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Regional scale evidence for improvements in surface water chemistry 1990–2001

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Data demonstrates a continued regional-scale chemical response of acid sensitive lakes and streams to emissions controls programs which is conducive to biological recovery.

Abstract

The main aim of the international UNECE monitoring program ICP Waters under the Convention of Long-range Transboundary Air Pollution (CLRTAP) is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. Regional trends are calculated for 12 geographical regions in Europe and North America, comprising 189 surface waters sites. From 1990–2001 sulphate concentrations decreased in all but one of the investigated regions. Nitrate increased in only one region, and decreased in three North American regions. Improvements in alkalinity and pH are widely observed. Results from the ICP Waters programme clearly show widespread improvement in surface water acid-base chemistry, in response to emissions controls programs and decreasing acidic deposition. Limited site-specific biological data suggest that continued improvement in the chemical status of acid-sensitive lakes and streams will lead to biological recovery in the future.
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Keywords: Acidification; Deposition; Trends; ICP waters; Sulphate; Nitrate; Alkalinity; Dissolved organic carbon

1. Introduction

Surface water acidification has been recognized as a major environmental problem in many parts of Europe and North America for several decades, resulting in the

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creation of emissions control programs at both national and international levels. These programs have produced widespread decreases in acidic deposition, and the expectation that surface waters in affected regions should be experiencing recovery from acidification. In this paper we examine data from the international UNECE monitoring program ICP Waters (International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes) under the Convention of Long-range Transboundary Air Pollution (UNECE, 1999; Bull et al., 2001) to determine whether such widespread recovery can be detected, and to put the more detailed results presented in this special issue for the UK Acid Waters Monitoring Network (AWMN) into a larger context. The ICP Waters network described in this paper covers most of the acid-sensitive terrain of the Northern Hemisphere, where emissions controls to control acidification have been focused. It is probably worth noting, however, that it does not cover areas (notably Asia) where acidic deposition is on the rise, and is of growing concern (Streets et al., 2001).

Our focus is primarily on trends in the chemistry of acid-sensitive surface waters. When these trends are shown to be moving in the correct direction (e.g., decreases in sulphate, SO_4^{2-}, or increases in pH), they indicate improvement in the acid-base chemistry of lakes and streams. It is important to note that these improvements or recovery process do not necessarily equate to recovery, for at least two important reasons:

1. Lakes and streams will have "recovered" only when their chemistry has returned to its pre-acidified status, such as pre-industrial levels of SO_4^{2-} or alkalinity, or to some status that no longer poses a risk to biotic integrity; trends indicate only that surface waters are moving toward this recovered status, not that they have reached it;
2. While the ultimate goal of emissions control programs is biological recovery, e.g., the return of sensitive species that have been eliminated and biological functioning that has been impaired during the course of acidification; chemical recovery is necessary before biological recovery can occur. Chemical data are more widely available and indicate weather the necessary chemical conditions to facilitate biological recovery is present or will be achieved.
3. This regional trend assessment is based on the premise that a consistent pattern of improvement (decreasing SO_4^{2-} and increasing pH and alkalinity) across a large number of sites represents the strongest evidence that emissions control programs are having their intended effect. For this reason, we aggregate data from numerous ICP Waters sites into regions, and conduct the trend tests on the region as a whole for all data collected in the time period 1990–2001. This period is one in which all of the regions covered by the ICP monitoring sites have experienced substantial reductions in sulphur (S) deposition (Barret et al., 2000; Stoddard et al., 2003; see also Davies et al., this issue), and this can be expected to be reflected in trends in surface water SO_4^{2-} concentrations and acidity (pH and alkalinity).

Our analysis of response to changing deposition focuses on the key variables that play major roles in surface water acidification and recovery:

1. SO_4^{2-} and NO_3^-, the acid anions of acidic deposition. Trends in the concentrations of these anions reflect recent trends in deposition (especially SO_4^{2-}) and in ecosystem response to long-term deposition (most notably NO_3^- and desorbed SO_4^{2-}).
2. Base cations - as represented by $\Sigma(Ca^{2+}+Mg^{2+})$ are mobilized by weathering reactions and cation exchange. Base cations will respond indirectly to decreases in SO_4^{2-} and NO_3^- because reduced input of acids will theoretically lead to reduction of neutralizing processes in the soil, such as weathering and ion-exchange, and thereby reduced release of base cations to soil- and runoff water.
3. Acidity, including pH, measured (Gran) alkalinity and calculated ANC, which reflects the outcome of interactions between changing concentrations of acid anions and base cations.
4. Concentrations of Dissolved Organic Carbon (DOC) or alternatively Total Organic Carbon (TOC), as a surrogate for organic acidity. Organic acids are common natural sources of acidity in surface waters.

The ICP Waters network consists of acid-sensitive lakes and streams in 23 countries of Europe and North America. Sites in the ICP Waters database exhibit a wide range of sampling frequencies, completeness of chemistry, and length of record. Although monitoring at some sites extends further back than 1988, when sampling on the AWMN was initiated, the ICP Waters Network only reached its current size in the early 1990s. As the focus for the remainder of this special issue is the 1988–2003 period in the UK it is therefore not possible to make precise temporal comparisons between the two datasets. In order to make a meaningful comparison of trends among these sites, we imposed a minimum set of requirements (e.g., for sampling frequency, completeness of major ion chemistry, etc.) for inclusion of data, which are described in detail in Skjelkvåle et al. (2003b). A total of 189 sites had sufficient data to be included in our analyses. Details of the ICP Waters program, data quality control, and the collection and measurement of the variables listed above, can be found in numerous ICP Waters reports

(International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes, 1995; Skjelkvåle et al., 2003b). Both SO_4^{2-} and base cation concentrations were sea-salt corrected prior to analysis, and the analyses of pH were made on values transformed to H^+ concentrations.

2. Statistical methods

Numerous statistical techniques are available to analyse trends in time series such as those presented here. In the two previous ICP Waters reports we have used the Seasonal Kendall test (SKT) (Hirsch and Slack, 1984; Hirsch et al., 1982). This method deals well with censored data, and with data collected at irregular intervals with marked seasonality (Loftis and Taylor, 1989). The SKT, however, is designed to estimate the statistical significance of trends, and does not include a direct estimate of the magnitude of the trends. The regional analyses we present in this report depend on the ability to calculate a robust estimator of slope for each site. Rather than utilizing a Theil or Sen estimator of slope, as is often done with the SKT, we have chosen to employ simple linear regression (SLR) to calculate a robust slope for trends at each monitoring site.

While the significance of individual tests conducted with SLR are questionable (due to lack of normality in the monitoring data, and the use of multiple comparisons when combining results from many sites in a region), we can use the estimated SLR slopes to indicate the range of behaviours (i.e., rates and directions of change) observed in each region. For any given variable in any given region, the collection of slopes represents a distribution whose central tendency is characterized by the median value (slope) for the region. We test for the significance of trends in the region by calculating confidence limits about the median value in the slope distribution (Altman et al., 2000; SAS Institute Inc., 1988), and testing whether these confidence limits include zero. For a distribution in which all of the slopes are negative, for example, the median value would be significantly less than zero, indicating a significant regional downward trend.

3. Regional trend results

Regional trends were calculated for 12 regions (6 in Europe and 6 in North America), comprising 189 ICP Waters sites (73 in Europe and 116 in North America); both regions and the locations of individual sites are illustrated in Fig. 1. The sites are grouped into geographic regions based on similar acid-sensitivity (e.g., similar geology, soil characteristics) and rates of deposition. In some cases, in order to reach sufficient sample sizes (i.e., number of sites), we have grouped sites into regions that are more heterogeneous than would be ideal. For example, the "Upper Midwest" region of the U.S. and Canada includes sites in central Ontario (the Turkey Lakes area), western Ontario (Experimental Lakes Area), northern Michigan and northern Wisconsin. While there are certainly many similarities in the geology of these areas, they comprise a very large geographic area with different climate and rate of change of atmospheric deposition. The list of regions on which we report is therefore based on both scientific and pragmatic decisions resulting from availability of data. The UK/Ireland group consists of six lakes from the AWMN and three from the Republic of Ireland.

Results of trend analyses in each region are shown in Table 1.

3.1. Sulphate

The most significant finding in this regional trend analysis, as in others conducted on earlier data (Skjelkvåle et al., 2001b; Stoddard et al., 1999), is the almost universal decrease in SO_4^{2-} concentrations in lakes and streams throughout Europe and North America (Table 1, Fig. 2). Only one region in this analysis failed to show a significant SO_4^{2-} decrease, and this is a region (the Virginia Blue Ridge) where strongly sulphur-adsorbing soils make a SO_4^{2-} decrease unlikely (Church et al., 1990; Cosby et al., 1986). Many decades of accumulated, atmospherically-deposited SO_4^{2-} is now slowly leaking out under reduced rates of SO_4^{2-} deposition. A small but significant increase in surface water SO_4^{2-} is most probably due to output of "old" stored SO_4^{2-} in the soils.

In Europe, regional rates of SO_4^{2-} decline ranged from ca. -1 μeq l^{-1} yr^{-1} in the U.K. and Ireland and the Northern Nordic region, to more than -6 μeq l^{-1} yr^{-1} in the Southern Nordic region. Rates in central Europe were intermediate, with both East- and West-Central Europe exhibiting regional SO_4^{2-} declines of ca. -4 μeq l^{-1} yr^{-1}. All of these changes are consistent with declines in rates of S deposition in Europe (see below).

Previous regional trend analyses of ICP data did not find decreases in SO_4^{2-} in the UK and Ireland, but the addition of data from the late 1990s and early 2000s leads to a highly significant rates of SO_4^{2-} decline (Table 1). This is consistent with the trends reported for the larger AWMN dataset over 1988–2003 (Davies et al., this issue).

In North America, rates of SO_4^{2-} decline ranged from ca. -1 μeq l^{-1} yr^{-1} in the region with the lowest rates of S deposition (Maine and Atlantic Canada), to more than -2 μeq l^{-1} yr^{-1} in the Adirondack Mountains, Appalachian Mountains, and the Upper Midwest (U.S. and Canada). In an analysis of recent trends in both surface waters and deposition, Stoddard et al. (2003)

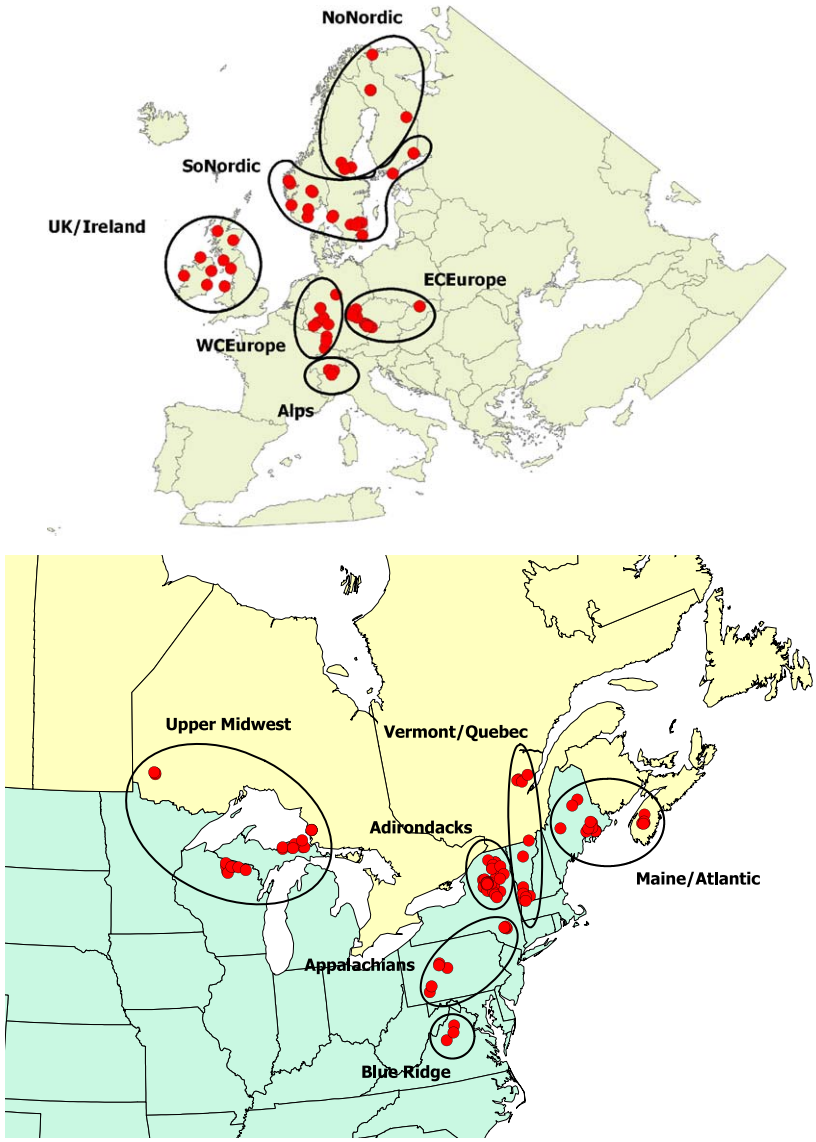

Fig. 1. Map showing location of ICP Waters sites used for trend analysis in this report and outline of geographical regions.

conclude that rates of SO_4^{2-} decline in surface waters follow the same geographic pattern, but are lower than, trends in regional SO_4^{2-} deposition.

3.2. Nitrate

Fewer than half of the ICP regions exhibited significant regional trends in NO_3^- (Table 1), and only the Alps region showed a significant increase. Regional declines in NO_3^- since ca. 1990 have been noted elsewhere (Skjelkvåle et al., 2001b; Stoddard et al., 1999), and need to be interpreted cautiously. The time period of data analysed in this analysis, and in previous reports, is on the order of a decade. While decadal trends in ions undergoing incremental and consistent changes (i.e., SO_4^{2-}) can be interpreted as an improvement in acid-base chemistry, they may not represent true long-term changes for ions actively affected by biotic processes and thus as temporally variable as NO_3^-. Both mathematical (Aber et al., 1997) and conceptual (Stoddard, 1994; Wright et al., 2001) models of nitrogen suggest that long-term catchment responses to N deposition may occur on the time scale of centuries, rather than decades. Several large scale analyses of NO_3^- data suggest the strong spatial patterns observed, with the highest NO_3^- concentrations occurring in regions of highest N deposition, can only be explained by long-term accumulation and eventual leakage of atmospherically-deposited NO_3^- from catchment soils and vegetation (Dise and Wright, 1995; Stoddard et al., 2001). A recent comprehensive assessment of North American data has shown that these spatial patterns are evident in forest foliage, soils and surface waters (Aber et al., 2003), and concludes that many of the trends

Table 1
Regional trend results for ICP Waters sites for the period 1990–2001

Region	Continent	# sites	Slope of regional trend in:						
			SO_4^{2-}	NO_3^-	Gran Alkalinity	ANC	H^+	Ca+Mg	DOC
Alps	Europe	6	***−1.80***	***+0.52***	***+1.05***	−0.02	+0.00	−1.35	*
East Central Europe	Europe	20	***−3.91***	−0.87	+0.41	***+2.55***	−0.13	***−2.26***	+0.06
Northern Nordic	Europe	7	***−1.68***	+0.00	***+0.72***	+0.26	−0.07	***−1.23***	***+0.05***
Southern Nordic	Europe	19	***−6.75***	−0.05	***+1.73***	***+3.30***	***−0.16***	***−2.58***	***+0.08***
UK/Ireland	Europe	9	***−1.45***	+0.02	+1.37	+0.33	−0.29	***−1.46***	***+0.13***
West Central Europe	Europe	12	***−3.95***	−1.00	*	***+6.02***	+0.02	−5.42	+0.03
Maine/Atlantic Canada	N. America	18	***−1.02***	+0.00	***−0.59***	−0.32	+0.00	***−1.39***	+0.04
Vermont/Quebec	N. America	15	***−2.20***	−0.20	+0.26	***+0.94***	−0.05	***−1.40***	***+0.06***
Adirondacks	N. America	48	***−2.26***	***−0.47***	***+1.03***	***+1.19***	***−0.19***	***−2.29***	***+0.06***
Appalachian Plateau	N. America	9	***−2.27***	***−1.37***	***+0.79***	+1.92	−0.08	***−2.97***	+0.03
Upper Midwest	N. America	23	***−2.47***	+0.02	+0.32	+0.90	−0.01	***−1.80***	***+0.06***
Virginia Blue Ridge	N. America	3	+0.35	***−1.36***	+0.06	*	−0.00	***−0.58***	***−0.04***

Values are median slope for the region, with significant results ($P<0.05$) shown in bold and italics. Units for sulphate, nitrate, base cations [$Ca^{2+}+Mg^{2+}$], Gran alkalinity, ANC and hydrogen are μeq l^{-1} $year^{-1}$. Units for DOC are mg l^{-1} $year^{-1}$. * insufficient data.

reported for lake and stream NO_3^- may represent only the short-term variation in a large-scale and long-term increase in NO_3^- due to N saturation (see also Curtis et al., 2005, in this issue).

Over the 12-year period 1990–2001, ICP sites show decreasing NO_3^- concentrations in the Adirondack Mountains, Appalachian Mountains and the Virginia Blue Ridge (all in North America), and increasing concentrations in the Alps (Fig. 3). The area in northwestern Italy where the ICP Waters sites are located is subject to a high atmospheric input of N compounds (25–30 kg ha^{-1} yr^{-1} as the sum of ammonium and NO_3^-) which has remained fairly constant in the last two decades causing increasing N saturation in forest ecosystems and increasing NO_3^- levels in rivers and lakes (Rogora et al., 2001). No other regions exhibit clear patterns (Fig. 3) and once more, the absence of trend in the UK/Ireland group is consistent with the observations of Davies et al. (this issue) for the wider UK.

Some sites in Central Europe show increasing trends due to forest disturbance (harvesting or insects), while other sites in sensitive areas show decreasing trends. Vesely et al. (2002) have shown that NO_3^- in stream waters with pH less than or equal to 6 has decreased up to 60% between 1984–1986 and 1996–2000 in the Czech Republic. This rate of decline is greater than the 35% decrease of N emission observed in central Europe in the same period.

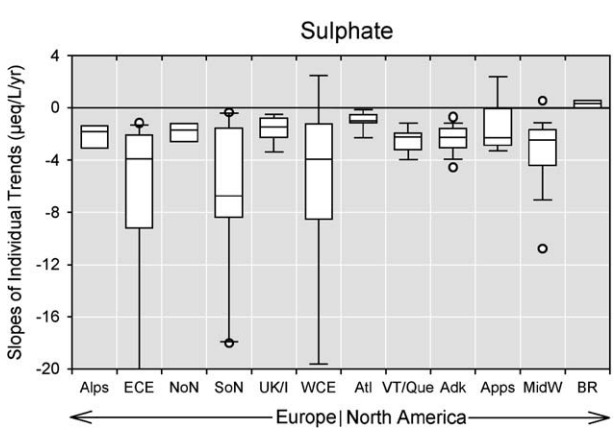

Fig. 2. Distributions of slopes for SO_4^{2-} trends in ICP regions in Europe and North America. Each box shows the range (25th to 75th percentiles, with line at median) of slopes; confidence intervals indicate 10th and 90th percentiles; dots indicate 5th and 95th percentiles. Significance of regional trend is indicated by preponderance of slope values (e.g., 95%) either above or below zero. Abbreviated region names are: ECE=East-Central Europe; NoN=Northern Nordic; SoN=Southern Nordic; UK/I=United Kingdom and Republic of Ireland; WCE=West-Central Europe; Atl=Maine and Atlantic Canada; VT/Que=Vermont and Quebec; Adk=Adirondack Mountains; Apps=Appalachian Plateau; MidW=Upper Midwestern U.S. and Canada; BR=Virginia Blue Ridge.

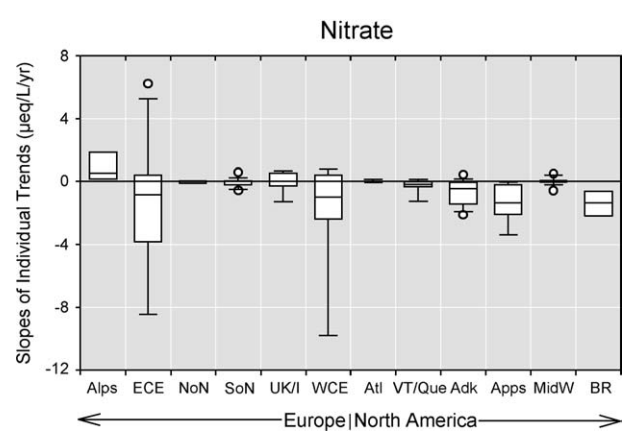

Fig. 3. Distributions of slopes for NO_3^- trends in ICP regions in Europe and North America. Interpretation of box and whiskers, as well as regional abbreviations, are as in Fig. 2.

3.3. Base cations

One of the expected responses of catchments to decreasing SO_4^{2-} is a decrease in base cation concentrations (Galloway et al., 1983). In this report, we use the sum of calcium and magnesium (Ca+Mg) as a surrogate for total base cations, because these cations are the most quantitatively important at the majority of acid sensitive monitoring sites, and because they exert the most control over alkalinity (Stoddard et al., 2003). As expected, all of the ICP regions show tendencies toward decreasing Ca+Mg (Fig. 4). One of the key findings of earlier regional assessments (Skjelkvåle et al., 2001b; Stoddard et al., 1999) is the larger-than-expected decreases in Ca+Mg in some regions, particularly in North America. When rates of Ca+Mg decline are equal, or nearly equal, to rates of SO_4^{2-} and NO_3^- decline, then chemical improvement (increasing alkalinity and pH) is negligible.

In the European regions, rates of Ca+Mg decrease are mostly smaller than those for SO_4^{2-} (Table 1, Fig. 4). One important exception is the U.K. and Ireland, where rates of rates of SO_4^{2-} and Ca+Mg decline were nearly equal for the time period 1990–2001—this has important implications for improvements in acidity in this region (see discussion below). One North America region (Maine and Atlantic Canada) exhibited stronger decreasing trends in Ca+Mg than in SO_4^{2-}.

3.4. Gran alkalinity and ANC

Because SO_4^{2-} is declining regionally in almost all ICP regions, and NO_3^- is either declining or unchanged in all but one region, we expect to see increases in the key indicators of recovery from acidification: Gran alkalinity, charge-balance ANC (acid neutralizing capacity) and pH (decline in H^+). Gran alkalinity is a measured variable that indicates the water's ability to buffer acidic inputs. ANC is calculated as an approximation for alkalinity. Charge-balance ANC is defined as the equivalent sum of base cations minus the equivalent sum of strong acid anions, and is particularly useful for regions where Gran alkalinity is not measured, and to compare to model outputs which are often made in terms of ANC rather than alkalinity. Most critical loads estimates depend on charge-balance ANC.

In the Alps, SO_4^{2-} is declining at a median rate of -1.8 μeq l^{-1} yr^{-1}. Combined with a median increase in NO_3^- of $+0.5$ μeq l^{-1} yr^{-1}, the Alps exhibit an overall change in acid anion concentrations of -1.3 μeq l^{-1} yr^{-1}, and a significant increase in Gran alkalinity of ca. $+1$ μeq l^{-1} yr^{-1} (Table 1, Fig. 5).

In East-Central Europe, the decline in SO_4^{2-} is -3.9 μeq l^{-1} yr^{-1}, considerably larger than the decline in base cations for this region (-2.3 μeq l^{-1} yr^{-1}); NO_3^- did not change significantly. While no significant increase in Gran alkalinity was observed for this region, calculated ANC increased strongly ($+2.6$ μeq l^{-1} yr^{-1}), consistent with the changes in SO_4^{2-} and Ca+Mg (Table 1)—more than 75% of the ICP sites in East-Central Europe showed increases in ANC for the period 1990–2001. This represents significant improvement in acid-base status for sites in Poland, the Czech Republic, and eastern parts of Germany. A handful of sites in this region do not report Gran alkalinity values, which may explain the lack of significant results for alkalinity.

In the more remote Northern Nordic areas, rates of deposition have historically been lower than in the rest of Europe; as a result, acidification is much less severe, and rates of chemical improvement are not expected to be large. Nonetheless, this region exhibited significant declines in SO_4^{2-} (-1.7 μeq l^{-1} yr^{-1}), smaller declines in Ca+Mg (-1.2 μeq l^{-1} yr^{-1}) and a significant, though

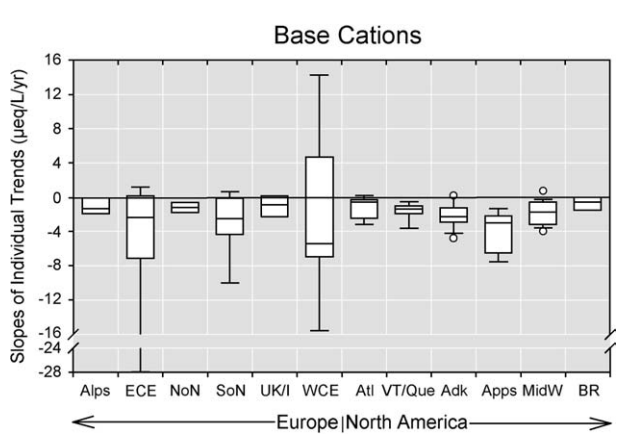

Fig. 4. Distributions of slopes for base cation (Ca+Mg) trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region abbreviations are as in Fig. 2.

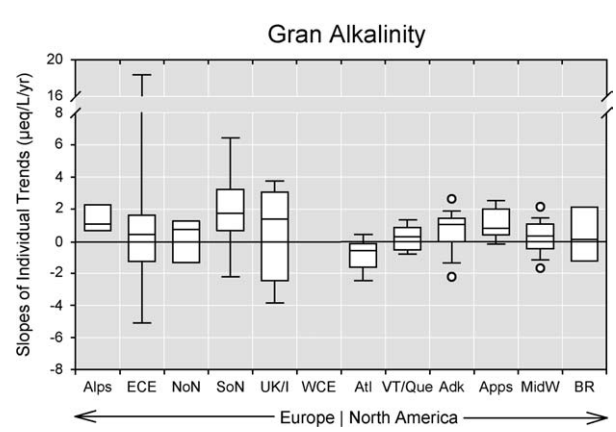

Fig. 5. Distributions of slopes for Gran alkalinity trends in ICP regions in Europe and North America. There were insufficient Gran alkalinity data available for West Central Europe to allow calculation of a regional trend. Interpretation of boxes and abbreviations as in Fig. 2.

modest, increase in Gran alkalinity (+0.7 μeq l^{-1} yr^{-1}) (Table 1, Fig. 5).

By contrast, the Southern Nordic region has experienced high rates of acidic deposition, especially in past decades, and significant surface water acidification (e.g., Henriksen et al., 1998; Kamari et al., 1991; Skjelkvåle et al., 2001a). Improving acid-base status has been observed since ca. 1990 in the southern portions of Norway, Sweden and Finland (Skjelkvåle et al., 2001a; Stoddard et al., 1999), and continues into the 2000s (Table 1). During the period 1990–2001, this region experienced the largest observed decreases in surface water SO_4^{2-}, no change in NO_3^-, and strongly increasing Gran alkalinity (+1.7 μeq l^{-1} yr^{-1}; Table 1). More than 75% of ICP sites in the Southern Nordic region exhibited upward trends in Gran alkalinity, and all sites exhibited upward trends in ANC (Fig. 6).

The U.K./Ireland region experienced the most modest decreases in surface water SO_4^{2-} of any European ICP region, and they were very closely balanced stoichiometrically by decreasing Ca+Mg (Table 1). As a result, we were unable to detect significant increases in either Gran alkalinity (Fig. 5) or calculated ANC (Fig. 6) in the UK and Ireland. These observations are largely in agreement with those of Davies et al. (this issue), although Davies et al. do demonstrate an apparent response to declining SO_4^{2-} when an alternative method of determining ANC is adopted based on DOC and labile Al. This latter method cannot be applied across the ICP dataset due to the absence of measured values of DOC and or labile Al data from some localities.

In West-Central Europe, we did not have sufficient Gran alkalinity data to perform reliable trend tests, and our conclusions regarding recovery are therefore based on calculated ANC (Table 1). This region exhibited substantial decreases in SO_4^{2-} (−4 μeq l^{-1} yr^{-1}), but widely variable changes in Ca+Mg (Fig. 4). Calculated ANC suggests a strong improvement in this region (+6 μeq l^{-1} yr^{-1}; Table 1, Fig. 6).

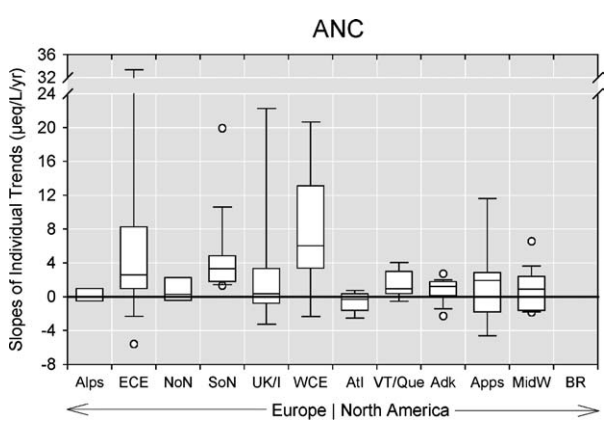

Fig. 6. Distributions of slopes for calculated ANC trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in Fig. 2. (ANC values were not calculated for the Blue Ridge sites.)

In North America three regions show significant improvement in either Gran alkalinity or ANC (Vermont/Quebec, Adirondacks and Appalachians), two exhibit no change (Upper Midwest and Virginia Blue Ridge), and one region is experiencing significant further acidification (Maine/Atlantic Canada). Movement toward recovery in the Adirondack and Appalachian mountains is an important finding, because neither of these regions showed significant improvement in previous regional analyses (e.g., Skjelkvåle et al., 2001b; Stoddard et al., 1999). All of these regions exhibit upward alkalinity trends that began in the early- to mid-1990s, and in all cases 75% or more of the individual sites have positive trend slopes (Fig. 5). In the Adirondacks, in particular, recent widespread improvement has received much attention, and includes increasing Gran alkalinity and pH, as well as significant decreases in toxic aluminium (Driscoll et al., 2003; Stoddard et al., 2003). Evaluation of the changing pattern of chemical trends observed in Canadian lakes over the past ten years shows that there has been a gradual shift from "no response" to "recovery" although the degree of improvement is still clearly at a very early stage (Jeffries et al., 2003).

The Virginia Blue Ridge region is not experiencing, nor is it expected to experience, decreasing SO_4^{2-} concentrations. As a result, there is no expectation that Gran alkalinity will increase in the immediate future; the current analysis indicates there has been no significant change in alkalinity during 1990–2001 (Table 1).

The region of Maine and Atlantic Canada is the only ICP region where significant acidification has occurred during the 1990s and early 2000s. Gran alkalinity decreased at a rate of −0.6 μeq l^{-1} yr^{-1} for the period 1990–2001 (Table 1, Fig. 5), and this acidification has occurred at the same time as significant (but small) decreases in surface water SO_4^{2-}. Importantly, Maine/Atlantic Canada is the only ICP region where Ca+Mg declines (−1.4 μeq l^{-1} yr^{-1}) exceeded observed decreases in acid anions (−1.0 μeq l^{-1} yr^{-1}). This somewhat extreme base cation behaviour has been noted previously in other regions now undergoing significant improvement (e.g., Couture, 1995; Jeffries et al., 2002; Kirchner and Lydersen, 1995; Lawrence et al., 1999; Wilander and Lundin, 2000), and still has no accepted geochemical explanation. It appears currently to be limiting the rate of recovery in Maine and Atlantic Canada.

3.5. pH

Chemical improvement of surface water acid-base chemistry involves a combination of changes toward

a historically more natural chemical composition. Included in these changes are decreases in SO_4^{2-} and potentially NO_3^- (in regions where NO_3^- has been a significant agent of acidification in the past), and increases in alkalinity and pH. Of these changes, increases in pH are perhaps the most biologically relevant, due to the relation between low pH and high concentrations of toxic aluminium. In the current assessment we analyse trends in hydrogen ion (calculated from pH measurements). A decrease in hydrogen ion concentration implies an increase in pH. Only two of the regions exhibit significant H^+ declines (the Southern Nordic and Adirondack regions; Table 1, Fig. 7). Both are among the regions showing the largest improvements in Gran alkalinity. pH is among the most difficult variables to measure well in the laboratory and variability in measurements makes it more difficult to detect trends. A longer data record might overcome inherent variability in the data, and lead to a conclusion of increasing pH in additional regions. The relatively large decrease in H^+ observed in UK/Ireland, for example, is not significant, possibly due to the small sample size used this analysis (see also Davies et al., this issue).

3.6. Dissolved organic carbon

Dissolved organic carbon (DOC) is of great interest in any analysis of surface water recovery, because it is an indicator of natural organic acidity (Driscoll et al., 1989). The previous ICP trends report (Skjelkvåle et al., 2001b) was one of the first to note the widespread increases in DOC now being observed throughout Europe and North America. All but one of the ICP regions included in this analysis exhibited positive slopes for DOC (Fig. 8), and six of these were considered

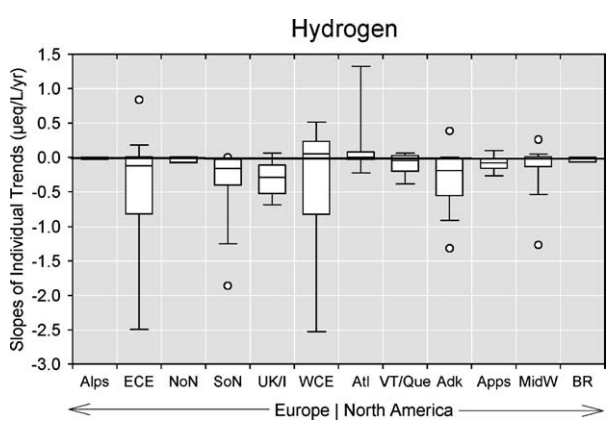

Fig. 7. Distributions of slopes for hydrogen ion trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in Fig. 2. Increasing pH (an indicator of recovery) is the same as decreasing H^+.

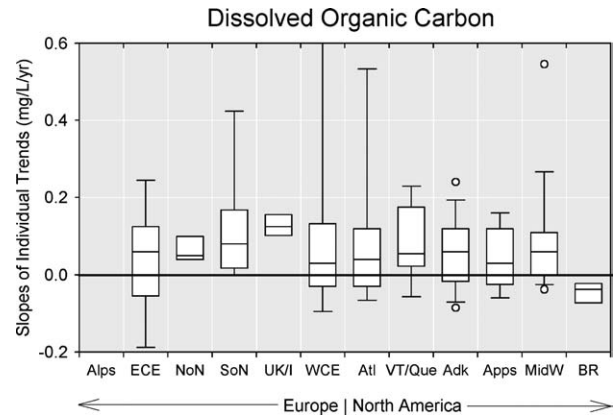

Fig. 8. Distributions of slopes for trends in dissolved organic carbon in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in Fig. 2. Increasing DOC is an indicator of the increased importance of organic acids in the acid/base chemistry of ICP sites.

significant. Overall, the results suggest an almost universal increase in the importance of organic acids.

Regional trends of increasing organic carbon through the 1990s have been documented from the UK (Freeman et al., 2001), the Nordic countries (Skjelkvåle et al., 2001a), elsewhere in Europe (Skjelkvåle et al., 2001b), and in the U.S. (Stoddard et al., 2003), while the picture is less straightforward in Canada (Jeffries et al., 2003). These increases may be coupled to warmer climate, particularly to elevated summer temperatures (Freeman et al., 2001), although the mechanism for observed changes is uncertain (e.g., Evans et al., 2002; Tranvik and Jansson, 2002) and may in part also be related to declining acid deposition (see Evans et al., this issue). If changes are temperature-driven, a warmer future climate may lead to further, and historically unprecedented, increases in DOC concentrations, with complex consequences for surface waters; these include increased organic acidity, increased buffering of changes in pH, increased water coloration, and decreased visible light and UV-B penetration within the water column. Alternatively, if declining acid deposition is having a major influence, the rise in DOC concentration may be seen as part of the recovery process, with "weak" organic acidity increasingly replacing "strong" mineral acidity.

3.7. Aluminium

Our interest in chemical recovery from acidification generally stems not from a desire to measure chemical change, but to observe and predict the process of biological recovery. For this reason, many of the chemical variables we choose to analyse are selected because of their relevance to the biota. Of the variables discussed thus far, both Gran alkalinity and pH have

important implications for biological recovery, both because of the direct toxic effects of elevated H^+, and because of their controlling effects on toxic aluminium concentrations. Unfortunately, most participants in the ICP Waters program do not routinely measure labile or inorganic monomeric aluminium (the form most toxic to biota), and we cannot infer regional patterns in aluminium behaviour from the ICP data. We can, however, observe the patterns at individual sites; while they do not give us the confidence that regional declines in aluminium would give us, declining concentrations of labile aluminium at single sites do suggest that our expectations of improving aluminium concentrations, based on declining alkalinity and H^+, are justified. An example of site-specific data for labile aluminium is shown in Fig. 9, for the Vikedal ICP site in western Norway. At Vikedal, pH began increasing ca. 1990, in response to a strong decline in SO_4^{2-}. Improvements in labile aluminium appear to have been simultaneous with increasing pH at this site. Regional declines in inorganic monomeric aluminium have also been reported for the Adirondack mountains (Driscoll et al., 2003).

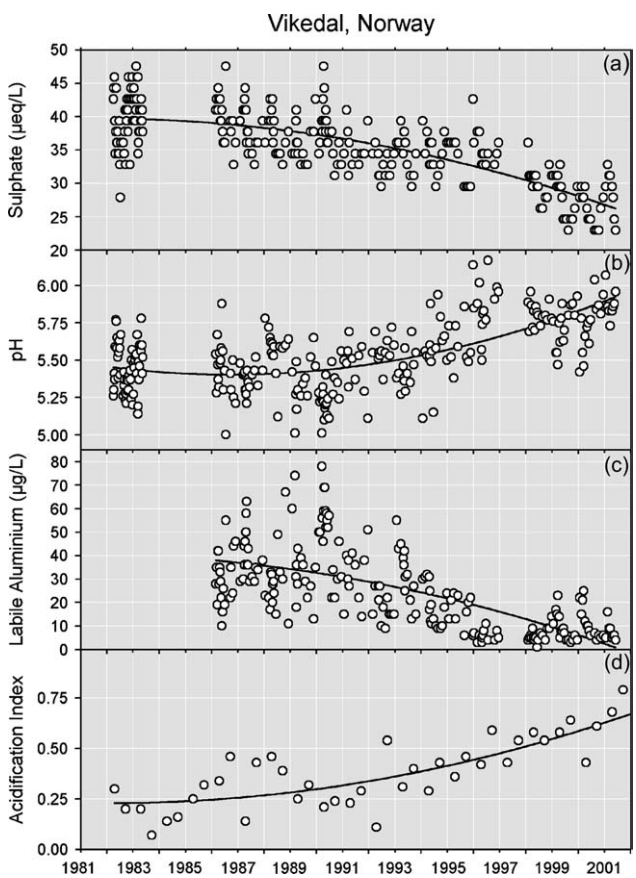

Fig. 9. Time series of (a) sulphate, (b) pH, (c) labile aluminium, and (d) Raddum invertebrate acidification index in Vikedal, an ICP Waters site in western Norway. Both sulphate and pH show improvement beginning in ca. 1990, a pattern common throughout the Nordic countries. Vikedal is one of the few ICP Waters sites with data for labile aluminium (c), which shows improvement beginning at the same time as sulphate and pH. The acidification index begins to improve in ca. 1992. An index score of zero indicates an acidophilic fauna assemblage, while and index score of 1 indicates a normal, undamaged assemblage (data from the ICP Waters database; see also Fjellheim and Raddum, 2001).

4. Do trends in deposition translate into trends in surface waters?

A major goal of the work of ICP Waters is to evaluate the changes in surface water chemistry in relation to reductions in emission and deposition of S and N.

It is difficult to compare absolute changes in SO_4^{2-} concentrations in surface waters and deposition, because of the effects of dry deposition and evapotranspiration. Both dry deposition and the evaporative concentration of ions in surface waters cause SO_4^{2-} concentrations in lakes and streams to be higher than those in precipitation. Higher concentrations lead to larger rates of change for SO_4^{2-} concentrations in surface waters than in precipitation. The percent change, however, should be relatively similar, assuming that dry deposition declines at the same rate as wet deposition, and that no changes in rates of evapotranspiration have occurred over time. There is a relatively good correlation between percentage change and concentration level, which means that sites with low concentrations of SO_4^{2-} show high percentage of change and sites with high concentrations of SO_4^{2-} show low percentage change. This will influence the comparison between regions, but the comparison between change in deposition and surface waters in the same region is unaffected.

We therefore present a comparison of percent change in SO_4^{2-} in precipitation and surface waters for each of the regions. European precipitation data are calculated for total deposition (wet plus dry) from EMEP Co-ordination Centre for Chemistry (CCC). Because no regional equivalent to EMEP exists in either the U.S. or Canada, we used wet deposition for North America and assume that percent changes in total deposition and wet deposition should be similar. U.S. data are from the U.S. National Atmospheric Deposition Program/National Trends Network (NADP/NTN; National Atmospheric Deposition Program/National Trends Network, 2002) and Canadian data from the Canadian Air and Deposition Monitoring Network (CAPMoN; Ro and Vet, 2003).

In general, rates of SO_4^{2-} decline are smaller in surface waters than in deposition for all regions in North America and most regions in Europe (Fig. 10) indicating a lagged response. This may reflect the desorption of S that has accumulated in catchment soils over the past century due to atmospheric deposition.

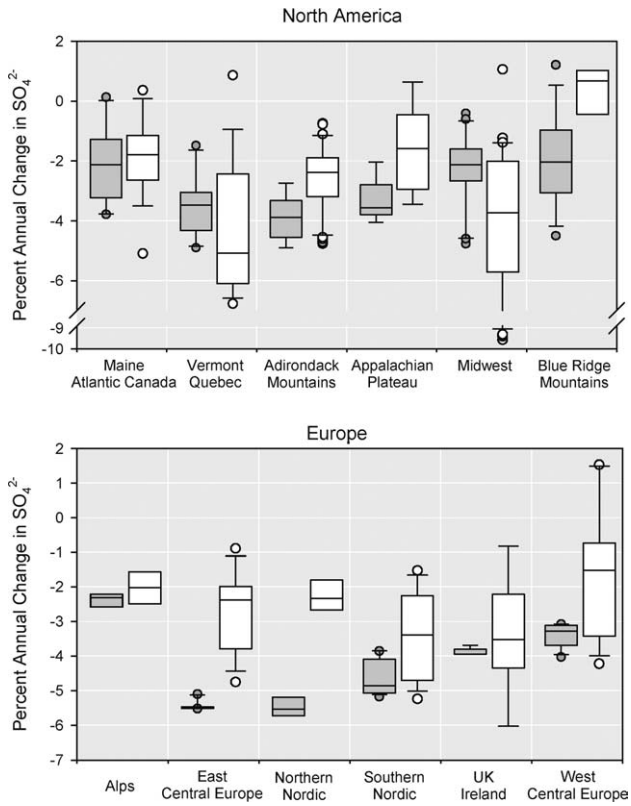

Fig. 10. Comparison of trend slopes for SO_4^{2-} in precipitation (left box – shaded) and SO_4^{2-} in surface waters (right box – clear) for the period 1990–2000 in acid sensitive regions of North America and Europe. North American deposition data are for trends in wet deposition concentrations. European deposition data are for trends in combined wet and dry deposition. Each box shows the range (25th to 75th percentiles, with line at median) of slopes; confidence intervals indicate 10th and 90th percentiles; dots indicate 5th and 95th percentiles.

Desorption of stored S has the effect of damping the trends in surface water SO_4^{2-} and slowing the rate of decline. One exception to the pattern in North America is in the Upper Midwest region of the U.S. (Fig. 10), where most lakes are seepage lakes. Here, the soils play only a minor role in controlling SO_4^{2-} concentrations, and declines in lake SO_4^{2-} concentrations are driven by dilution, following the drought that affected this area in the late 1980s and early 1990s (Stoddard et al., 2003). In Europe, both the Alps and the UK/Ireland regions show approximately the same percentage change in precipitation and surface waters indicating a very direct response on surface waters to changes in precipitation (see also Cooper, this issue).

5. Does chemical improvement lead to biological recovery?

As mentioned earlier, the ultimate goal of emissions reductions programs aimed at reducing the effects of acidic deposition is biological recovery—the re-establishment of sensitive taxa that were harmed or lost during the process of acidification. While we have the luxury of being able to assess chemical improvement over large regions and many monitoring sites, the existence of biological data relevant to biological recovery is much more limited. We may try to infer biological recovery from the stages of improvement in biologically-relevant chemistry (e.g., especially H^+ and aluminium), but those inferences will always be uncertain in the absence of actual biological data.

Although regional biological data are not generally available (but see Monteith et al., this issue), good monitoring data for single sites do exist, and can help us determine whether our expectations of biological recovery following chemical improvement are warranted (Raddum, 2003). An example is shown in Fig. 9 for Vikedal, one of the ICP Waters sites in western Norway. Strong declines in SO_4^{2-} have led to improvement in pH beginning in ca. 1990. Results for Raddum's acidification index (Raddum and Fjellheim, 1984) suggest that acid-sensitive invertebrates began to return in ca. 1992, and their abundance has continued to increase through the present. The Raddum index is a measure of acidification status based on presence/absence of sensitive invertebrate species. Similar results were found in Swedish lakes where statistically significant increase in another acidity biotic index was found for 11 out of 20 lakes (Wilander and Lundin, 2000).

6. Conclusions

The results from this work show that emission controls are working. Overall, the extent of recovery from acidification in Europe and North America varies over time, between regions, and between sites within regions, depending on a range of factors including the magnitude of deposition change and catchment characteristics. In general, however, there is clear evidence that reduced S deposition has led to significant improvements in the chemical status of acidified surface waters throughout Europe and North America. However future recovery can be changed by many factors, such as climate change and increased leaching of N (Skjelkvåle et al., 2003a). Specifically, for the key indicators of recovery:

- SO_4^{2-} concentrations are declining in 11 of 12 regions examined. The Blue Ridge region of the U.S., where decreases in SO_4^{2-} are not expected, is the only region not exhibiting significant regional decreases in SO_4^{2-}.
- In general, SO_4^{2-} declines in surface waters are smaller than the declines observed in precipitation, suggesting some buffering of the SO_4^{2-} decline by soil processes.

- NO_3^- concentrations increased in one region (the Alps), decreased in three North American regions, and were unchanged in all other regions examined.
- Most regions (7 out of 12) showed improvement in at least one indicator of chemical recovery: Gran alkalinity (measured), acid neutralizing capacity (calculated) and pH. The Maine and Atlantic Canada region was unusual in showing increasing acidification.
- DOC (an indicator of natural organic acidity) increased significantly in 6 out of 12 regions. All but one region had trends suggestive of increasing DOC. The mechanisms responsible for widespread increases in DOC are not currently known.
- While this paper focused on chemical trends, because chemical data are much more available, the observed trends in biologically-relevant chemistry should be facilitating biological recovery. Limited biological monitoring data from the ICP Waters network indicate that biological improvement may begin to occur after some lag time. Invertebrate data from one Norwegian stream suggest biological improvement lags chemical improvement by one or two years.

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