in this sensitive near-source upland region, despite reductions in sulphur deposition; 2) plantation forestry has exacerbated the effects of atmospheric pollution, and triggered nitrogen saturation; 3) the lack of any formal long-term monitoring in the North York Moors represents a major gap in the current evidence base for the effects of long-range air pollutants on UK upland ecosystems.

Keywords: *Acidification, water quality, peat, sulphur, nitrogen, DOC, North York Moors, long-term monitoring*

1. INTRODUCTION

Acid deposition has detrimentally impacted on the chemical and biological status of upland terrestrial and aquatic ecosystems across much of the UK, as well as Scandinavia, Central Europe and North-eastern North America. In all these areas, atmospheric sulphur pollution have declined substantially from 1970s-80s peaks; in the UK S emissions have decreased by around 90% since the 1970s (RoTAP, 2011). Long-term surface water monitoring studies, most initiated in the 1980s, have shown clear evidence of recovery from acidification (e.g. Evans et al., 2001; Stoddard et al., 2004; Davies et al., 2005; Kopáček et al., 2006) although in most cases current levels of acidity remain higher than background values inferred from palaeolimnological studies (e.g. Battarbee et al., 2005), and biological recovery of damaged ecosystems in general appears less advanced than chemical recovery (Monteith et al., 2005; RoTAP, 2011).

In the UK, the chemical and biological monitoring undertaken by the UK Acid Waters Monitoring Network (AWMN; Shilland et al, this issue) provides a national-scale assessment of the status of acid-sensitive waters. However, the 22 lakes and streams in the network are mostly located within the large acid-sensitive upland areas of Scotland, Wales and Northwest England. Conversely, the more distributed network of sites in the UK Acid Deposition Monitoring Network (Lawrence et al., 2008) indicate that the highest historic and current sulphur (S) deposition has occurred in eastern areas of England, close to industrial sources such as coal-burning power stations. Fowler et al. (2005) classified the UK into four deposition zones, from Zone 1 (most polluted) in eastern England to Zone 4 (least polluted) in remote North-western areas of Scotland and Northern Ireland. Based on this classification, the majority of AWMN sites are located in Zone 3, with only two sites located within Zone 1. To an extent, this reflects the limited extent of acid-sensitive upland ecosystems within this predominantly lowland and intensively agricultural region. Exceptions occur along the Pennine upland chain in Northern England; in isolated areas of sandstone and glacial sands and gravels in Southeast England; and in the North York Moors of Northeast England. While the Pennines are represented by the River Etherow AWMN site and the Moor House Environmental Change Network (ECN) site, and Southeast England by the Old Lodge stream AWMN site, no formal long-term monitoring of acid-sensitive surface waters has taken place in the North York Moors.

The lack of long-term water quality monitoring in the North York Moors is surprising given the sensitivity of the region to acid deposition, and its proximity to major emission sources. Indeed, there is a general lack of published data on atmospheric pollutants for this area. The UK Freshwater Critical Loads dataset, which is used to quantify the national extent and severity of atmospheric deposition impacts on surface waters, comprises a total of 1722 sampled lakes and streams. Prior to this study, only 11 sites were within the North York Moors National Park, all of which were sampled between 1991 and 1994. Of these, five (all of which were moorland pools) had an Acid Neutralising Capacity (ANC) of less than -50 μeq l^{-1}. This compares to the UK's critical damage threshold of 20 μeq l^{-1} (Hall et al., 2004) and thus suggests severe, biologically damaging acidification at this time. A one-year measurement study of the Brocka Beck catchment by McNish et al. (1997) recorded high pH during summer baseflows (6.5 or higher) but highly acidic high flows (pH minima below 4.0).

Overall, the limited available evidence suggests that some surface waters in the North York Moors were strongly acidified when water chemistry measurements were first taken in the 1990s, consistent with their geological sensitivity and proximity to emission sources. This is supported by preliminary analysis of a sediment record from Grey Heugh's Slack, a moorland pool on Fylingdale Moor, that shows strongly increasing contamination of the pool by heavy metal deposition, especially lead and zinc, over the last 150 years (Battarbee et al. unpublished). However, the extent of acidification is unknown, as is the degree to which surface waters may have recovered as S deposition has fallen. There is also little information on whether nitrogen (N) deposition has resulted in ecosystem nitrogen saturation (Stoddard et al., 1994) and consequent nitrate (NO_3^-) leaching to surface waters. In this study, we attempt to resolve these uncertainties through an integrated analysis of 1) 20 years of voluntarily-collected pH data from three surface waters in the region, and 2) a snapshot survey of 51 surface waters undertaken in 2005, focusing on sensitive heathland and forest-dominated catchments.

2. METHODS

2.1. Study area

The North York Moors National Park covers an area of 1436 km^2, of which 34% is moorland and 22% woodland, mainly coniferous plantation forest. The moorland area predominantly comprises heathland, the largest such area in England, with some areas of blanket bog. Most of the moorland area (440 km^2) has been designated as the North York Moors Special Area of Conservation. The upland area has a maximum elevation of 450m, and receives an annual rainfall of around 1000 mm, less than most other UK upland areas. The upland plateau is underlain by base-poor Jurassic sandstones, while surrounding valleys have incised into older, more weatherable shales and ironstones. Well-buffered limestones and clays are present at lower elevations to the south of the National Park. Moorland soils are acidic, organic or organo-mineral, with the central plateau occupied by blanket peat (Winter Hill association), grading into stagnohumic gleys soils (Wilcocks association), humus-ironpan stagnopodzols (Maw association) and humo-ferric podzols (Anglezarke association) towards the moorland edge (Jarvis et al., 1984). Deeper valleys contain more alkaline pelosols, brown earths and stagnogleys. Blanket peat is mostly shallow (< 1 m depth), as the region is close to the climatic limit for blanket peat formation in Great Britain (Clark et al., 2010). The moorland area has been affected by a range of current and historic land-management, including short-rotation burning for grouse production, extensive sheep grazing, drainage and forest planting, and is also susceptible to occasional wildfires (North York Moors National Park Authority, 2008a).

Of the two major rivers draining the upland area, the Esk (to the north) is the only river in Northeast England to support economically important salmon and sea trout fisheries. However, the fishery has been in decline since the 1960s (North York Moors National Park Authority, 2001). The Esk and the Derwent (draining the southeast of the National Park) support five threatened/declining species listed in the UK Biodiversity Action Plan: otter, water vole, kingfisher, dipper and freshwater pearl mussel. The River Esk Regeneration Programme (North York Moors National Park Authority, 2001) classified biological water quality in some headwater streams in Environment Agency classes D-F (Fair to Bad) due to

high levels of acidity in moorland tributaries, however this was considered a natural feature of runoff from the peatland.

Unlike most of the other acid-sensitive UK upland areas (exceptions being the Southern Pennines and the uplands of South Wales), the North York Moors are close to industrial areas, and downwind of several major emissions sources; three large coal-fired power stations (Drax, Ferrybridge and Eggborough) are located within 70 km to the southwest while the industrial area of Teesside, 25 km to the north, includes steel works and chemical plants. Mean estimated non-marine S deposition to the moorland area for 2004-06 (including estimated dry and occult deposition) was around 17 kg S ha^{-1} yr^{-1} (RoTAP, 2011; www.atmosci.ceh.ac.uk). In combination with relatively low rainfall volumes, this results in high effective rainfall sulphate (SO_4^{2-}) concentrations. Moorland Total N deposition for the same period was around 22 kg N ha^{-1} yr^{-1}, 40% as oxidised N and 60% in reduced forms. For forested areas, S deposition is estimated to be around 32% higher, and total N deposition 43% higher.

2.2. Long-term precipitation and surface water pH monitoring

The High Muffles Acid Deposition Monitoring Network site is located in the Southeast of the National Park (54°20′03″ N, 0°48′25″ W, 267 m above sea level) and has been measuring precipitation chemistry on a two-weekly basis since 1986. Annual volume-weighted mean concentrations of non-marine sulphate (xSO_4^{2-}), total inorganic nitrogen (the sum of NO_3^-, and ammonium, NH_4^+), sodium (Na^+) and chloride (Cl^-) were obtained from the UK Air Quality Archive (www.airquality.co.uk). Concentrations of non-marine Cl^- (xCl^-) were calculated from sea-salt ratios, assuming that all Na^+ is marine-derived, and that any additional Cl^- must derive from pollutant sources, e.g. hydrochloric acid (HCl) emissions from coal-burning. This follows the method used by the ADMN to calculate xSO_4^{2-}, and was recently used in an assessment of UK deposition data that revealed evidence of significant HCl deposition to UK upland areas (Evans et al., 2011).

In 1990 a local volunteer group, Environet, began monitoring precipitation and surface water acidity at several sites in Danby Dale, a catchment draining the northern edge of the moorland plateau. Measurements have been maintained on a frequent (normally weekly) basis for two streams. Danby Beck (54° 24.8' N, 0° 55.7' W) is a peat-dominated moorland headwater stream with a catchment area of 0.77 km^2, which also formed part of the spatial survey. Brownhill Spring (54° 26.4' N, 0° 56.5' W) is a downstream tributary of Danby Beck; the sampled location drains Castleton Rigg, a moorland ridge overlain by well-drained humus-ironpan stagnopodzols of the Maw Association. In 1992 an additional site, Botton Pond, was added; this small artificial water body (area 400 m^2, depth 2-3 m) lies close to the Danby Beck sampling point, but drains a separate areas of hillslope, the lower part comprising conifer plantation and bracken-covered hillslope on mineral soils, and the upper part the edge of the moorland plateau, on organic soils. The continuous twenty-year pH record provided by this voluntary monitoring programme is unique within the North York Moors National Park, and provides the only robust basis by which to infer long-term changes in stream acidification. The dataset has not previously been published in the peer-reviewed literature.

2.3. Surface water survey

A snapshot survey of surface waters was carried out between March 1st and March 4th 2005. A total of 51 surface waters were sampled, comprising 46 headwater streams, four moorland pools and one reservoir. A subset of the stream catchments contained substantial areas of coniferous forestry, the rest were dominated by heather moorland (Figure 1). Sites were selected within the area of the National Park underlain by acid-sensitive soils (i.e. peats, peaty gleys and podzols), to exclude any local anthropogenic solute sources (in particular areas of improved agricultural land); and to provide a reasonably representative geographical spread across the upland part of the National Park, within the constraints of site accessibility (Figure 1). The water bodies sampled reflected the character of the region, which is dominated by streams, with natural standing waters limited to moorland pools. The sites sampled, their locations, and summary characteristics, are listed in Table A.1.

The survey coincided with a substantial accumulation of snow across most of the region. However, because air temperatures remained close to 0 °C throughout the sampling period, the effects of snowmelt on river flows or chemistry was limited, and flows remained moderately low and stable through the sampling period.

2.4. Chemical analysis

All samples from the survey were filtered immediately in the field, and refrigerated prior to analysis at the Centre for Ecology and Hydrology, Bangor. Major anions (SO_4^{2-}, NO_3^-, and chloride, Cl^-) and ammonium (NH_4^+) were analysed on a Dionex Ion Chromatograph. The main base cations (calcium, Ca^{2+}; magnesium, Mg^{2+}; sodium, Na^+; potassium, K^+) and total aluminium (Al) were analysed on a Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer. Alkalinity was measured by Gran titration, analysed along with pH on a Metrohm SM 702 Titrino. Dissolved organic carbon (DOC) was measured on a Thermalox TOC/TN analyser after acidifying the sample to pH 2.0 and purging with oxygen to drive off any inorganic carbon present.

Exploratory sulphur (S) isotope analyses were undertaken on a subset of survey sites using residual samples following bulk chemistry analyses. In most cases it was necessary to combine samples from two or more sites in order to provide sufficient S for isotope analysis, with the combination based on similarity of site characteristics, chemistry, and geographical proximity (Table A.1). Samples were acidified to pH 3 and SO_4^{2-} precipitated by addition of excess barium chloride. The barium sulphate was combusted to SO_2 in an EA-1120 elemental analyser on-line to a Delta+XL isotope ratio mass spectrometer (ThermoFinnigan, Bremen, Germany), with $^{34}S/^{32}S$ ratios calculated as $\delta^{34}S$ values versus CDT by comparison with standards IAEA SO5 ($\delta^{34}S$ = +0.5) and NBS-127 ($\delta^{34}S$ = +21.1). Analytical precision of standards was <0.3‰ (1 SD).

2.5. Stream diatom measurements

Samples for epilithic diatom analysis were collected from Danby Beck on the 27th August 2009 and 1st September 2010. The 2010 sample was taken from the same location as the routine water sample (Figure 1) and the 2009 sample approximately 1 km upstream.

Sample collection and processing followed standard AWMN protocols for diatom analysis (Battarbee et al., this volume).

2.6. Data analysis

Annual volume-weighted mean precipitation chemistry from the High Muffles deposition monitoring site were analysed by simple linear regression against time, to give an indication of overall changes in pollutant loading. The higher resolution rainfall and surface water pH datasets showed clear non-linear variation over the monitoring period, so to illustrate the underlying pattern of temporal change, LOWESS curves (Minitab Version 16) were fitted to each dataset, with a smoothing parameter of 0.15. In addition, time series data were grouped into 5-year periods (1990-1994, 1995-1999, 2000-2004 and 2005-2009) to examine differences in the distribution of measured pH between sites, and over time. Since pH distributions were often skewed, a 3-parameter Weibull distribution (which provides flexibility in terms of shape and possible asymettry) was found to give the best fit to observations.

Data from the 2005 spatial survey data were classified into three broad groups, based on catchment type. Moorland catchments, which comprised the majority of those sampled, were subdivided based on measured alkalinity into 'acid' sites with negative alkalinity (36 sites), and a smaller set of 6 'alkaline' sites with positive alkalinity. Although these latter sites were difficult to pre-define based on available catchment information, they tended to occur on the moorland fringe, presumably at the transition between acid-sensitive and better-buffered bedrock and soils. Nine catchments in which 10% or more of the land area was occupied by conifer plantation were grouped together as 'forest' catchments. The small number of moorland pools sampled did not emerge as a chemically distinct group, and were therefore included within the acid moorland class. Differences between the chemical characteristics of the three catchment groups were analysed using two-sample t-tests, assuming unequal variances, and a significance threshold of 0.05.

For the 10 composite samples analysed for $^{34}S/^{32}S$ isotopes, total SO_4^{2-} concentrations were calculated as the average of the measured concentrations of the individual component samples. Total SO_4^{2-} $\delta^{34}S$ values were measured on the composite samples. The isotopic composition of the non-marine component, xSO_4^{2-}, was estimated by assuming that the marine component of SO_4^{2-} had a concentration $0.119 \times Na^+$ concentration (assuming all measured Na^+ was of marine origin), and that marine SO_4^{2-} had a $\delta^{34}S$ value of +21‰.

3. RESULTS

3.1. Temporal changes in rainfall chemistry

Data from the High Muffles ADMN site show a steady decline in volume-weighted precipitation xSO_4^{2-} concentrations since 1988. Based on a linear regression against time, concentrations have declined by approximately 2.5 $\mu eq\ l^{-1}\ yr^{-1}$, from a 1986-1990 mean of 52 $\mu eq\ l^{-1}\ yr^{-1}$ to a 2003-2007 mean of 31 $\mu eq\ l^{-1}\ yr^{-1}$. Over the same period, concentrations of xCl^- have fallen from around 10 $\mu eq\ l^{-1}\ yr^{-1}$, to values consistently at or below zero since

2002. A recent analysis of UK-wide precipitation xCl^- concentrations (Evans et al., 2011) suggests that this pattern of xCl^- reduction is widespread, and associated with the near-cessation of HCl emissions from coal-burning power stations following flue gas desulphurisation. Given the proximity of the North York Moors to several coal-burning power stations, HCl deposition appears to have been high in the past, and its disappearance has therefore contributed significantly to the overall reduction in acidifying pollutant loadings to the region (the reduction in xCl is around half of that in xSO_4). Slightly negative values of calculated xCl in recent years could be explained by a small input of Na derived from terrestrial sources, and/or the dechlorination of sea-salt aerosol during atmospheric transport (Evans et al., 2011). On the other hand, total inorganic N concentrations in precipitation have shown only a modest reduction over the same period, and now form by far the largest component of acidifying pollutant deposition. The ratio of wet reduced to wet oxidised N concentration in rainfall has remained approximately constant, with an average of 1.2. The pH of rainfall (based on volume-weighted mean hydrogen ion concentration) has increased from 4.2 to 4.8 during the monitoring period.

The Danby Dale rainfall monitoring data (Figure 3a) show a high short-term variability, with a mean pH of 4.75 for the 1990-2010 monitoring period (compared to 4.49 for the same period at High Muffles, although the Danby data are not volume weighted). There was a general increase in pH between 1994 and 2007, since when acidity has remained approximately constant (mean of last 4 years data 5.37). Rising rainfall pH, and the current relatively high values, are attributable to decreases in xSO_4^{2-} and xCl^-, and to the increasingly large proportional contribution of NH_4^+ to the overall pollutant load.

3.2. Temporal changes in surface water chemistry

Danby Beck, the peat-dominated headwater stream, has an exceptionally low pH; the mean for the full 20 year dataset is 3.81 (Figure 3b). This compares to a 20-year mean pH range among AWMN lakes and streams of 4.66 to 6.54. Stream pH variations show a consistent, skewed seasonal pattern, with pH low and relatively stable (between 3.0 and 4.0 prior to 2005) for most of the year, with brief periods each year when pH is considerably higher, typically > 5.0. These peaks all occur between May and September, but rarely persist for more than 1-2 months. The positively skewed pH variation at Danby Beck is reflected in the five-year frequency distributions (Figure 4a). The time series data suggest that the most acid conditions occurred in around 1997, since when there has been a gradual rise in pH, interrupted by intervals of re-acidification in 1999-2001 and 2003-2005. Since 2006, pH appears to have stabilised, with a mean for the last four years of 4.14. The increase in pH is also reflected in a progressive upward shift in the frequency distribution since 1995-1999 (Figure 4a).

Brownhill Spring, which drains moorland organo-mineral soils, is considerably less acid than Danby Beck, with a mean of pH 5.63. Within-year pH variations show less consistent seasonality, but are more evenly distributed around the mean, with short periods of both high and low pH observed (Figure 3c, 4b). The long-term pattern resembles that for Danby Beck, with an apparent pH decline until the late 1990s, followed by a period of recovery, which was interrupted by pronounced but temporary re-acidification during 2003-2005. Since 2005, stream pH appears to have stabilised at a mean of around 6.0. However a more

negative frequency distribution during this period shows that occasional acid episodes persist.

Based on the slightly shorter (1992-2010) monitoring dataset, Botton Pond has a mean pH of 5.88. Despite being located adjacent to Danby Beck, Botton Pond has highly contrasting short-term pH dynamics, characterised by high pH (5.5 to 7.0) for most of the time, interspersed with large acid episodes during which pH often drops below 4.5 (Figure 3d). The pH distribution consequently shows a strong negative skew during all time periods (Figure 4c). There is no clear seasonal pattern to the occurrence of acid episodes, although the majority occur between November and March. The long-term pattern of pH change at Botton Pond resembles that at the other sites; although it is difficult to identify clear overall trends, the pattern of rising pH from the late 1990s to 2003, followed by a period of re-acidification from 2003-2005, is synchronous with that for Danby Beck and Brownhill Spring. At both Botton Pond and Brownhill Spring, pH appears to have declined slightly in the last 4 years.

3.3. Spatial variations in surface water chemistry

The March 2005 surface water survey revealed evidence of widespread, severe acid conditions at the time of sampling. Of 51 sites sampled, 44 had pH < 5.0, and 45 had ANC < 0 $\mu eq\ l^{-1}$ (Figure 5; Table A.2), indicative of highly adverse conditions for aquatic biota (Lien et al., 1996; Henriksen et al., 1999). Of these sites, 33 had an ANC below -100 $\mu eq\ l^{-1}$. By comparison, in a survey of 64 surface waters in the South Pennines, which has been considered the most acidification-impacted regions in the UK, only 21 sites sampled has a negative ANC, and none had an ANC below -100 $\mu eq\ l^{-1}$ (Evans et al., 2000). Excluding sites from the North York Moors, 15% of the 1719 lakes and streams in UK Freshwater Critical Loads dataset had a negative ANC, but only 0.7% had ANC < -100 $\mu eq\ l^{-1}$ (1719 sites sampled between 1990 and 2002; www.freshwaters.org.uk). Concentrations of SO_4^{2-} were extremely high (mean 218 $\mu eq\ l^{-1}$) compared to other UK upland areas (e.g. Evans et al., 2000; Helliwell et al., 2002; Helliwell et al. 2007), whereas NO_3^- leaching was relatively low (mean 15 $\mu eq\ l^{-1}$) despite sampling during spring, when concentrations typically peak. Concentrations of NH_4^+ were < 4 $\mu eq\ l^{-1}$ at all but one site, a peat pool (Brian's Pond) which had a concentration of 18 $\mu eq\ l^{-1}$. Total Al concentrations were also high at most sites (mean 400 $\mu g\ l^{-1}$). Although it is not possible to fully evaluate whether conditions at the time of sampling were representative of long-term conditions, the pH of 4.1 measured in Danby Beck during the survey was similar to the 2005 annual mean of 3.9, suggesting that conditions were not highly atypical.

Comparisons between the three catchment classes (see Methods) highlight pronounced contrasts in mean water chemistry (Figure 5). Comparing acid moorland and forest catchments, there was no significant difference in alkalinity, ANC or pH, but the forested catchments had 70% higher SO_4^{2-} concentrations (forest mean 306 $\mu eq\ l^{-1}$, acid moorland mean 180 $\mu eq\ l^{-1}$), and fivefold higher mean NO_3^- concentrations (forest mean 44 $\mu eq\ l^{-1}$, acid moorland mean 8 $\mu eq\ l^{-1}$). The increased acid anion leaching from the forested catchments was accompanied by a combination of higher base cation concentrations (e.g. Ca^{2+}, Figure 5d) and almost threefold higher Al concentrations (Figure 5g). DOC and DON concentrations were not significantly different between the two sets of sites, but slightly

higher mean DOC and lower mean DON in the forest streams resulted in significantly higher DOC/DON ratios.

Differences between the acid and alkaline moorland catchments must be analysed with caution, insofar as measured alkalinity was used to differentiate the two groups. However, it is clear that the 36 acid moorland catchments (i.e. those with negative alkalinity) spanned a much narrower range of observed water chemistry than the 6 sites with positive alkalinity. The shift from negative to positive alkalinity coincided with a major pH transition, with all acid moorland sites having pH < 5.0, and all alkaline moorland sites having pH > 6.0. Higher alkalinity was also associated with higher concentrations of Ca^{2+} and SO_4^{2-}, and lower Al. NO_3^- concentrations were significantly higher at alkaline moorland versus acid moorland sites, but significantly lower than in the forested streams. DOC and DON concentrations were similar between the two moorland categories.

3.4. Sulphur isotope analysis

Sulphur isotopes were analysed on seven composite samples from acid moorland streams, one composite from moorland pools, two composites from forested catchments, and a single sample from an alkaline moorland stream, Darnholme. Concentrations of xSO_4^{2-} in the 10 composite samples ranged from 104 to 342 μeq l^{-1}, whilst Darnholme had a higher concentration of 712 μeq l^{-1}. After subtracting the marine SO_4^{2-} contribution to measured $\delta^{34}S$ (see Methods), estimated $\delta^{34}S$ values for the xSO_4^{2-} component of the 10 composite samples fell within a narrow range of +2.7 to +6.1‰ (Table A.3). These values correspond closely to the range of +2 to +6‰ previously measured on rainfall SO_4^{2-} in Yorkshire (Heaton et al., 1997; Novak et al., 2001), and to measurements from non-coastal areas in other parts of the world (Wadleigh, 2001; Tichomirowa, 2007). There was no evidence of a relationship between $\delta^{34}S$ and either xSO_4^{2-} or land-cover type for these samples (Figure 6).

By contrast, the sample from Darnholme had a markedly lower $\delta^{34}S$ value of -9.1‰. This appears likely to be associated with a geological source; SO_4^{2-} formed from the oxidation of sulphides in clays and shales commonly has very low $\delta^{34}S$ values; sulphides in the Kimmeridge Clay of the Cleveland Basin have $\delta^{34}S$ values of -25 to -12‰ (Lallier-Verges et al., 1997). Given that the Darnholme sample almost certainly included some SO_4^{2-} from rainwater, the pure reduced S end-member could have a $\delta^{34}S$ value as low as -20‰. The location of the Darnholme Stream, in an incised valley (as opposed to the more plateau-like locations of the acid moorland and forested sites) provides the potential for significant inputs of groundwater from sulphide-bearing shales.

3.5. Stream diatom measurements

The epilithic diatom assemblages obtained from Danby Beck in 2009 and 2010 have a very similar composition. Both are strongly dominated by *Eunotia exigua* (Bréb) Rabh. Other taxa present in both samples are *E. curvata* (Kütz.) Lagerstedt, *Frustulia rhomboides* var. *saxonica* (Rabh.) de Toni, and *Pinnularia viridis* (Nitzsch) Ehr. All are taxa typical of extremely acidic environments and tolerate high concentrations of heavy metals (Renberg 1986, van Dam & Mertens 1990). The assemblages are exceptionally species poor with only six taxa in the 2009 sample and three taxa in the 2010 sample occurring in a count of 300 valves. This low

diversity is typical of extreme environments and indicates water quality even more acidic than the most acidified streams in the AWMN such as Old Lodge, and the Afon Gwy and Afon Hafren (Shilland et al., 2010).

4. DISCUSSION

4.1. Drivers of spatial variation in water chemistry

Compared to previous surface water surveys in UK acid-sensitive regions (e.g. Evans et al., 2000; Helliwell et al., 2002; Helliwell et al. 2007) the relative uniformity of surface water quality across the moorland plateau of the North York Moors is striking, as is the severity of acidification across this area. Although low pH values can partly be attributed to high concentrations of DOC (and hence organic acids) from the peaty soils, this has clearly been exacerbated by very high SO_4^{2-} leaching, resulting in strongly negative alkalinity and ANC. S isotope data for the acidified sites suggest a predominantly atmospheric, anthropogenic SO_4^{2-} source, but the extremely high concentrations are remarkable given that the survey was undertaken in 2005, by which time UK SO_4^{2-} deposition, and surface water concentrations in other acidified areas of the UK, had fallen considerably from their 1970s-80s peaks (Fowler et al., 2005; Davies et al., 2005). On average, xSO_4^{2-} in acid moorland and forested streams was around five times higher than mean rainfall concentrations at High Muffles during the same period. This discrepancy could be explained by a combination of dry deposition and high evapotranspiration rates, and/or by the release of stored S from the soil. Atmospherically-deposited SO_4^{2-} can be reduced and assimilated in soil organic matter, and subsequently re-oxidised and leached. Previous studies have shown substantial release of SO_4^{2-} from peats following drought (Adamson et al., 2001; Bottrell et al, 2004) or water table drawdown via gully erosion (Daniels et al., 2008). The assimilation of rainfall SO_4^{2-} by plant-soil systems to form organic S compounds, and their subsequent re-oxidation to SO_4^{2-}, are not thought to result in a significant change in $\delta^{34}S$ (Mayer et al., 1995; Schiff et al., 2005). Thus, S isotope data cannot differentiate between directly and indirectly derived atmospheric SO_4^{2-}. Ratios of Cl^- to xSO_4^{2-} in the acid moorland and forested sites are similar to those in rainfall, suggesting that evaporative concentration remains a possible explanation for high observed SO_4^{2-} concentrations. However, this would require a ca. 80% evapotranspiration rate, whereas flow gauging stations in the region (http://www.ceh.ac.uk/data/nrfa/index.html) suggest an actual value of around 50%. The overall contribution of SO_4^{2-} release from organic soils is thus uncertain, but may be significant; this is discussed further below.

Whilst xSO_4^{2-} concentrations were exceptionally high, inorganic N leaching from the moorland area (over 90% as NO_3^-) was notably low. Several studies have shown a general inverse relationship between NO_3^- leaching and soil carbon richness, as reflected in DOC concentrations (Goodale et al., 2005; Evans et al., 2006; Taylor and Townsend, 2010). The high-DOC streams of the North York Moors might therefore be expected to show low rates of NO_3^- leaching. However, peaty catchments in the South Pennines exposed to similarly high rates of N deposition have much higher rates of NO_3^- leaching (Helliwell et al., 2007). This has been attributed to the degradation of peatlands in the Pennines, in particular the loss of *Sphagnum* cover (Curtis et al., 2005), in part due to S deposition (Tallis, 1987), which has greatly decreased peat formation and contributed to widespread gully erosion. In

comparison, despite similarly high S deposition and reduced *Sphagnum* due to rotational moorland burning, the North York Moors appear to retain their N sink function. It has been suggested that low-intensity moorland burning can slow the onset of N saturation (e.g. Carroll et al., 1999), although other studies have shown substantially increased NO_3^- leaching following more intensive burns (e.g. Cresser et al., 2004). The reasons for continued high atmospheric N retention in the North York Moors thus remain uncertain.

Compared to streams draining moorland areas, those draining conifer plantations have strongly contrasting chemistry. Both SO_4^{2-} and NO_3^- concentrations were greatly elevated, which can partly be attributed to increased canopy interception of atmospheric pollutants, along with increased evapotranspiration by the forest. However the proportionally greater (fivefold) increase in NO_3^- leaching suggests that afforestation has led to a more dramatic shift in ecosystem status, from strong N retention to severe N saturation. This does not appear simply to reflect greater soil N-enrichment, since the C/N ratio of organic matter in runoff is actually higher in the forest streams. Topsoil radiocarbon measurements (Tipping et al., 2010; E. Tipping pers comm.) suggest that forests develop a larger pool of actively cycling organic matter, which leads to greater N mineralisation, and therefore greater potential for inorganic N leaching. A further possibility is that deeper rooting depths and water table drawdown in afforested soils may lead to more runoff passing through deeper (mineral) soil flowpaths, which has been shown to lead to greater mineralisation, nitrification and subsequent NO_3^- leaching (Evans et al., 2008a). Some evidence in support of this mechanism is provided by higher base cation concentrations and, in particular, much higher Al concentrations in forest streams. Higher Al concentrations cannot be explained simply by more acid conditions, since the mean pH of forest streams is similar to that of acid moorlands (Figure 5g). In other words, there has been an increase in the ratio of Al to hydrogen ions (often expressed via the 'Gibbsite' constant, which assumes a pH-dependent solubility control on Al concentrations, e.g. Reuss and Johnson, 1987). This strongly suggests greater routing of water through Al-rich mineral soils in the forest catchments.

The survey data suggest an abrupt transition between acid (pH < 5) and alkaline (pH > 6) surface waters at the moorland fringe, highlighting the crucial role of geology and soil type in determining surface water chemistry. The long-term pH data from Danby Dale illustrate this transition within a single catchment draining the moorland fringe. The Danby Beck monitoring site, draining the moorland plateau, has a mean pH of 3.8. Botton Pond, although adjacent to the Danby Beck sampling point, drains mainly mineral soils on the valley sides, and has a mean pH of 5.9. We interpret this chemical transition as a shift from shallow runoff through blanket peats and organic horizons on the moorland plateau, to deeper runoff through more well-buffered mineral soils in the valleys, coinciding with the transition from base-poor sandstone to more base-rich shale bedrock. Our results are consistent with previously noted hydrochemical variations through upland-lowland and peat-mineral soil transitions (e.g. Soulsby et al., 2003, Clark et al., 2007), and with the contrasting temporal pattern of pH variation of the two sites. Sustained low pH at Danby Beck suggests that runoff from the peats remains hydrologically isolated from more alkaline underlying mineral soils and bedrock for most of the year. Short periods of elevated summer pH at Danby Beck can be explained by a higher proportion of runoff deriving from this underlying mineral material during dry periods. This pattern of pH variation is similar to other catchments where blanket peats overlie more alkaline bedrock, including Moor House

in the North Pennines (Monteith et al., this issue), the River Etherow in the South Pennines (Monteith and Evans, 2000), and the Upper Conwy in North Wales (Austnes et al., 2010). However, Danby Beck appears more severely and consistently acidic than any other UK monitoring site. At Botton Pond, pH is generally circumneutral, but with severe episodic pH depressions. This can be explained by predominantly mineral soil-derived runoff during most flow conditions, interspersed with periods of rapid, acidic runoff from headwater peats. Surface water chemistry in this moorland-edge transition zone are thus likely to be temporally as well as spatially variable, as was also observed in a one-year pH monitoring study at the Brocka Beck (located 1 km downstream of our sampling site on this stream) by McNish et al. (1997).

4.2. Drivers of acidification and recovery

In the moorland area of the North York Moors, it is clear that N deposition makes only a marginal contribution to acidification, due to high soil N retention. NO_3^- leaching is a more important cause of acidification in the afforested areas, but the long-term trajectory of NO_3^- change in these areas is unknown. Measurements in forest catchments in Wales show that NO_3^- leaching is strongly influenced by forest age and management, tending to peak as the trees mature and immediately after felling, and to decrease during the early stages of forest regrowth (e.g. Stevens et al., 1995). In the past, it is likely that HCl deposition, emitted by coal-burning power stations to the southwest, contributed to acidification, and that the removal of HCl during the 1990s therefore contributed to recovery (Figure 2c; Evans et al., 2011). However, the survey data suggest that the dominant cause of acidification in this area, as elsewhere, has been S deposition, as reflected in exceptionally high surface water SO_4^{2-} concentrations.

Given the sharp reduction in S deposition over the last two decades (Figure 2a), the very modest pH increases observed at the Danby Dale monitoring sites, particularly the acidic Danby Beck, are surprising. Two factors could help to explain the apparent persistence of acidification. First, SO_4^{2-} retention in organic soils may have led to a 'pollution legacy' of accumulated S, which is vulnerable to later release, as has been recognised in other polluted peatland areas such as the South Pennines (Daniels et al., 2008). Re-oxidation and leaching of SO_4^{2-} can occur during and after periods of water table drawdown, and given the low rainfall and shallow peats of the North York Moors, these periods may be frequent and persistent here. High observed SO_4^{2-} concentrations relative to contemporary S deposition, and to surface waters in other peatland areas, provide some support for this explanation. Furthermore, periods of observed surface water re-acidification in the mid 1990s and in 2003-2005 (Figure 3) coincide with drought events in 1994-1995 and 2003, which triggered pulses of SO_4^{2-} release at the Moor House peatland monitoring site (Adamson et al., 2001; Evans et al., 2011). Although we cannot be certain in the absence of long-term surface water SO_4^{2-} data from the North York Moors, release of 'legacy' S from the peats appears a likely explanation for the slow recovery of this region.

Two further, perhaps parallel, explanations for limited change in surface water pH are possible. Firstly, given the extreme degree of acidification, much of the reduction in acid anion leaching may have been counterbalanced by (unmeasured) decreases in inorganic Al, rather than in H^+ concentration. This has been observed at the Scoat Tarn AWMN site in the

Lake District (Monteith et al., this volume), although this site drains comparatively mineral soils with higher inorganic Al leaching. A second factor could be an increase in organic acidity associated with rising DOC concentrations. Although we do not have DOC time series data from the region, DOC increases appear near-ubiquitous in the UK uplands during the last 20 years, including the nearby Pennines (Worrall et al., 2004; Monteith et al., 2007). These increases have been linked to reductions in S deposition (e.g. Monteith et al., 2007), based on a solubility-related mechanism first proposed by Krug and Frink (1983). They argued that the replacement of (natural) organic acidity by (anthropogenic) mineral acidity would buffer organic soils and waters against any acidification, an argument which was subsequently refuted (e.g. Reuss et al., 1987). However, subsequent data have shown that the mechanism does represent a *partial* buffer to pH change; for UK streams, increases in organic acidity associated with rising DOC have buffered on average one third of the reductions SO_4^{2-} deposition (Evans et al., 2008b). In the organic soils of the North York Moors, this proportion could be higher, but it is doubtful whether this mechanism alone could explain the very low rates of pH change at Danby Beck.

Finally, large intra- and inter-annual pH variations at the Danby monitoring sites highlight the important influence of climatic factors on runoff acidity. As noted above, drought-rewetting periods lead to release of stored SO_4^{2-} and to sustained periods of re-acidification. Although the store of S available for mobilisation is finite, it may be sufficient to cause prolonged acid pulses for years or decades to come (Aherne et al., 2006; Wright, 2008). Furthermore, increasing severity of droughts, or even the long-term degradation of the peatland due to climate change (Clark et al., 2010), may release progressively greater amounts of the S accumulated over more than a century of deposition, with detrimental consequences for runoff acidity. Similarly, the acid episodes which characterise lower-elevation catchments such as Botton Pond may persist in the future, for as long as the peatland headwaters and organic horizons remain acidified. Again, these episodes could be exacerbated by climate change if this leads to more frequent or extreme rain events (Evans et al., 2008c).

4.3. Ecological impacts of past and current water quality in the North York Moors

Our results suggest that acidification has been, and remains, a serious cause of water quality degradation in the North York Moors. The survey data suggest that chronic acidification extends across most of the moorland area, where elevated Al concentrations and consistently negative ANC indicate toxic conditions for fish, invertebrates and other aquatic biota. These conditions are intensified by conifer afforestation, with streams draining forest plantations having exceptionally high Al concentrations. Data on the status of aquatic biota across the region are sparse, but a recent survey of the upper Derwent and Esk catchments (North York Moors National Park Authority, 2008b) concluded that some watercourses were too acidic to support significant fish stocks, attributing this to a combination of acid deposition, forestry, and mine drainage (to our knowledge, the latter did not affect any of our study catchments).

For the Danby Dale sites, some additional information is available. Botton Pond was stocked with 180 two-year old brown trout in 1992. In September 1993, during an acid episode in which pH fell to 3.9 (Figure 3d), many of these fish were killed. The remainder gradually died

out and the pond was not restocked. Acid episodes of a similar magnitude have continued through the monitoring period, most recently a value of 3.8 recorded in February 2010, which occurred despite the pond having a circumneutral mean pH of 6.2 during the last 5 years (Figure 3d). Based on these observations, as well similar (albeit less severe) pH depressions at Brownhill Spring and the data of McNish et al. (1997), we speculate that acid episodes continue to have negative effects on aquatic biota in many streams around the moorland fringe. These conditions cannot be attributed to 'natural' acidity, to which poor water quality in headwaters of the Esk (a river which has seen severe salmon fishery decline since the 1960s) was previously attributed (North York Moors National Park Authority, 2001). Indirect evidence of acidification impacts on aquatic invertebrates is provided by a survey of the diet of shrews living adjacent to Danby Beck and Botton Pond, undertaken by Capes (2005). Under favourable conditions, aquatic prey would be expected to comprise over 50% of their diet at these locations, but the survey found no evidence of any aquatic prey consumption. Finally, the diatom survey of Danby Beck matched the chemical data; the very few species present were all typical of highly acidic environments, in the UK and elsewhere in Europe (e.g. van Dam et al. 1981, Kwandrans 1989). *Eunotia exigua* in particular is often abundant in acid mine drainage water (cf Hargreaves et al. 1975) and its dominance in Danby Beck and other sites in the North Yorkshire Moors (Battarbee, unpublished), almost to the exclusion of other taxa, is consistent with the interpretation that these moorland streams have been severely acidified. Provisional palaeoecological data from Grey Heugh's Slack, a moorland pool on Fylingdales Moor (Battarbee, unpublished) also indicate that *E. exigua* has become increasingly abundant in the sediment record. These observations support the inference that surface waters in the North York Moors, although naturally acidic, have become more so as a result of long term pollution by acid deposition. Collectively, the biological evidence suggests severe impoverishment of the aquatic ecosystem at all trophic levels due to anthropogenic acidification.

4.4. Implications for upland monitoring

The 2005 survey, together with 20-year pH records from Danby Dale, demonstrate that acidification in the North York Moors is extensive, and exceptionally severe. Furthermore, the long-term data suggest that recovery may be progressing more slowly than in other upland areas. The lack of any formalised or comprehensive water quality monitoring from the North York Moors represents a major gap in current UK upland monitoring programmes such as the AWMN and ECN, with implications for accurate national-scale quantification of the extent of atmospheric pollutant impacts on upland ecosystems. The existence of a robust, continuous pH record for the Danby Dale sites is a testament to the remarkable efforts of volunteers over a 20 year period. With declining research and monitoring budgets, and a growing emphasis on voluntary activities at a UK national scale, these efforts could provide a template for environmental monitoring more widely. The careful integration of such voluntary activities into structured national-scale programmes would add greatly to their value.

The pH monitoring data also have implications for the design of water quality monitoring programmes. Over short distances, streams draining acid uplands such as Danby Beck can undergo a rapid chemical transitions, from near-continuous (chronic) acidification in the headwaters, to circumneutral conditions interspersed with acidic episodes downstream.

Because intensive monitoring usually occurs at single locations within a catchment, this longitudinal change in water quality dynamics is rarely recorded. In practice, monitoring sites are often selected based on logistical factors such as road access, or on regulatory factors such as the emphasis of the Water Framework Directive (WFD) on catchments greater than 10 km^2. Bishop et al. (2008) noted that WFD requirements on minimum catchment size excluded over 90% of the river length from monitoring programmes in Sweden. Monitoring larger catchments will lead to the under-representation of, or even failure to detect, upland water quality problems which may be acute, as well as environmentally and (in the case of commercial fisheries) economically significant. This issue is of particular concern in the heterogeneous UK landscape, where it is rare to find catchments greater than 10 km^2 that include only upland semi-natural ecosystems. Better representation and siting of upland monitoring sites within existing regulatory programmes would greatly enhance our ability to detect and attribute environmental change in upland landscapes, areas which are critically important to biodiversity, and to ecosystem services ranging from the provision of drinking water and aquatic habitat provision to recreation and carbon sequestration.

ACKNOWLEDGEMENTS

The North York Moors water survey and analysis of data were supported by the UK Department for Environment, Food and Rural Affairs (Defra) as part of the Critical Loads and Dynamic Modelling programme, Contract No. AQ0801. The long-term monitoring of sites in Danby Dale has been undertaken voluntarily by Tom Chadwick, Philip Brown and others over a 20 year period. We appreciate the positive suggestions of two anonymous reviewers.

REFERENCES

Adamson, J.K., Scott, W.A., Rowland, A. ., Beard, G.R. 2001. Ionic concentrations in a blanket peat bog in northern England and correlations with deposition and climate variables, Eur. J. Soil Sci. 52, 69-79.

Aherne, J., Larssen, T., Cosby, B.J., Dillon, P.J. 2006. Climate variability and forecasting surface water recovery from acidification: Modelling drought-induced sulphate release from wetlands. Sci. Total Environ. 365, 186-199.

Austnes, K., Evans, C.D., Eliot-Laize, C., Naden, P.S., Old, G.H. 2009. Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. Biogeochemistry, 99, 157-173.

Battarbee, R.W., Monteith, D.T., Juggins, S., Evans, C.D., Jenkins, A., Simpson, G.L. 2005. Reconstructing pre-acidification pH for an acidified Scottish loch: a comparison of palaeolimnological and modelling approaches. Environ. Pollut. 137, 135-149

Battarbee et al. this volume

van Dam, H., Suurmond, G., ter Braak, C.J.F. 1981. Impact of acidification on diatoms and chemistry of Dutch moorland pools. Hydrobiologia, 83, 425-459.

van Dam, H., Mertens, A. 1990. A comparison of recent epilithic diatom assemblages from the industrially acidified and copper polluted Lake Orta (Northern Italy) with old literature data. Diatom Research, 5, 1-13.

Bishop K, Buffam I, Erlandsson M, Fölster J, Laudon H, Seibert J, Temnerud J. 2007. Aqua Incognita: the unknown headwaters. Hydrol. Process. 22, 1239-1242

Bottrell, S., Coulson, J., Spence, M., Roworth, P., Novak, M., Forbes, L. 2004. Impacts of pollutant loading, climate variability and site management on the surface water quality of a lowland raised bog, Thorne Moors, E. England, UK, Appl. Geochem. 19, 413-422.

Capes, D. 2005. Water Shrews in Danby Dale, North Yorkshire - Their Diet and Habitat. J. Yorkshire Mammal Group 32, 36-41.

Carroll, J.A., Caporn, S.J.M., Cawley, L., Read, D.J., Lee, J.A. 1999. The effect of increased deposition of atmospheric nitrogen on *Calluna vulgaris* in upland Britain. New Phytol. 141, 423-431

Chadwick, T. 2001. Monitoring acid rain on the North York Moors: Summary report of a ten year programme of monitoring from 1990 to 2000. Environet Environmental Monitoring, Whitby.

Clark, J.M., Lane, S.N., Chapman, P.J., Adamson, J.K., 2007. Export of dissolved organic carbon from an upland peatland during storm events: implications for flux estimates. J. Hydrol. 346, 438-447.

Clark, J.M., Gallego-Sala, A.V., Allott, T.E.H., Chapman, S.J., Farewell, T., Freeman, C., House, J.I., Orr, H.G., Prentice, C., Smith, P. 2010. Assessing the vulnerability of blanket peat to climate change using an ensemble of statistical bioclimatic envelope models. Clim. Res. 45, 131-150.

Cresser, M.S., Smart, R.P., Clark, M., Crowe, A., Holden, D., Chapman, P.J., Edwards, A.C. 2004. Controls on leaching of N species in upland moorland catchments. Water, Air, Soil Pollut.: Focus 4, 85-05.

Curtis, C.J., Emmett, B.A., Grant, H., Kernan, M., Reynolds, B., Shilland, E. 2005. Nitrogen saturation in UK moorlands: the critical role of bryophytes and lichens in determining retention of atmospheric N deposition. J. Appl. Ecol. 42, 507-517.

Daniels, S.M., Evans, M.G., Agnew, C.T., Allott, T.E.H. 2008. Sulphur leaching from headwater catchments in an eroded peatland, South Pennines, U.K. Sci. Total Environ. 407, 481-496.

Davies, J.J.L, Jenkins, A., Monteith, D.T., Evans, C.D. and Cooper, D.M., 2005. Trends in surface water chemistry of acidified UK freshwaters, 1988-2002. Environ. Pollut. 137, 27-39

Evans, C.D., Jenkins, A., Wright, R.F. 2000. Surface water acidification in the South Pennines I. Current status and spatial variability. Environ. Pollut. 109, 11-20

Evans, C.D., Cullen, J.M., Alewell, C., Kopáček, J, Marchetto, A., Moldan, F., Prechtel, A., Rogora, M., Veselý, J. Wright, R. 2001. Recovery from acidification in European surface waters. Hydrol. Earth Syst. Sci. 5, 283-298

Evans, C.D., Reynolds, B., Jenkins, A., Helliwell, R.C., Curtis, C.J., Goodale, C.L., Ferrier, R.C., Emmett, B.A., Pilkington, M.G., Caporn, S.J.M., Carroll, J.A., Norris, D., Davies, J., Coull, M.C. 2006. Evidence that soil carbon pool determines susceptibility of semi-natural ecosystems to elevated nitrogen leaching. Ecosystems 9, 453-462.

Evans, C.D., Norris, D., Ostle, N., Grant, H., Rowe, E., Curtis, C.J., Reynolds, B. 2008a. Rapid immobilisation and leaching of wet-deposited nitrate in upland organic soils. Environ. Pollut. 156, 636-643.

Evans, C.D., Monteith, D.T., Reynolds, B., Clark, J.M. 2008b. Buffering of recovery from acidification by organic acids. Sci. Total Environ. 404, 316-325.

Evans, C.D., Reynolds, B., Hinton, C., Hughes, S., Norris, D., Grant, S., Williams, B. 2008c. Effects of decreasing acid deposition and climate change on acid extremes in an upland stream. Hydrol. Earth Syst. Sci. 12, 337-351.

Evans, C.D., Monteith, D.T., Fowler, D., Cape, J.N., Brayshaw, S. 2011. Hydrochloric acid: An overlooked driver of environmental change. Environ. Sci. Technol. (in press).

Fowler, D., Smith, R.I., Muller, J.B.A., Hayman, G., Vincent, K.J. 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environ. Pollut. 137, 15-25.

Goodale, C.L., Aber, J.D., Vitousek, P.M., McDowell, W.M. 2005. Long-term decreases in stream nitrate: Successional causes unlikely; possible links to DOC? Ecosystems 8, 334-337.

Hall J., Ullyett, J., Heywood, L., Broughton, R. 2004. Update to: The Status of UK Critical Loads – Critical Loads Methods, Data and Maps. February 2004. Report to Defra (Contract EPG 1/3/185). (http://cldm.defra.gov.uk).

Hargreaves, J. W., Lloyd, E.J.H., Whitton, B.A. (1975). Chemistry and vegetation of highly acidic streams. Freshwater Biology, 5, 563–576.

Heaton, T.H.E., Spiro, B. and Robertson, S.M.C. 1997. Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition. Oecologia, 109, 600-607.

Helliwell, R.C., Wright, R.F., Evans, C.D., Jenkins, A., Ferrier, R.C. 2002. A comparison of loch chemistry from 1955 and 1999 in the Cairngorms, N.E. Scotland Water Air Soil Pollut.: Focus 2, 47-59.

Helliwell, R.C., Coull, M.C., Davies, J.J.L., Evans, C.D., Norris, D., Ferrier, R.C., Jenkins, A., Reynolds, B. 2007. The role of catchment characteristics in determining surface water nitrogen in four upland regions in the UK. Hydrol. Earth Syst. Sci. 11, 356-371.

Henriksen, A., Fjeld, E., Hesthagen, T. 1999. Critical load exceedance and damage to fish populations. Ambio 28, 583-586.

Hornung, M., Bull, K.R., Cresser, M., Ullyett, J., Hall, J.R., Langan, S., Loveland, P.J. 1995. The sensitivity of surface waters of Great Britain to acidification predicted from catchment characteristics. Environ. Pollut. 87, 207-214.

Jarvis, R.A, Bendelow, V.C., Bradley, R.I., Carroll, D.M., Furness, R.R., Kilgour, I.N.L., King, S.J. 1984. Soils and their use in Northern England. Soil Survey of Envland and Wales, Bulletin No. 10, Harpenden, UK.

Kopáček, J., Stuchlík, E., Hardekopf, D., 2006. Chemical composition of the Tatra Mountains lakes: recovery from acidification. Biologia Bratislava 61 (Suppl 18), 21–33.

Kwandrans, J. (1993). Diatom communities of acidic mountain streams in Poland. Hydrobiologia 269/270, 335-342

Krug, E.C., Frink, C.R. 1983. Acid rain on acid soil: a new perspective. Science 221, 520-5.

Lallier-Vergès, E., Hayes, J.M., Boussafir, M., Zaback, D.A., Tribovillard, N.P., Connan, J., and Bertrand, P. 1997. Productivity-induced sulphur enrichment of hydrocarbon-rich sediments from the Kimmeridge Clay Formation. Chemical Geology, 134, 277-288.

Lawrence, H., Vincent, K., Donovan, B., Davies, M., Smith, M., Colbeck, C., Tang, Y.S., van Dijk, N., Anderson, M., Simmons, I., R.I., Smith, Cape, J.N., Fowler, D., Sutton M.A., 2008. UK Acid Deposition Monitoring Network: Data Summary 2007. Report to the Department for Environment, Food and Rural Affairs and the Devolved Administrations, AEAT/ENV/R/2706.
(http://www.airquality.co.uk/reports/cat04/0812231140_Acid_dep_2007_Issue_1.pdf)

Lien, L., Raddum, G. G., Fjellheim, A., and Henriksen, A. 1996. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Sci. Total Environ. 177, 173–193.

McNish, J.H., Labadz, J.C., Butcher, D.P. 1997. Assessing variability of acidity in Yorkshire rivers, with special reference to the acid sensitive headwaters of the Esk catchment. British Hydrological Society 6th National Hydrology Symposium, Salford, pp. 2.1-2.7.

Mayer, B., Feger, K.H., Giesemann, A. and Jager, H-J. 1995. Interpretation of sulfur cycling in two catchments in the Black Forest (Germany) using stable sulfur and oxygen isotope data. Biogeochemistry, 30, 31-58.

Monteith, D.T., Evans, C.D. (Eds.) 2000. The UK Acid Waters Monitoring Network: Ten Year Report. Analysis and interpretation of results, 1988-1998. ENSIS Publishing, London (ISBN 1 871275 26 1). 363 pp.

North York Moors National Park Authority, 2001. River Esk Regeneration Programme, July 1997 - October 2001, Final Report, 37 pp.

North York Moors National Park Authority, 2008a. Moorland Habitat Action Plan, 2008-2012, 6 pp. (http://www.northyorkmoors.org.uk/uploads/publication/8478.pdf)

North York Moors National Park Authority, 2008b. Rivers and Streams Habitat Action Plan, 2008-2012, 4 pp. (http://www.northyorkmoors.org.uk/uploads/publication/8480.pdf)

Novak, M., Bottrell, S.H., and Prechova, E., 2001. Sulphur isotope inventories of atrmospheric deposition, spruce forest floor and living Sphagnum along a NW-SE transect across Europe. Biogeochemistry, 53, 23-50.

Renberg, I., 1986. A sedimentary diatom record of severe acidification in Lake Blåmissusjön, N. Sweden, through natural processes. In Diatoms and Lake Acidity, ed. J.P. Smol, R.W. Battarbee, R.B. Davis, & J. Meriläinen. Dordrecht, The Netherlands: Dr. W. Junk, pp. 213-219

Reuss, J.O., Cosby, B.J., Wright, R.F. 1987. Chemical processes governing soil and water acidification. Nature 329, 27-33.

RoTAP. Review of Transboundary Air Pollution. 2011. Report to the Department of Environment, Food and Rural Affairs, Centre for Ecology and Hydrology, Edinburgh.

Schiff, S.L., Spoelstra, J., Semkin, R.G. and Jeffries, D.S. 2005. Drought induced pulses of SO_4^{2-} from a Canadian shield wetland: use of δ34S and δ18O in SO_4^{2-} to determine sources of sulfur. Applied Geochemistry, 20, 691-700.

Shilland, E.M., Kernan, M, Monteith, D.T., Curtis, C.J., Battarbee, R. 2011. Surface water acidification in the UK and the Acid Waters Monitoring Network. Ecol. Indicat (this issue)

Shilland E.M., Irvine, L., Malcolm, I.A. (Eds.) (2010) UKAWMN Summary of Data for Year 21 (2008-2009). Report to the Department for Environment, Food and Rural Affairs (Contract EPG 1/3/160)

Soulsby C., Rodgers P., Smart R., Dawson J., Dunn, S. 2003. A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. Hydrol. Process. 17, 759-777

Stevens, P.A., Norris, D.A., Williams, T.G., Hughes, S., Durrant, D.W.H., Anderson, M.A., Weatherley, N.S., Hornung, M., Woods, C. 1995. Nutrient losses after clearfelling in Beddgelert Forest: A comparison of the effects of conventional and whole-tree harvest on soil water chemistry. Forestry, 68, 115-131.

Stoddard, J.L., Kahl, J.S., Deviney, F.A., De Walle, D.R., Driscoll, C.T., Herlihy, A.T., Kellogg, J.H., Murdoch, P.S., Webb, J.R., Webster, K.E. 2003. Response of surface water chemistry to the clean air act amendments of 1990. Report EPA 620/R-03/001. United States Environmental Protection Agency, North Carolina.

Tallis, J.H. 1987. Fire and flood at Holme Moss: erosion processes in an upland blanket mire. J. Ecol. 75, 1099-1129.

Taylor, P.G., Townsend, A.T. 2010. Stoichiometric control of organic carbon-nitrate relationships from soils to the sea. Nature 464, 1178-1181.

Tichomirowa, M., Haubrich, F., Klemm, W. and Matschullat, J. 2007. Regional and temporal (1992–2004) evolution of air-borne sulphur isotope composition in Saxony, southeastern Germany, central Europe. Isotopes Environ. Health Studies, 43, 295-305.

Tipping, E., Smith, E.J., Lawlor, A.J., Hughes, S., Stevens, P.A. 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. Environ. Pollut. 123, 239-253

Tipping, E., Chamberlain, P.M., Bryant, C.L., Buckingham, S. 2010. Soil organic matter turnover in British deciduous woodlands, quantified with radiocarbon. Geoderma 155, 10-18.

Wadleigh, M.A., Schwarcz, H.P. and Kramer, J.R. 2001. Areal distribution of sulphur and oxygen isotopes in sulphate of rain over eastern North America. Journal of Geophysical Research, 106, 20883-20895.

Wright, R.F. 2008. The decreasing importance of acidification episodes with recovery from acidification: an analysis of the 30-year record from Birkenes, Norway. Hydrol. Earth Syst. Sci. 12, 353-362.

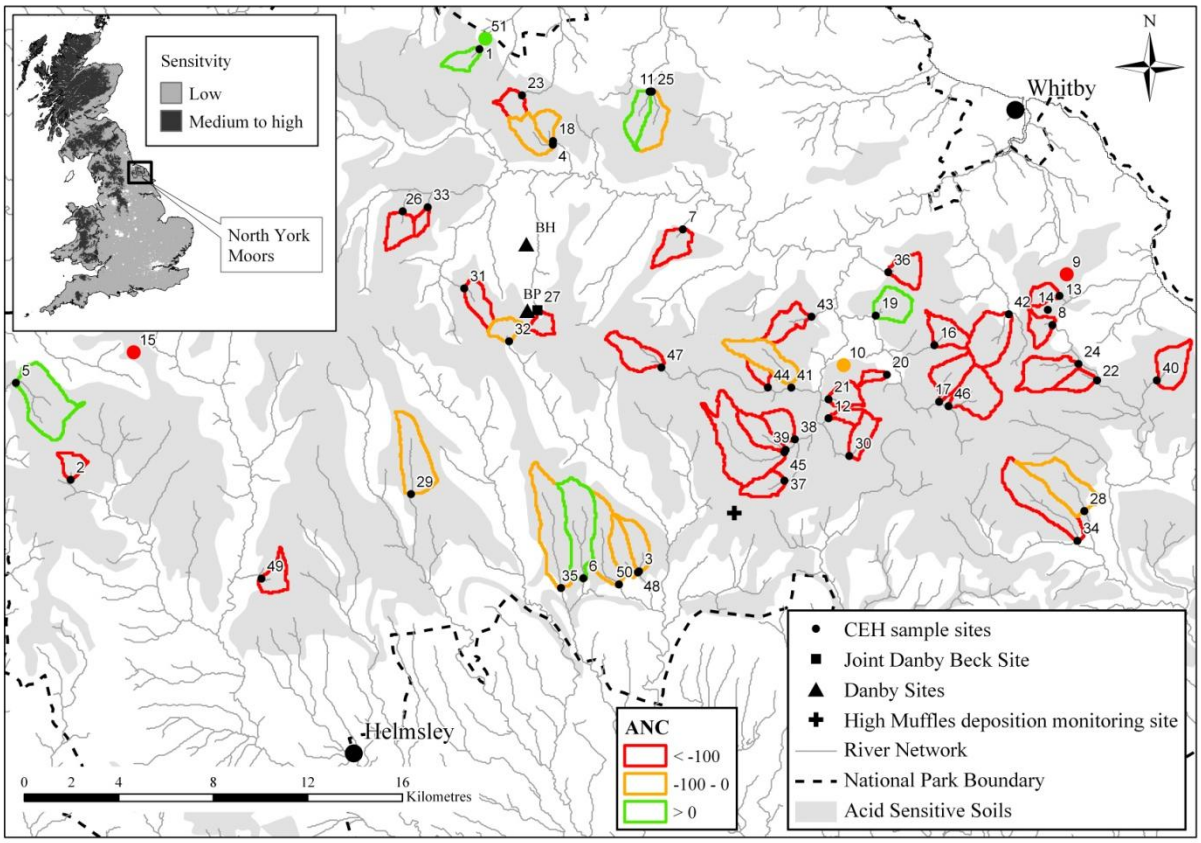

Figure 1. Areas of acid sensitive moorland and forest, and sampled catchments in the North York Moors acid waters survey. Site numbers correspond to listed sites in Table A.1., and catchment boundary colours indicate measured ANC. Circles denote sampling points, and moorland pools (sites 9, 10, 15) with small catchments and are denoted by coloured circles only. Danby Dale pH monitoring sites are denoted by a square (Danby Beck, survey site 27) and triangles (Botton Pond, BP, and Brownhill Spring, BH). The High Muffles deposition monitoring site is also shown. Acid sensitive areas in both the North York Moors and UK inset maps are derived from the low/medium sensitivity classes mapped by Hornung et al. (1995) based on soil type and geology.

ALTERNATIVE GREYSCALE FIGURE FOR PRINT VERSION

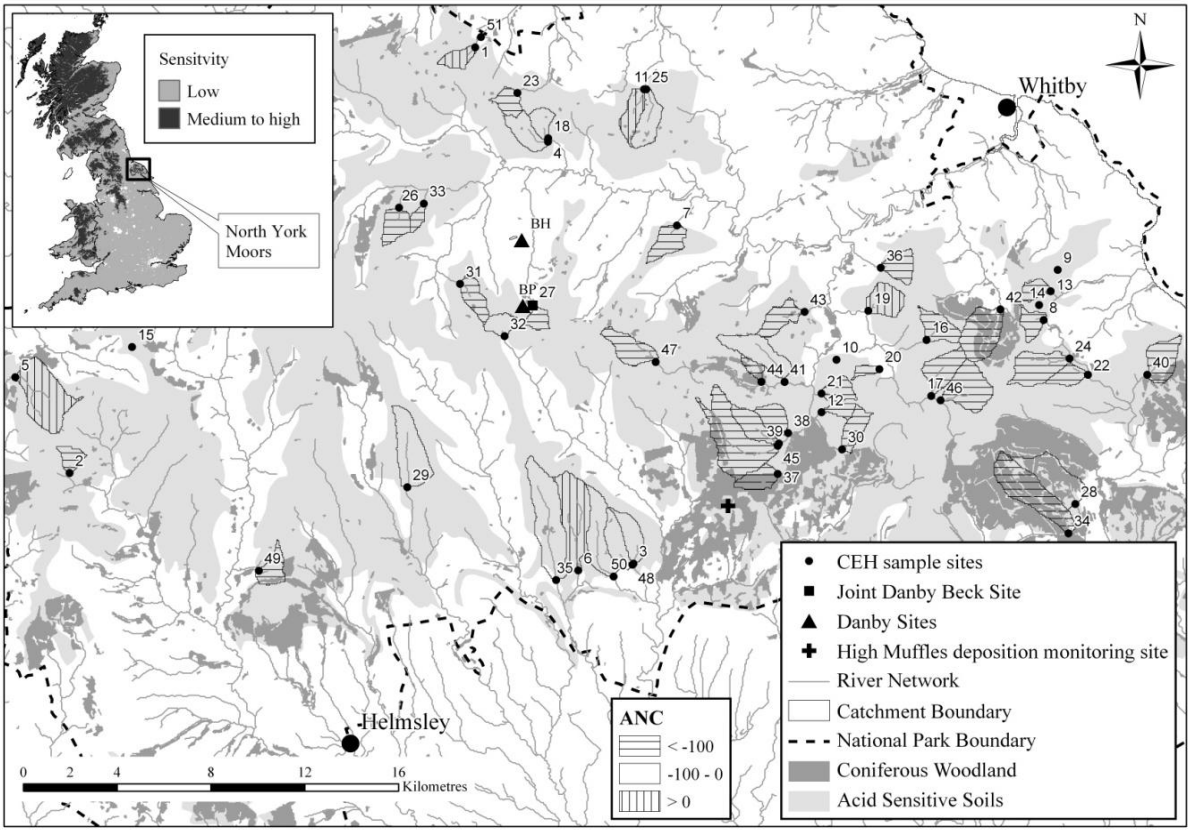

Figure 1. Areas of acid sensitive moorland and forest, and sampled catchments in the North York Moors acid waters survey. Site numbers correspond to listed sites in Table A.1., and catchment shading indicates measured ANC. Circles denote sampling points, and moorland pools (sites 9, 10, 15) with small catchments and are denoted by circles only. Danby Dale pH monitoring sites are denoted by a square (Danby Beck, survey site 27) and triangles (Botton Pond, BP, and Brownhill Spring, BH). The High Muffles deposition monitoring site is also shown. Acid sensitive areas in both the North York Moors and UK inset maps are derived from the low/medium sensitivity classes mapped by Hornung et al. (1995) based on soil type and geology.

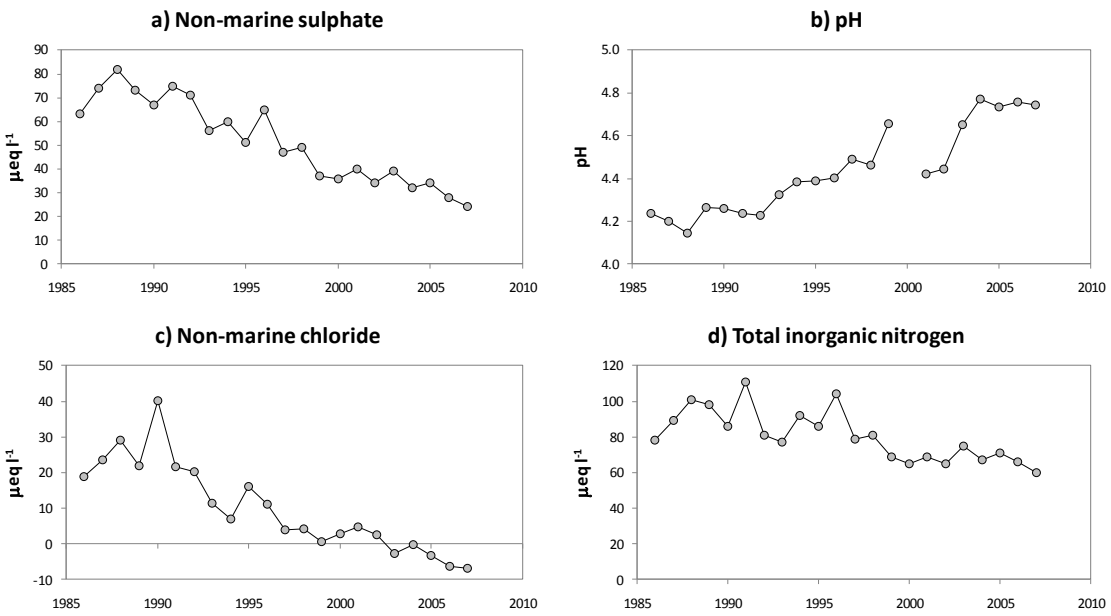

Figure 2. Annual mean precipitation chemistry at the High Muffles Acid Deposition Monitoring Network site (www.airquality.co.uk).

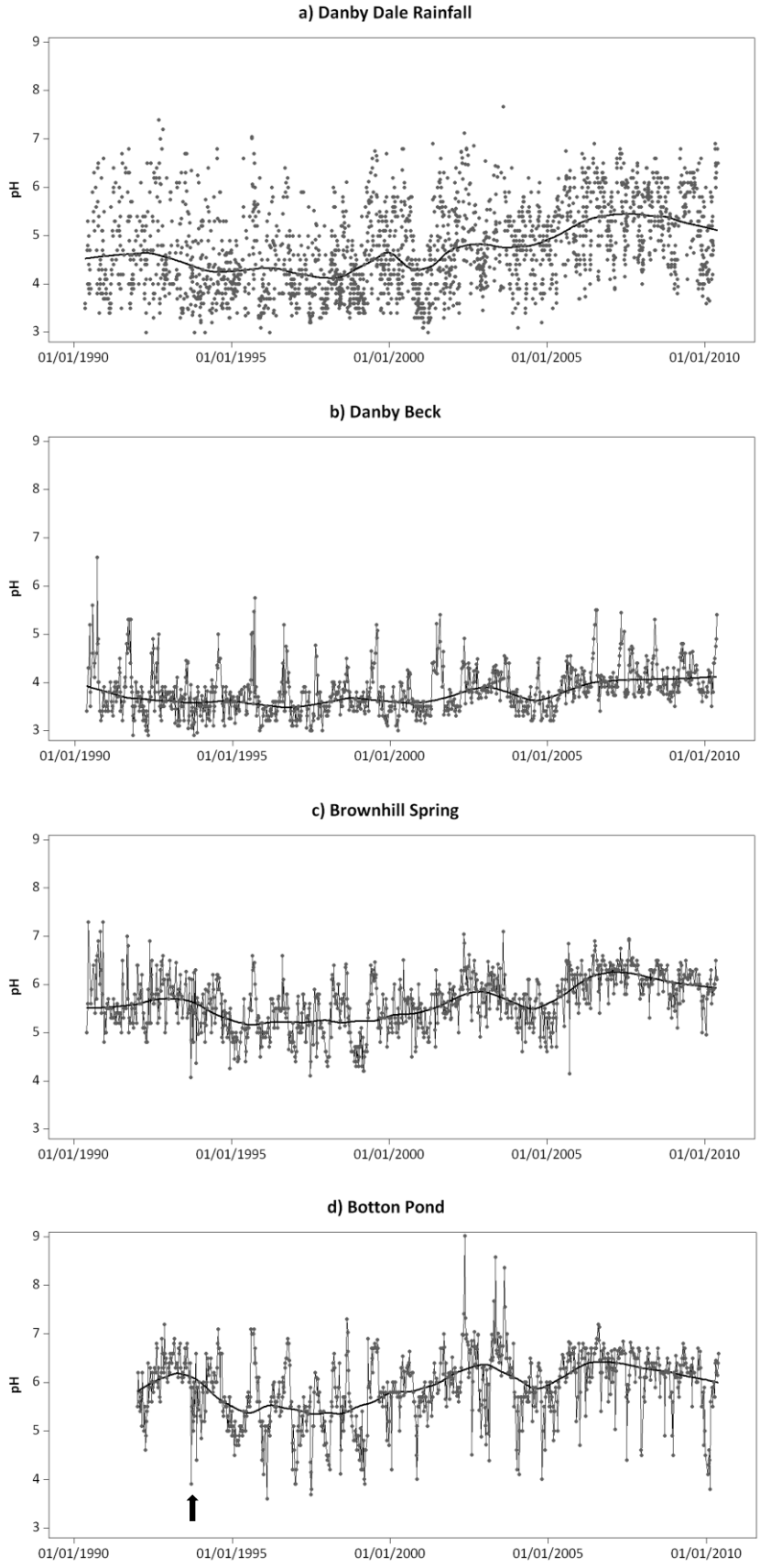

Figure 3. Rainfall and surface water pH from 1990 to 2010, Danby Dale monitoring sites. Solid lines are LOWESS best fit lines (smoothing parameter set to 0.15). Arrow in d) indicates timing of recorded fish kill event at this site.

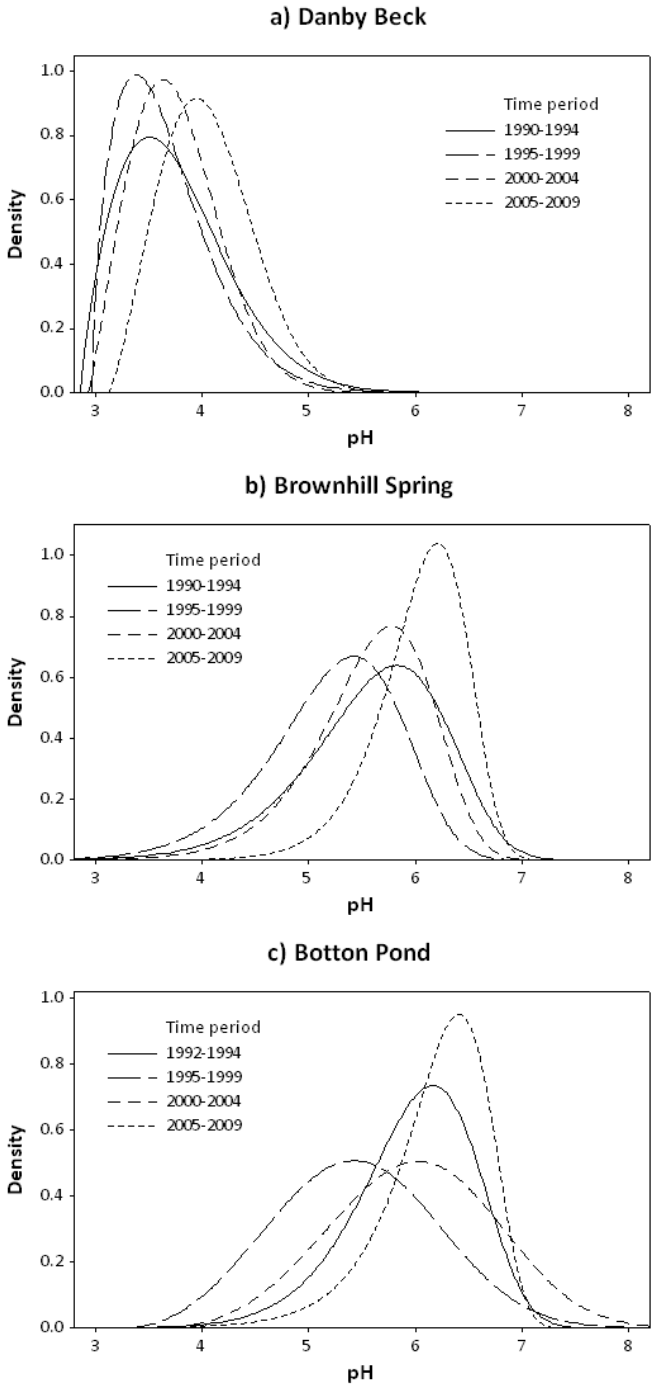

Figure 4. Frequency distribution of surface water pH data in five-year blocks, from 1990 to 2009 (1992 to 2009 at Botton Pond).

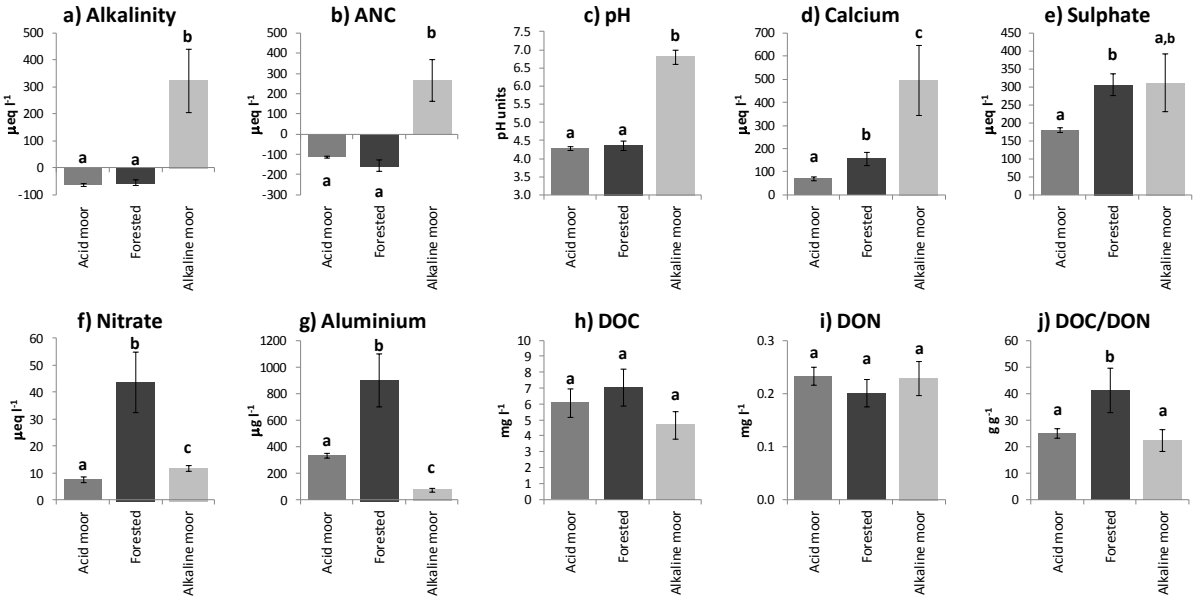

Figure 5. Mean and standard error of a range of water chemistry parameters measured during the 2005 spatial survey, classified into acid moorland (36), alkaline moorland (6) and forested (9) catchments. Error bars show standard error of mean, different letters indicate a significant ($p < 0.05$) concentrations difference between catchment classes, based on two-sample t-tests.

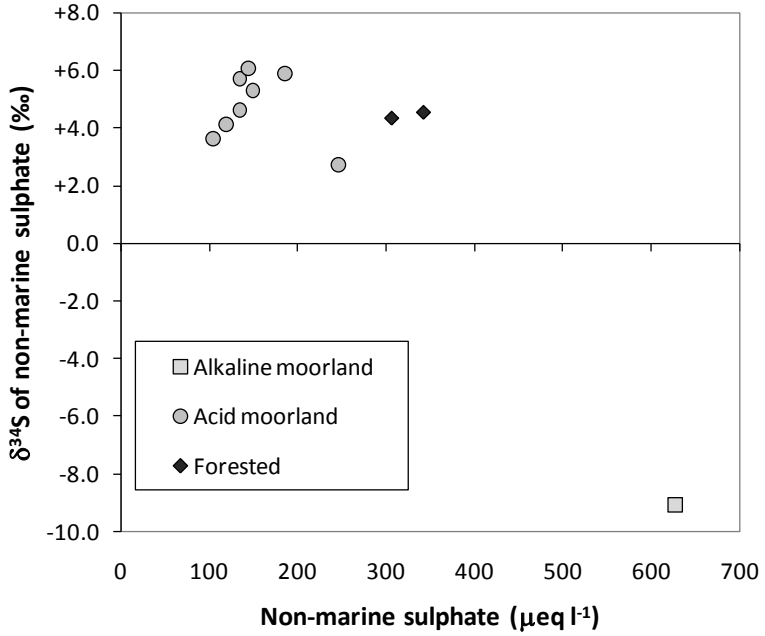

Figure 6. Sulphur isotope signature of non-marine sulphate in composite North York Moors surface water samples, versus non-marine SO_4^{2-} concentration, of samples (see Table A.3 for details of sites and measurements)

APPENDIX

Table A.1. Survey catchment names, locations and summary characteristics

Site Number	Site name	Easting	Northing	Type	Catchment area (km^2)	Mean altitude (m)	Forest %
1	Lockwood Beck	466820	513580	Stream	0.94	260	0
2	Cringle Ing Slack	449520	495300	Stream	0.85	292	10
3	Grain Beck	473570	491420	Stream	1.58	208	0
4	Haw Rigg Slack	469920	509520	Stream	1.60	242	1
5	Crab Dale Beck	447200	499420	Stream	4.62	282	1
6	Loskey Beck	471210	491120	Stream	4.26	255	0
7	Busco Beck	475420	505930	Stream	1.56	242	0
8	Biller Howe Dale Slack	491060	501870	Stream	1.02	210	0
9	Graystone Hills Pond	491670	504020	Pond	0.00	204	0
10	The Tarn	482230	500170	Pond	0.06	216	0
11	Bog House Beck	474020	511780	Stream	1.47	235	5
12	Hollin Gill	492170	500220	Stream	2.62	226	0
13	Kirkmoor Beck	491370	503110	Stream	0.83	209	0
14	Grey Heugh Slack	490880	502520	Stream	0.35	209	0
15	Brians Pond	452180	500710	Pond	0.01	335	0
16	Brocka Beck	486070	501020	Stream	1.61	255	0
17	Sliving Sike	486270	498620	Stream	1.99	252	0
18	Ewe Crag Beck	469930	509670	Stream	0.97	238	1
19	Darnholme	483590	502270	Stream	1.77	226	0
20	Moss Dike	484060	499770	Stream	0.40	202	0
21	Hunt House	481590	498720	Stream	1.10	226	0
22	Stream S of the Island	492960	499520	Stream	1.00	200	0
23	Haw Beck	468620	511620	Stream	1.04	253	0
24	Howl Moor Dike	481590	497920	Stream	0.61	229	0
25	Bella Dale Slack	474120	511770	Stream	1.85	241	6
26	Great Hograh Beck	463570	506690	Stream	1.39	343	0
27	Danby Beck	469270	502500	Stream	0.77	398	0
28	Hipperly Beck	492420	493980	Stream	3.39	192	75
29	Ouse Gill	463920	494700	Stream	3.54	332	0
30	Simon Howe Moss	482470	496320	Stream	1.38	239	1
31	Clough Gill	466170	503420	Stream	1.36	369	2
32	River Seven	468070	501180	Stream	0.95	400	1
33	Little Hograh Beck	464620	506870	Stream	0.49	324	0
34	Stockland Beck	492120	492720	Stream	4.36	196	78
35	Hutton Beck	470270	490710	Stream	5.26	248	2
36	Spa Hill Slack	484120	504110	Stream	1.41	262	0
37	Keys Beck	479720	495270	Stream	1.32	256	78
38	Sod Fold Slack	480160	497020	Stream	1.28	228	0
39	Black Rigg Beck	479770	496570	Stream	1.61	248	0
40	Helwarth Gains	495490	499520	Stream	2.05	217	17
41	Collier Gill	480020	499220	Stream	2.68	267	1
42	May Beck	489220	502330	Stream	3.15	242	59
43	Oakly Beck	480870	502220	Stream	1.57	238	3
44	Wheel Dale	479030	499230	Stream	0.55	263	40
45	Rutmoor Beck	479720	496480	Stream	5.57	258	16
46	Little Eller Beck	486670	498430	Stream	2.95	263	0
47	Bluewath Beck	474510	500070	Stream	2.02	363	0
48	Tranmire Beck	473530	491370	Stream	1.63	209	1
49	Tod Hill Slack	457580	491110	Stream	1.27	255	16
50	Hole Beck	472720	490860	Stream	2.88	223	0
51	Lockwood Beck Res	467070	514020	Reservoir	2.27	241	1

Table A.2. Measured values of key water quality determinands at survey sites

Site Number	Site name	pH	Alkalinity μeq l^{-1}	ANC μeq l^{-1}	Aluminium μg l^{-1}	Calcium μeq l^{-1}	Sulphate μeq l^{-1}	Nitrate μeq l^{-1}	DOC mg l^{-1}
1	Lockwood Beck	6.84	236	193	110	375	241	8	8.0
2	Cringle Ing Slack	4.38	-46	-107	660	142	204	41	8.6
3	Grain Beck	4.25	-76	-98	380	45	183	12	3.5
4	Haw Rigg Slack	4.53	-29	-58	210	119	165	3	5.4
5	Crab Dale Beck	6.59	158	130	120	318	232	15	5.9
6	Loskey Beck	6.62	143	97	60	243	210	14	3.4
7	Busco Beck	4.21	-77	-115	380	42	211	1	5.5
8	Biller Howe Dale Slack	4.21	-75	-104	200	60	165	2	5.8
9	Graystone Hills Pond	3.86	-94	-127	130	55	174	0	14.0
10	The Tarn	4.35	-55	-95	330	47	180	6	7.2
11	Bog House Beck	6.1	69	19	90	182	193	12	4.6
12	Hollin Gill	4.22	-74	-139	370	49	173	4	4.3
13	Kirkmoor Beck	4.11	-83	-163	410	44	176	1	5.1
14	Grey Heugh Slack	4.1	-84	-119	220	35	157	1	7.6
15	Brians Pond	3.84	-91	-110	40	32	105	10	27.5
16	Brocka Beck	4.18	-80	-141	420	40	146	8	5.1
17	Sliving Sike	4.28	-63	-117	430	38	130	1	4.5
18	Ewe Crag Beck	4.66	-14	-75	290	109	219	1	4.1
19	Darnholme	7.51	805	667	50	1161	712	11	1.6
20	Moss Dike	4.35	-53	-151	180	65	194	5	3.3
21	Hunt House	4.11	-83	-132	480	36	129	8	6.7
22	Stream S of the Island	4.33	-58	-120	340	59	209	3	3.5
23	Haw Beck	4.45	-42	-115	310	73	156	1	3.9
24	Howl Moor Dike	4.13	-83	-126	480	47	127	4	6.6
25	Bella Dale Slack	4.92	-13	-81	210	98	208	9	2.4
26	Great Hograh Beck	4.06	-85	-151	430	31	170	8	5.5
27	Danby Beck	4.08	-83	-108	290	75	165	21	7.0
28	Hipperly Beck	5.21	12	-16	280	310	401	31	15.3
29	Ouse Gill	4.53	-23	-81	400	61	211	16	3.9
30	Simon Howe Moss	4.16	-82	-111	410	104	193	8	6.0
31	Clough Gill	4.39	-45	-103	430	109	257	16	4.0
32	River Seven	4.83	-11	-77	180	318	327	23	0.9
33	Little Hograh Beck	4.18	-78	-127	230	45	199	1	3.6
34	Stockland Beck	4.46	-35	-128	780	213	400	50	5.2
35	Hutton Beck	4.78	-9	-52	320	125	180	15	4.0
36	Spa Hill Slack	4.26	-66	-132	470	74	228	4	2.2
37	Keys Beck	4.16	-82	-248	1730	171	344	84	6.9
38	Sod Fold Slack	4.21	-74	-100	480	46	141	7	5.1
39	Black Rigg Beck	4.25	-67	-102	500	46	147	3	4.1
40	Helwarth Gains	4.12	-82	-172	510	96	288	4	4.5
41	Collier Gill	3.99	-100	-77	280	123	160	9	24.3
42	May Beck	4.67	-10	-148	1350	247	375	67	4.8
43	Oakly Beck	4.26	-65	-110	380	52	191	2	2.8
44	Wheel Dale	3.93	-91	-317	1880	89	376	95	7.9
45	Rutmoor Beck	4.27	-64	-116	490	94	175	12	5.6
46	Little Eller Beck	4.32	-55	-109	390	78	145	4	3.9
47	Bluewath Beck	3.96	-92	-165	400	40	185	9	8.6
48	Tranmire Beck	4.36	-49	-84	410	79	198	20	3.5
49	Tod Hill Slack	4.14	-80	-123	440	55	198	9	4.7
50	Hole Beck	4.66	-18	-50	260	122	177	29	4.0
51	Lockwood Beck Res	7.21	533	500	30	697	288	11	4.7

Table A.3. $^{34}S/^{32}S$ composition of composite samples (for details of sample aggregation and calculation of non-marine SO_4^{2-} $\delta^{34}S$, see Methods)

Site No.	Site name	Site type	Composite sample number	Values for composite samples: Total SO_4^{2-} μeq l^{-1}	Measured total SO_4^{2-} $\delta^{34}S$ (‰)	Estimated non-marine SO_4^{2-} (μeq l^{-1})	Estimated non-marine SO_4^{2-} $\delta^{34}S$ (‰)
19	Darnholme	Alkaline moorland stream	1	712	-5.5	627	-9.1
28	Hipperly Beck	Acid forest stream	2	400	+6.9	343	+4.5
34	Stockland Beck						
32	River Severn	Acid moorland stream	3	292	+5.6	246	+2.7
31	Clough Gill						
35	Hutton Beck	Acid moorland stream	4	184	+8.3	149	+5.3
50	Hole Beck						
3	Grain Beck						
48	Tranmire Beck						
4	Haw Rigg Slack	Acid moorland stream	5	180	+8.8	134	+4.6
23	Haw Beck						
18	Ewe Crag Beck						
24	Hullin Gill	Acid moorland stream	6	182	+9.7	135	+5.7
8	Biller Howe						
22	The Island						
21	Hunt House	Acid moorland stream	7	161	+8.5	119	+4.1
12	Howl Moor Dyke						
20	Moss Dike						
30	Simon Howe Moss						
10	The Tarn	Acid moorland pond	8	153	+9.2	104	+3.6
9	Graystone Hills						
15	Brians Pond						
44	Wheeldale Plant	Acid forest stream	9	360	+6.8	307	+4.3
37	Keys Beck						
33	Little Hograh beck	Acid moorland stream	10	178	+8.9	145	+6.1
26	Great Hograh Beck						
27	Danby Beck						
5	Crab Dale Beck	Acid moorland stream	11	214	+7.9	185	+5.9
29	Ousegill Beck						
16	Tod Hill Slack						