Trends in Surface Water Chemistry in Acidified Areas in Europe and North America from 1990 to 2008

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Abstract Acidification of lakes and rivers is still an environmental concern despite reduced emissions of acidifying compounds. We analysed trends in surface water chemistry of 173 acid-sensitive sites from 12 regions in Europe and North America. In 11 of 12 regions, non-marine sulphate (SO_4*) declined

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significantly between 1990 and 2008 (−15 to −59 %). In contrast, regional and temporal trends in nitrate were smaller and less uniform. In 11 of 12 regions, chemical recovery was demonstrated in the form of positive trends in pH and/or alkalinity and/or acid neutralising capacity (ANC). The positive trends in these indicators of chemical recovery were regionally and temporally less distinct than the decline in SO_4^* and tended to flatten after 1999. From an ecological perspective, the chemical quality of surface waters in acid-sensitive areas in these regions has clearly improved as a consequence of emission abatement strategies, paving the way for some biological recovery.

Keywords Acid deposition · Surface waters · Trend analysis · Monitoring network · Chemical recovery

1 Introduction

Over the past 30 years, acid atmospheric deposition (often referred to as "acid rain") has received considerable attention as an international environmental problem in Europe and North America (Likens et al. 1979). Polluted air masses containing sulphur and nitrogen compounds travel long distances across national boundaries. Acidifying compounds thus affect surface waters, groundwaters, and acid-sensitive soils far beyond their country of origin. Acidification of the environment has lead to fish death and extinction of fish populations (Haines and Baker 1986), soil acidification (Matzner and Murach 1995), and reduced forest vitality (Fischer et al. 2007). Recently, deposition of reactive nitrogen has also been shown to pose a threat to remote terrestrial and aquatic ecosystems through nutrient enrichment (Lepori and Keck 2012; Stevens et al. 2011; Phoenix et al. 2012).

The Convention on Long-Range Transboundary Air Pollution (CLRTAP) came into effect in 1983 to control air pollutant emissions in Europe and North America and thereby improve the environmental status of natural ecosystems. Under the CLTRAP, international cooperative monitoring programmes were initiated to assess the impact of atmospheric pollution on ecosystems. For surface waters, the International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) has been an important contributor documenting the effects

of the implemented Protocols under CLRTAP since 1985 (Kvaeven et al. 2001).

The ICP Waters programme is designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. The collected data provide information on dose/response relationships for a wide range of acid-sensitive lakes and streams under varying deposition regimes by correlating changes in acidic deposition with the physical, chemical, and biological status of lakes and rivers. Data collected by various monitoring schemes are integrated and interpreted, and inter-laboratory quality control systems are run to ensure data are comparable across participating countries. Previous trend analyses of ICP Waters data on surface water chemistry have provided important indications of the geographic extent of acidification and recovery of lakes and streams for the 1980s (Newell and Skjelkvåle 1997), the 1980s and 1990s (Stoddard et al. 1999), and up to the start of 2000 (Skjelkvåle et al. 2001, 2005). Early assessments provided little evidence for chemical recovery during the 1980s. Subsequently, however, patterns of widespread chemical recovery became clear during the 1990s, as indicated by reduced sulphate (SO_4) concentrations and increases in pH and alkalinity. The reduction in sulphur deposition is considered to be the main driver of the improved acidification status of surface waters and is also substantiated by catchment input–output budgets (Prechtel et al. 2001) and acidification models (Jenkins et al. 2003).

Whether continued reduction in emissions of sulphur and nitrogen will lead to further improvement of surface water quality in acid-sensitive regions, sufficient to sustain biological recovery, depends on a number of factors (Wright et al. 2005). In some regions, base cations have declined at a similar or greater rate than SO_4, preventing chemical recovery (Skjelkvåle et al. 2005; Stoddard et al. 1999). Catchments continue to be enriched by nitrogen deposition with possible consequences for enhanced leaching of nitrate (NO_3) (Curtis et al. 2005; Moldan et al. 2006; Oulehle et al. 2008; Stoddard et al. 2001), especially under climate change. Additionally, widespread increases in concentrations of dissolved organic carbon (DOC) have also been documented and related to changes in atmospheric chemistry, most prominently the decline in sulphur deposition (Monteith et al. 2007). The increase in DOC may dampen expected reductions in acidity as humic substances are naturally acidifying agents (Erlandsson et al. 2011). Thus, ground truth data on the environmental status and

recovery of acid-sensitive surface waters remain important for assessing the effects of emission controls.

Here, we report trends in key variables of surface water chemistry from 173 monitoring sites from 1990 to 2008. Trends for individual sites, as well as aggregated trends by regions, are presented.

2 Methods

2.1 Selection of Variables

The analysis of surface water response to changing deposition comprises variables that are sensitive to acidification and recovery:

- Non-marine SO_4 and NO_3 are strong acid anions. As ICP Waters sites are selected to be remote from the influence of direct terrestrial pollution, elevated concentrations largely reflect the combined effects of recent trends in deposition and ecosystem responses. The nitrogen acidification ratio (NAR), defined as the ratio of equivalent concentrations of NO_3 to the sum of NO_3 and SO_4, is used to indicate the relative importance of nitrogen as a driver for acidification.
- Non-marine base cations are mobilised by geological weathering and cation exchange reactions that neutralise acids in watersheds, and their concentrations will therefore be influenced by changes in acid deposition. Base cations will respond indirectly to changes in SO_4 and NO_3. The sum of non-marine Ca and Mg equivalents comprise the major fraction of non-marine cations at the majority of acid-sensitive monitoring sites and was therefore used as a surrogate for total non-marine base cation concentration.
- pH, measured alkalinity and calculated acid neutralising capacity (ANC), reflects the outcome of interactions between changing concentrations of acid anions and base cations. Alkalinity is measured by titration and indicates the capacity of the water to buffer acidic inputs. ANC, calculated from sum of base cations (Ca+Mg+Na+K) minus the sum of acid anions (SO_4+Cl+NO_3), is an approximate surrogate for alkalinity in waters with relatively low concentrations of DOC. For waters where DOC is higher, alkalinity is normally significantly lower than ANC.
- The concentration of DOC (i.e., the fraction passing through a filter typically with a pore size of

0.45 μm) is considered as a surrogate for organic acids, mostly derived through degradation of natural organic matter in catchment soils. The Nordic countries report total organic carbon (TOC), but we do not discuss these results separately as the dissolved fraction is expected to be large (>90 %) in most of the samples.

Both SO_4 and base cation concentrations were sea salt corrected by subtracting the marine contribution estimated from the ratio of the ion to Cl in seawater (Lyman and Fleming 1940). Non-marine ions are hereafter denoted by an asterisk (SO_4*, Ca*+Mg*). Water pH was transformed to H^+ concentration (assumed to be equal to activity), prior to statistical analysis.

2.2 ICP Waters Sites Selected for Trend Analysis

ICP Waters data are provided by national and provincial monitoring programmes in the participating countries. Sampling frequencies, analytical methods, lengths of record, and site sensitivity to acidification vary between and within programmes. It was therefore necessary to define criteria for inclusion of data in the analysis and comparison of trends among sites. Sites were selected if

1. data were available for at least 14 out of 19 years between 1990 and 2008
2. data were available for at least 7 years between 1990 and 1999 and at least 7 years between 1999 and 2008 (i.e., 1999 was included in both periods in order to be able to compare trends from two time spans of 10 years length with just 19 years of data available)
3. they were sensitive to acidification (ANC<300 μEq/L and/or alkalinity<300 μEq/L)
4. they had relatively undisturbed catchments (i.e., no known point sources of pollution, agricultural influence, or commercial forestry)

The number of sites that met the criteria ranged from 132 for DOC to 173 for SO_4* (Table 1, Fig. 1), i.e., availability of data (criteria 1 and 2) was considered for each parameter in isolation and sites did not have to meet the data criteria for all parameters in order to be included.

For the purpose of regional comparison, sites are grouped into geographic regions which, where

Table 1 Number of ICP Water sites with significantly ($p<0.05$) increasing or decreasing trends for the time span 1990 to 2008. Not significant means that no monotonic trend was detected. Variables are non-marine SO_4 (SO_4^*), NO_3, $NO_3/(NO_3+SO_4^*)$ (NAR), sum of base cations (Ca^*+Mg^*), alkalinity, acid neutralising capacity (ANC), H^+, and dissolved organic carbon[a] (DOC)

		SO_4^*	NO_3	NAR	Ca^*+Mg^*	Alkalinity	ANC	H^+	DOC^a
Europe	Increasing	0	2	14	2	16	29	0	15
	Not significant	8	38	36	29	37	24	33	22
	Decreasing	55	10	0	33	1	0	30	0
North America	Increasing	0	1	11	0	29	26	2	14
	Not significant	14	92	94	41	72	67	92	78
	Decreasing	96	17	5	54	2	1	15	3
	Total	173	160	160	159	157	147	172	132
All sites	% increasing	0	2	16	1	29	37	1	22
	% not significant	13	81	81	44	69	62	73	76
	% decreasing	87	17	3	55	2	1	26	2

[a] DOC was measured as DOC or as TOC

necessary, were constrained by attributes including similar acid sensitivity (e.g., similar geology and soil characteristics) and rates of deposition (Fig. 1). The list of regions on which we report is based on scientific and pragmatic decisions resulting from availability of data. Thirteen sites from Ontario, which do not contribute to the ICP Waters database, were nevertheless included in order to provide a sufficient number of sites to justify analysis as a separate region.

2.3 Analytical Methods and Quality Assurance of Data

Standardisation of sample collection and analytical methodologies is addressed in the ICP Waters Programme Manual (ICP Waters Programme Centre 2013, http://www.icp-waters.no). Aspects of site selection, water chemistry/biological monitoring, and data handling are also described in detail in the manual. Each country is responsible for sampling and analytical work, and the data are submitted to the ICP Waters database hosted by NIVA.

Three levels of quality control of the data are distinguished: in-laboratory controls in individual countries, between-laboratory controls (intercomparisons), and a technical quality control before data are entered into the database. The last step includes looking for outliers, evaluation of continuity in time series, and calculation of ionic balance.

2.4 Statistical Methods Used for Trend Analysis

Statistical analyses were performed on annual means only. The sampling frequency per station varied from a single annual sample for some lake sites, to weekly sampling, and the frequency of observations for some stations differed between years. For each site, the annual arithmetic mean for each parameter was calculated, thus minimising the effect of variable sampling frequency on the ability to detect trends. Seasonality in the data could affect the annual mean but not the choice of statistical test.

The Mann Kendall test (MKT) (Hirsch and Slack 1984) was used to evaluate temporal trends of solute concentrations. This method is robust against outliers, missing data, and does not require normal distribution of data. The method was used to determine monotonic trends based on the values of the test statistic (Z-score). Slopes were calculated using the Sen estimator (Sen 1968).

We compiled the results of the MKT for the individual sites and calculated the total number of "increasing," "decreasing," and "no trend" occurrences for each parameter. This procedure is not strictly valid because the risk of falsely rejecting null hypotheses increases when individual results are summed. However, if each test is regarded as a Bernoulli trial with a success probability of 0.05, the total number of false rejections can still be expected to be relatively low. We therefore assume that the compilation of MKT results by region gives a good overview of trends in the data.
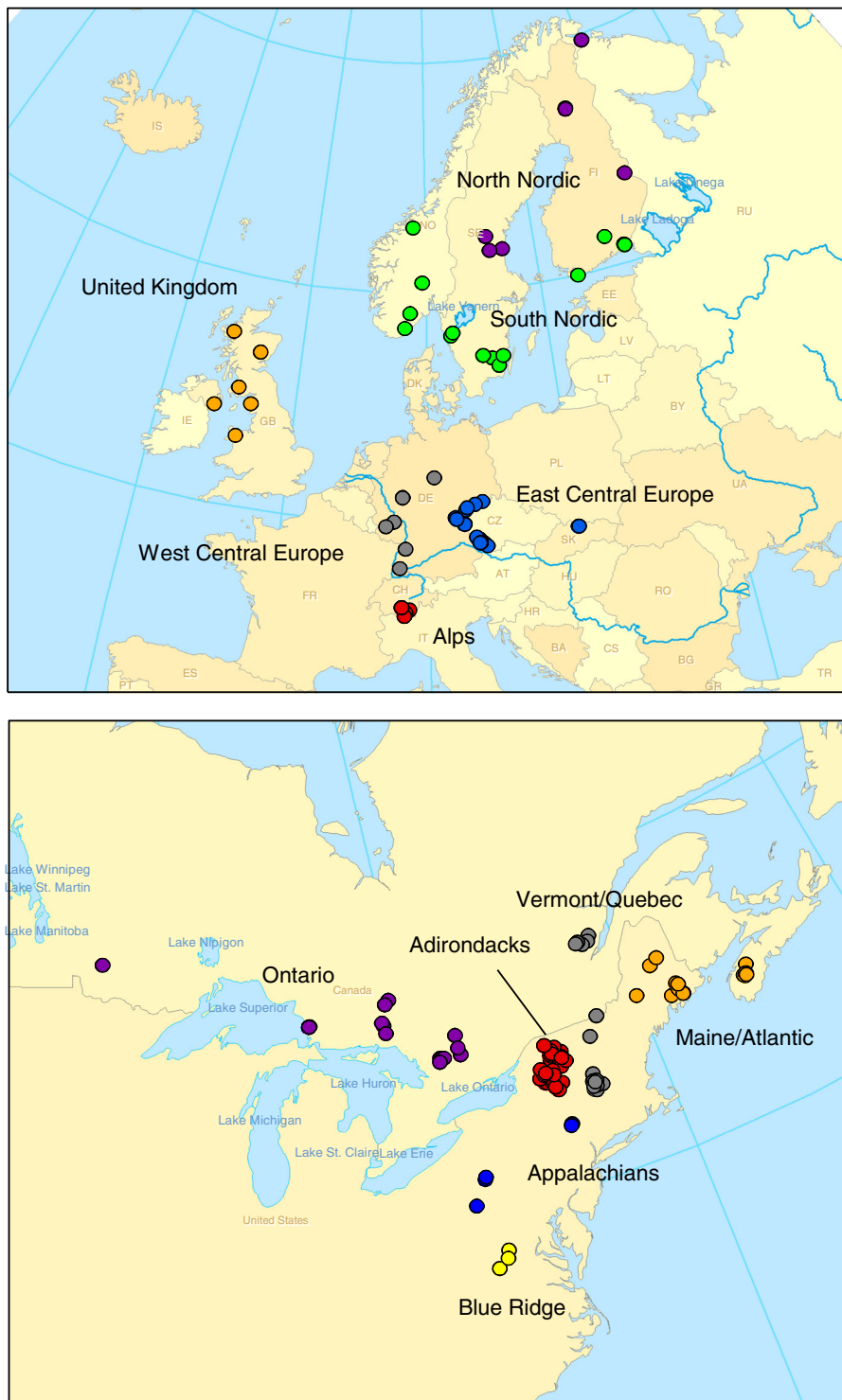
Fig. 1 Map showing location of the monitoring stations (*coloured circles*). Different colouring of the circles indicates that stations belong to separate regions

While the significance of sums of individual MKT tests are questionable from a statistical viewpoint, the slopes calculated for multiple sites within a region represent a distribution of results, which can in turn be

examined and analysed for patterns. The non-parametric Wilcoxon test was used to test for different distributions of slopes (calculated with the Sen slope estimator) between two time periods of 10 years, i.e., 1990–1999 and 1999–2008 (1999 is included in both periods). The sites were grouped in the regions used for the regional trend analysis (see below), and all sites that met the criteria (see above) were included in the analysis. The time intervals were chosen to minimise overlap between the time spans.

Regional trends in the data were assessed using the Regional Kendall Test (Helsel and Frans 2006), which provides median slopes and a *p* value for the trend's significance. The Regional Kendall Test has similar strengths as the MKT and does not require normal distribution of the data.

3 Results and Discussion

3.1 Trends in Individual Sites

Patterns and qualitative results of the trend analyses for individual sites are summarised in Table 1. A significant decrease in SO_4* concentration was observed at 87 % of sites; no significant increases were observed. Most sites (81 %) had no trend in NO_3 concentration, but most trends for the remaining sites were negative. A decreasing trend in non-marine base cations $(Ca+Mg)$* was observed at 55 % of the sites. A majority of sites did not show trends in NAR, alkalinity, ANC, DOC, or H^+ concentration. However, increasing trends in NAR, alkalinity, ANC, and DOC were more common than decreasing trends, while the opposite was true for H^+ concentration.

3.2 Trends in Sulphate by Region

Concentrations of SO_4* decreased significantly in all regions included in this analysis, except Virginia Blue Ridge in North America (Fig. 2, Tables 2 and 3). Previous trend analyses (Skjelkvåle et al. 2005; Stoddard et al. 1999) have shown similar regional patterns. In most catchments, responses of aquatic SO_4* concentrations appear to respond rapidly to changes in atmospheric inputs of SO_4* (Prechtel et al. 2001) because of limited capacity of the soil to adsorb SO_4. However, in the Virginia Blue Ridge region, deeply weathered soils with a large capacity to adsorb SO_4 delay the response (Church et al. 1990), and the three sites follow the pattern revealed by a more

Fig. 2 Relative change of annual means of SO_4*, NO_3, sum of base cations $(Ca+Mg)$*, H^+, and organic carbon (DOC)[a] in regions of Europe and North America from 1990 to 2008. Each annual mean is divided by the first annual mean (i.e., between 1990 and 1993) of each time series. The line is a cubic spline with a lambda of 0.05. Region names are abbreviated in the following way: *NoN* North Nordic, *SoN* South Nordic, *UK* United Kingdom, *WCE* West Central Europe, *ECE* East Central Europe, *Atl* Maine and Atlantic Canada, *Vt/Que* Vermont and Quebec, *Ads* Adirondacks, *App* Appalachians, *BRi* Blue Ridge Mountains, and *Ont* Ontario

comprehensive assessment of streams in the region (Stoddard et al. 2003). Soils with large sulphur adsorption capacity also occur at stations from the Harz and Fichtel mountains in Germany (West and East Central European region, respectively), where again there is little evidence for reductions in surface water SO_4 despite decreasing rates of acidic deposition (see Alewell et al. 2001 for more detailed descriptions). A delayed response in surface waters can be caused by release of previously deposited sulphur stored in wetland and/or forest soils (see Mitchell et al. 2011 for a discussion of this and other potential confounding factors). Such release can affect surface water trends in SO_4* as well as pH and ANC.

The largest rates of decline in SO_4* concentration were observed in Europe (Table 2) and especially in South Nordic region. Trends in most regions tended to be more gradual in the second decade, but only differed significantly in Vermont/Quebec and Ontario (Table 4). Trend analyses of SO_4 in precipitation have indicated substantial decreases of sulphur deposition, especially in the areas that previously received the highest loads (Tørseth et al. 2012). Regional and temporal patterns in changes of SO_4* in surface water in North America and Europe were similar to those observed in precipitation, indicating that reduced deposition of sulphur has been the main driver of decreasing SO_4* concentrations in surface waters.

3.3 Trends in Nitrate by Region

The regional and temporal patterns in NO_3 concentration were more varied than for SO_4* (Fig. 2). Even so, NO_3 concentrations were found to be decreasing in 7 of the 12 regions (Tables 2 and 3). The Alps was the only region that showed increasing concentrations. However, in the Alps as well as in the North Nordic and Maine/Atlantic Canada regions, slopes were significantly smaller for the
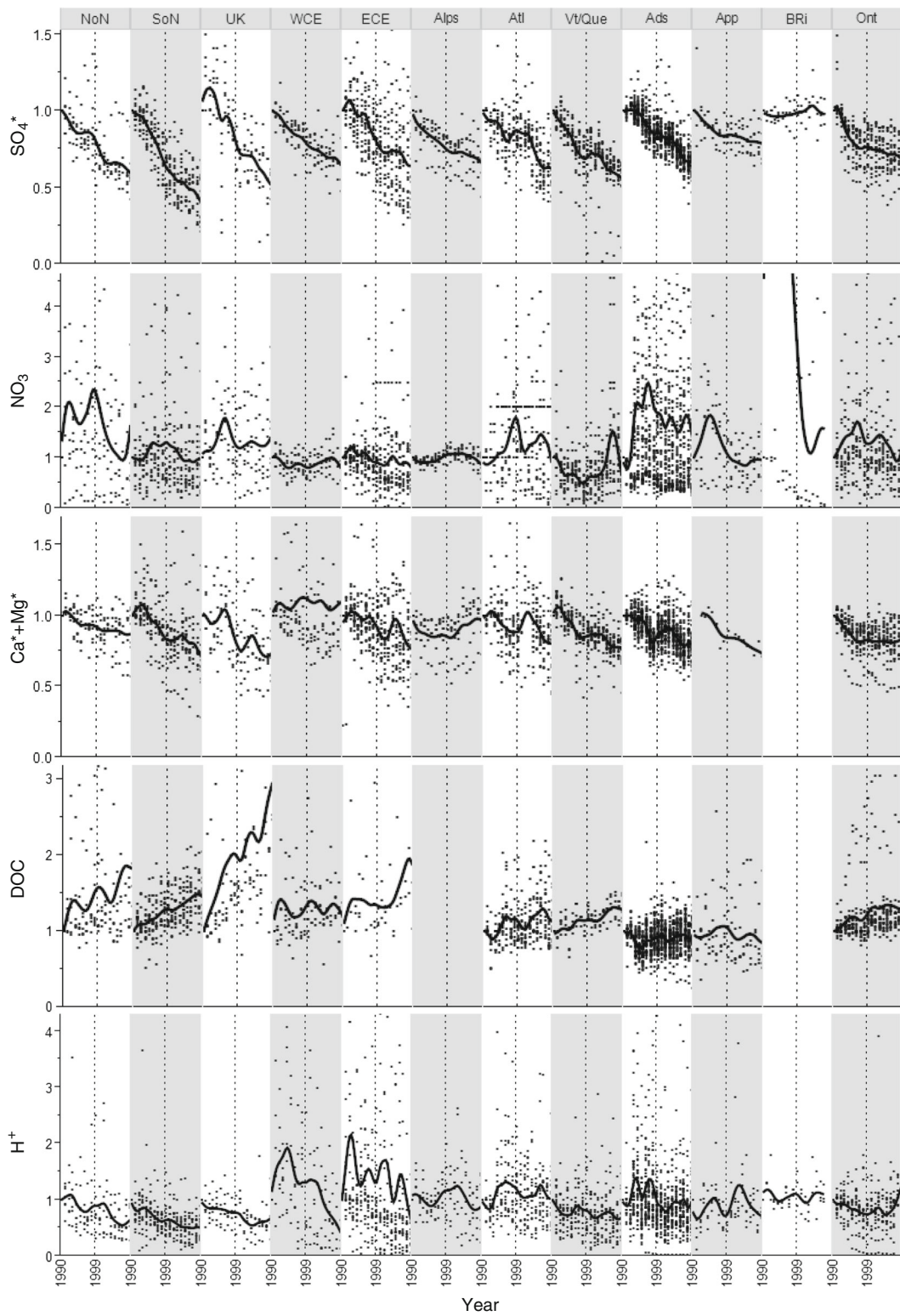
Table 2 Results from the Regional Kendall trend analysis for 1990 to 2008. For each region, median trend slope is shown for SO_4^*, NO_3, NAR, sum of base cations $(Ca+Mg)^*$, acid neutralising capacity (ANC), H^+, and organic carbon (DOC)[a].

SO_4 and base cations were sea salt corrected. Significant ($p < 0.05$) upward trends in dark grey shade, significant downward trends in light grey shade, and non-significant in white. Units: µEq/L/yr for all except DOC: mg C/L/yr. nd, no data

		SO_4^*	NO_3	NAR	Ca^*+Mg^*	Alkalinity	ANC	H^+	DOC^1
Europe	North Nordic	-1.42	-0.04	0.000	-0.54	0.88	1.19	-0.02	0.04
	South Nordic	-4.58	-0.04	0.001	-2.12	0.48	2.64	-0.04	0.09
	United Kingdom	-1.22	-0.09	0.007	-0.81	0.26	0.14	-0.25	0.11
	West Central Europe	-3.74	0.13	0.005	-1.60	0.45	5.84	-0.08	0.05
	East Central Europe	-3.03	-0.21	0.001	-1.54	0.92	3.23	-0.33	0.04
	Alps	-1.27	0.37	0.006	0.88	2.22	1.92	0.00	nd
N. America	Maine & Atlantic Canada	-0.95	0.00	0.000	-0.28	0.30	0.51	-0.01	0.03
	Vermont & Quebec	-1.76	0.00	0.001	-1.11	0.14	0.42	-0.03	0.06
	Adirondacks	-2.14	-0.18	0.000	-1.40	0.74	1.07	-0.04	0.03
	Appalachians	-1.48	-0.33	-0.001	nd	0.41	nd	0.01	-0.02
	Blue Ridge Mountains	0.15	-0.73	-0.009	nd	0.22	nd	0.00	nd
	Ontario	-1.93	-0.03	0.000	-1.65	0.60	0.72	0.00	0.03

[a] DOC was measured as TOC or DOC

period 1999–2008 than 1990–1999 (Table 4) and appear to have levelled out or changed from positive to negative (Fig. 2, see also Tables S1 and S2 in supporting information). The results for Vermont/Quebec and possibly West Central Europe indicate that the opposite has occurred in these regions.

While reduced deposition of sulphur is the main driver behind the extensive decline of freshwater SO_4^*, the

controls of NO_3 concentration are complex as a result of the biogeochemical cycling of nitrogen in soils. Factors that have been invoked to explain trends include changes in deposition of nitrogen (Curtis and Simpson 2014; Oulehle et al. 2008; Rogora et al. 2012), progressive N saturation (Curtis et al. 2011), and changes in snow cover (Brooks et al. 1999; De Wit et al. 2008) and temperature (Brookshire et al. 2011; Monteith et al. 2000).

Table 3 Relative regional change (percent) in key variables of surface water chemistry in ICP Waters sites for 1990 to 2008. See caption of Table 2 for explanation of variables. Relative change was calculated using median slope and median 1990-value of the

specific variable for each region. Significant ($p < 0.05$) upward trends in dark grey shade, significant downward trends in light grey shade, and non-sigificant in white. Units: µeq/L/yr for all except DOC: mg C/L/yr

		SO_4^*	NO_3	Ca^*+Mg^*	H^+	DOC^1
Europe	North Nordic	-46	-42	-10	-35	15
	South Nordic	-59	-19	-27	-23	35
	United Kingdom	-48	-12	-34	-51	113
	West Central Europe	-31	5	-9	-69	22
	East Central Europe	-37	-13	-17	-73	16
	Alps	-25	15	6	-3	nd
N. America	Maine & Atlantic Canada	-35	0	-13	-7	14
	Vermont & Quebec	-41	0	-24	-24	30
	Adirondacks	-35	-20	-21	-19	11
	Appalachians	-15	-34	nd	2	-18
	Blue Ridge Mountains	4	-132	nd	-2	nd
	Ontario	-27	-19	-17	-7	20

[a] DOC was measured as TOC or DOC

Table 4 Comparison of trends in surface water chemistry (key variables) for the periods 1990–1999 and 1999–2008 for regions in Europe and North America. A Wilcoxon test was used to test for different distribution of slopes between the two periods. Near significant (* $p<0.10$) and significant (** $p<0.05$) differences are indicated (n.d., no data). A plus or minus sign indicate whether slopes for the period 1999–2008 are higher or lower, respectively, than for the period 1990–1999 (i.e., signs refer to inflection not trend direction)

		SO$_4$*	NO$_3$	NAR	Ca*+Mg*	Alkalinity	ANC	DOC	H$^+$
Europe	North Nordic		**(−)	**(−)					
	South Nordic	* (+)					**(−)		
	United Kingdom						*(−)		
	West Central Europe	*(+)	*(+)						
	East Central Europe			**(−)	**(+)				
	Alps	*(+)	**(−)	**(−)	**(+)	**(+)	**(+)	nd.	
North America	Maine and Atlantic Canada		**(−)	**(−)	**(+)		*(−)		*(−)
	Vermont and Quebec	**(+)	**(+)	**(+)	**(+)		**(−)		
	Adirondacks				**(+)	**(−)	**(+)		**(+)
	Appalachians				nd.		nd.		
	Blue Ridge Mountains			*(+)	nd		nd.	nd	
	Ontario	**(+)		**(−)	**(+)				

Furthermore, insect attack on vegetation can cause large temporal variation in NO$_3$ concentration as observed in sites from Blue Ridge Mountains and East Central Europe (Eshleman et al. 1998; Oulehle et al. 2013). Thus, trends in NO$_3$ remain poorly understood, but at present, declining trends are more prominent than increases.

The relative importance of NO$_3$ for acidification of surface waters, i.e., the NAR, has increased somewhat in most regions (Table 2, Fig. 3). Exceptions are the Appalachian and Virginia Blue Ridge region where NAR showed a significant decrease. The relative importance of NO$_3$ as an acid anion was greatest in the non-Nordic European regions where NAR was 0.3 to 0.5.

3.4 Trends in Non-marine Base Cations by Region

One of the expected responses of catchments to decreasing SO$_4$ inputs is the reduced leaching of base cations because of increased pH and cation scavenging by cation exchange sites (Galloway et al. 1983).

Almost all regions showed decreasing concentrations of Ca*+Mg* between 1990 and 2008 (Table 2, Fig. 2). However, in six of the regions, the trend slopes were significantly less negative in the latter half of the time span (Table 4), indicating that the rate of decline is decreasing. In contrast to the other regions and despite a significant reduction in SO4*, the Alps showed increasing concentrations of Ca*+Mg*, while the rate of increase was greater in the more recent decade. While

NO$_3$ concentrations have increased slightly, there has been an overall reduction in acid anion concentration and other mechanisms are therefore required to explain this tendency. Possible explanations for the observed recent increase in base cations in the Alps include hydrological effects (i.e., drought), increased weathering rates caused by climate change (Rogora et al. 2003), and contribution from Saharan dust deposition episodes (Rogora et al. 2004).

For most regions, the median decrease in Ca*+Mg* was lower than the equivalent decline in SO$_4$* (Table 2), creating likely conditions for recovery in pH and alkalinity. This was most distinct in Europe. If the decrease in SO$_4$* is entirely balanced by a decrease in base cations, no improvement of water quality (increase in pH, alkalinity, and ANC) would be expected.

3.5 Trends in Measured Alkalinity and Calculated ANC by Region

Measured alkalinity and calculated charge balance ANC are widely used as indices of the extent of acidification and the susceptibility of natural waters to acidification. The steeper negative regional trends for SO$_4$* relative to those for base cations, combined with the regional signal of either no change or decreasing NO$_3$, should result in increasing ANC and alkalinity. Indeed, all regions except Virginia Blue Ridge, the only region not to show a significant decline in SO$_4$*, show positive regional
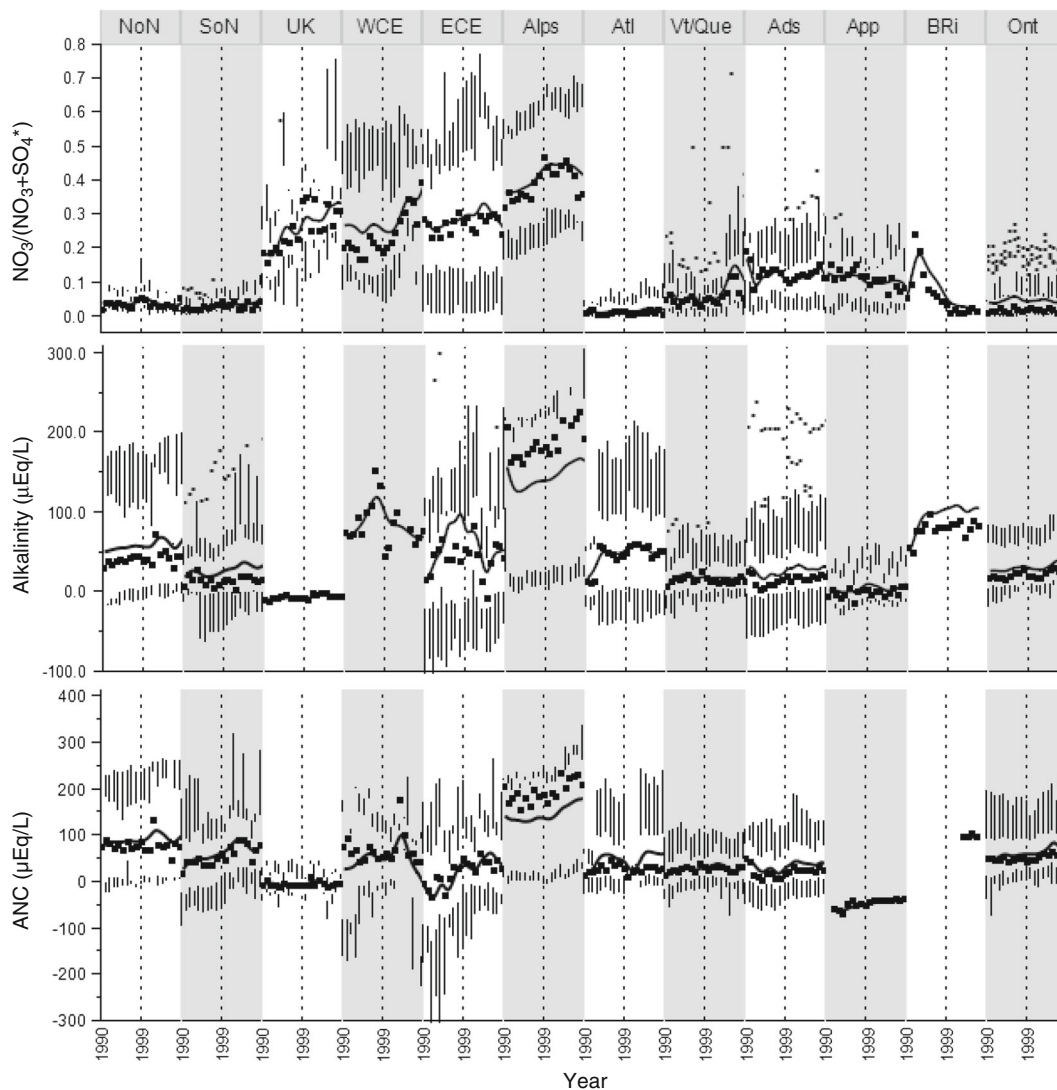
Fig. 3 Absolute change of nitrate acidification ratio (NAR), alkalinity, and ANC in regions of Europe and North America between 1990 and 2008. The *line* is a cubic spline with a lambda of 0.05. The *points* represent the median value, and the *vertical black lines* extends from the 75th percentile+the interquartile range multiplied by 1.5 and the 25th percentile – the interquartile range multiplied by 1.5

trends in alkalinity and/or ANC between 1990 and 2008 (Table 2, Fig. 3), indicating chemical recovery from acidification. In the South Nordic region and Vermont/Quebec, the increases in ANC were larger for1990–1999 than 1999–2008 (Table 4, Fig. 3), while in the Alps, the largest increase in ANC and alkalinity occurred in the latter time span. In the Adirondacks, there was a discrepancy between trends in measured alkalinity and calculated ANC. The former indicate larger improvement for 1990–1999 than 1999–2008, while the latter suggest the opposite (Table 4). The rates of change are, however, small (Fig. 3). The discrepancy is possibly due to the influence of changes in aluminium and DOC, which are not included in the calculation of ANC, but which do influence measured (Gran) alkalinity (Driscoll et al. 1994; Waller et al. 2012).

3.6 Trends in DOC by Region

DOC is a key component of aquatic chemistry, e.g., as an indicator of natural organic acidity (Erlandsson et al. 2011). In this respect, it has received considerable

attention in recent years because of rising levels in many regions (Hruška et al. 2009; Monteith et al. 2007). The drivers of rising DOC are still debated in the scientific literature, but analysis of ICP Waters and associated data has demonstrated that DOC trends are strongly correlated with trends in deposition chemistry and catchment acid sensitivity (Monteith et al. 2007). While changes in sulphur and sea salt deposition appear to control monotonic trends, climatic factors can exert strong influence on seasonal and interannual variations (Clark et al. 2010) and longer term climate change is therefore also likely to affect DOC trends. All regions where DOC data were available, except East Central Europe and the Appalachians, showed increasing DOC concentrations between 1990 and 2008 with median rates varying between 0.03 and 0.11 mg/L/y (Table 2). None of the regions showed a significant difference in the distribution of slopes between the first and second half of the time span (Table 4), i.e., there are few indications that the rise in DOC concentrations is beginning to plateau. If the increase has mainly been driven by reduced acidification, DOC levels are likely to stabilise in the near future, because further reductions in SO_4* concentrations are expected to be relatively slight.

The link between rising DOC and declining SO_4* concentrations indicates that rising DOC concentrations may be integral to the process of chemical recovery from acidification. This partial replacement of mineral acidity by organic acidity may explain why pH and alkalinity responses are more muted than had once been anticipated and predicted by process-based models of acidification dynamics such as MAGIC (Battarbee et al. 2005; Erlandsson et al. 2010).

3.7 Trends in pH by Region

Most processes in natural aqueous systems are pH-dependent, and pH is an important parameter for understanding biological consequences of acid deposition. However, trends in pH can be difficult to detect because of high measurement uncertainty in the low ionic strength water typical for most of the ICP Waters sites (Hovind 2010).

All regions, except the Alps, Appalachians, and Virginia Blue Ridge, showed decreasing H^+ concentration between 1990 and 2008 (Table 2). The H^+ trends in the Adirondacks were steeper between 1990 and 1999 than between 1999 and 2008 (Table 4, Fig. 2), confirming the findings of Lawrence et al. (2011). Elsewhere, however, there is little evidence that trends in H^+ concentrations are

levelling off. The relative change is smaller in North American regions than in most European regions.

The trends in H^+ are consistent with those observed for other parameters on a regional scale. In the European regions, the median decreases in base cations have been appreciably smaller than the equivalent declines in acid anions. Consequently, ANC, alkalinity, and pH have increased here. An exception is the UK where increases in alkalinity and ANC were small and insignificant, respectively, despite significant decrease in H^+. However, trends in alkalinity over the period 1988–2008 for a wider set of UK lakes and streams than assessed here (Monteith et al. 2014) averaged 0.63 µEq L^{-1} yr^{-1} which is similar to the average of all European regions in this analysis. The apparent lack of response in ANC in UK may result from the effect of large long-term variability in sea salt deposition and compound analytical errors affecting the ANC calculation in waters with relatively high concentrations of sea salt (Evans et al. 2001a; b). When ANC for these UK sites is calculated using an alternative, alkalinity-based method, trends for the period 1988–2008 have been found to be statistically significant and are similar in magnitude to trends in other regions (Monteith et al. 2014). In the North American regions, the rates of decrease of base cations are closer to those observed for acid anions (see also, e.g., Driscoll et al. 2007; Stoddard et al. 2003). Changes in ANC/alkalinity are therefore relatively small and so is the decrease in H^+.

Inorganic monomeric aluminium (Al_i), which is an important parameter associated with acidification, was not included in this analysis as it is not routinely measured across the ICP Waters network. The speciation of aluminium is highly dependent on pH, and decreasing trends in Al_i concentration are likely to have occurred at strongly acidified sites with decreasing H^+ concentration across the ICP Waters network. The implication of these trends in hydrochemical parameters is that conditions for sensitive biota in many of these waters have improved and various communities of organisms are responding (see, e.g., the articles in a recent special issue on recovery from acidification in the UK, Ecological Indicators 37B, 2014).

4 Conclusions

A pattern of chemical recovery from acidification of surface waters across a large number of rivers and lakes

in Europe and North America is shown by trend analysis of SO_4*, pH, ANC, and alkalinity data from 173 acid-sensitive ICP Waters monitoring sites. This recovery appears to be driven primarily by the reduction of sulphur deposition, confirming that emission control programmes are having their intended effect on aquatic chemistry, even though improvements are not as universally clear, or rapid, as were once expected.

Downward trends also dominated temporal patterns in NO_3 concentration, but their slopes tended to be smaller and the pattern more complex than for SO_4*. The lack of a clear pattern of regional decline in NO_3 leaching remains poorly understood, and the potential for gradual nitrogen saturation of catchments, and consequences for these vulnerable systems, remains a concern, especially in areas receiving high deposition.

Water chemistry responses to changed precipitation chemistry are delayed by catchment processes. In several regions, trends in indicators of chemical recovery tended to be less pronounced after 1999, suggesting that the rate of improvement of water quality has slowed. Overall, the regional increases in pH, alkalinity, and ANC which we have reported here should be creating the conditions conducive to partial biological recovery.

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