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

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1 **Abstract**

2 Acidification of lakes and rivers is still an environmental concern despite reduced emissions of  
3 acidifying compounds. We analysed trends in surface water chemistry of 173 acid-sensitive sites from  
4 12 regions in Europe and North America. In 11 of 12 regions, non-marine sulphate (SO<sub>4</sub><sup>\*</sup>) declined  
5 significantly between 1990 and 2008 (-15% to -59%). In contrast, regional and temporal trends in  
6 nitrate were smaller and less uniform. In 11 of 12 regions, chemical recovery was demonstrated in the  
7 form of positive trends in pH and/or alkalinity and/or acid neutralizing capacity (ANC). The positive  
8 trends in these indicators of chemical recovery were regionally and temporally less distinct than the  
9 decline in SO<sub>4</sub><sup>\*</sup>, and tended to flatten after 1999. From an ecological perspective, the chemical quality  
10 of surface waters in acid-sensitive areas in these regions has clearly improved as a consequence of  
11 emission abatement strategies, paving the way for some biological recovery.

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15 **Keywords:** acid deposition; surface waters; trend analysis; monitoring network; chemical recovery

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## 19 **1. Introduction**

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

30 The Convention on Long-Range Transboundary Air Pollution (CLRTAP) came into effect in  
31 1983 to control air pollutant emissions in Europe and North America, and thereby improve  
32 the environmental status of natural ecosystems. Under the CLTRAP, international cooperative  
33 monitoring programmes were initiated to assess the impact of atmospheric pollution on  
34 ecosystems. For surface waters, the International Cooperative Programme on Assessment and  
35 Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) has been an important  
36 contributor documenting the effects of the implemented Protocols under CLRTAP since 1985  
37 (Kvaeven et al. 2001).

38 The ICP Waters programme is designed to assess, on a regional basis, the degree and  
39 geographical extent of acidification of surface waters. The collected data provide information  
40 on dose/response relationships for a wide range of acid-sensitive lakes and streams under  
41 varying deposition regimes by correlating changes in acidic deposition with the physical,  
42 chemical and biological status of lakes and rivers. Data collected by various monitoring  
43 schemes are integrated and interpreted, and inter-laboratory quality control systems are run to  
44 ensure data are comparable across participating countries. Previous trend analyses of ICP  
45 Waters data on surface water chemistry have provided important indications of the geographic  
46 extent of acidification and recovery of lakes and streams for the 1980s (Newell and Skjelkvåle  
47 1997), the 1980s and 1990s (Stoddard et al. 1999), and up to the start of 2000 (Skjelkvåle et  
48 al. 2005; Skjelkvåle et al. 2001). Early assessments provided little evidence for chemical  
49 recovery during the 1980s. Subsequently, however, patterns of widespread chemical recovery

50 became clear during the 1990s, as indicated by reduced sulphate (SO<sub>4</sub>) concentrations and  
51 increases in pH and alkalinity. The reduction in sulphur deposition is considered to be the  
52 main driver of the improved acidification status of surface waters and is also substantiated by  
53 catchment input – output budgets (Prechtel et al. 2001) and acidification models (Jenkins et  
54 al. 2003).

55 Whether continued reduction in emissions of sulphur and nitrogen will lead to further  
56 improvement of surface water quality in acid-sensitive regions, sufficient to sustain biological  
57 recovery, depends on a number of factors (Wright et al. 2005). In some regions, base cations  
58 have declined at a similar or greater rate than SO<sub>4</sub>, preventing chemical recovery (Skjelkvåle  
59 et al. 2005; Stoddard et al. 1999). Catchments continue to be enriched by nitrogen deposition  
60 with possible consequences for enhanced leaching of nitrate (NO<sub>3</sub>) (Curtis et al. 2005;  
61 Moldan et al. 2006; Oulehle et al. 2008; Stoddard et al. 2001), especially under climate  
62 change. Additionally, widespread increases in concentrations of dissolved organic carbon  
63 (DOC) have also been documented and related to changes in atmospheric chemistry, most  
64 prominently the decline in sulphur deposition (Monteith et al. 2007). The increase in DOC  
65 may dampen expected reductions in acidity as humic substances are naturally acidifying  
66 agents (Erlandsson et al. 2011). Thus, ground truth data on the environmental status and  
67 recovery of acid-sensitive surface waters remain important for assessing the effects of  
68 emission controls.

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

## 72 **2. Methods**

### 73 2.1 Selection of variables

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

- 76 • Non-marine SO<sub>4</sub> and NO<sub>3</sub> are strong acid anions. As ICP Waters sites are selected to  
77 be remote from the influence of direct terrestrial pollution, elevated concentrations  
78 largely reflect the combined effects of recent trends in deposition and ecosystem

79 responses. The nitrogen acidification ratio (NAR), defined as the ratio of equivalent  
80 concentrations of  $\text{NO}_3$  to the sum of  $\text{NO}_3$  and  $\text{SO}_4$ , is used to indicate the relative  
81 importance of nitrogen as a driver for acidification.

- 82 • Non-marine base cations are mobilised by geological weathering and cation exchange  
83 reactions that neutralise acids in watersheds, and their concentrations will therefore be  
84 influenced by changes in acid deposition. Base cations will respond indirectly to  
85 changes in  $\text{SO}_4$  and  $\text{NO}_3$ . The sum of non-marine Ca and Mg equivalents comprise the  
86 major fraction of non-marine cations at the majority of acid-sensitive monitoring sites,  
87 and was therefore used as a surrogate for total non-marine base cation concentration.
- 88 • pH, measured alkalinity and calculated acid neutralizing capacity (ANC), reflect the  
89 outcome of interactions between changing concentrations of acid anions and base  
90 cations. Alkalinity is measured by titration and indicates the capacity of the water to  
91 buffer acidic inputs. ANC, calculated from sum of base cations ( $\text{Ca}+\text{Mg}+\text{Na}+\text{K}$ )  
92 minus the sum of acid anions ( $\text{SO}_4+\text{Cl}+\text{NO}_3$ ), is an approximate surrogate for  
93 alkalinity in waters with relatively low concentrations of DOC. For waters where DOC  
94 is higher, alkalinity is normally significantly lower than ANC.
- 95 • The concentration of dissolved organic carbon (DOC) (i.e., the fraction passing  
96 through a filter typically with a pore size of  $0.45\ \mu\text{m}$ ) is considered as a surrogate for  
97 organic acids, mostly derived through degradation of natural organic matter in  
98 catchment soils. The Nordic countries report total organic carbon (TOC), but we do  
99 not discuss these results separately as the dissolved fraction is expected to be large (>  
100 90 percent) in most of the samples.

101 Both  $\text{SO}_4$  and base cation concentrations were sea-salt corrected by subtracting the marine  
102 contribution estimated from the ratio of the ion to Cl in seawater (Lyman and Fleming 1940).  
103 Non-marine ions are hereafter denoted by an asterisk ( $\text{SO}_4^*$ ,  $\text{Ca}^*+\text{Mg}^*$ ). Water pH was  
104 transformed to  $\text{H}^+$  concentration (assumed to be equal to activity), prior to statistical analysis.

## 105 2.2 ICP Waters sites selected for trend analysis

106 ICP Waters data are provided by national and provincial monitoring programmes in the  
107 participating countries. Sampling frequencies, analytical methods, lengths of record, and site  
108 sensitivity to acidification vary between and within programmes. It was therefore necessary to

109 define criteria for inclusion of data in the analysis and comparison of trends among sites. Sites  
110 were selected if:

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

119

120 The number of sites that met the criteria ranged from 132 for DOC to 173 for  $\text{SO}_4^*$  (Table 1,  
121 Fig. 1), i.e. availability of data (criteria 1 and 2) was considered for each parameter in  
122 isolation and sites did not have to meet the data criteria for all parameters in order to be  
123 included.

124 For the purpose of regional comparison, sites are grouped into geographic regions which,  
125 where necessary, were constrained by attributes including similar acid-sensitivity (e.g.,  
126 similar geology, soil characteristics) and rates of deposition (Fig. 1). The list of regions on  
127 which we report is based on scientific and pragmatic decisions resulting from availability of  
128 data. Thirteen sites from Ontario, that do not contribute to the ICP Waters database, were  
129 nevertheless included in order to provide a sufficient number of sites to justify analysis as a  
130 separate region.

### 131 2.3 Analytical methods and quality assurance of data

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

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

#### 141 2.4 Statistical methods used for trend analysis

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

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

153 We compiled the results of the MKT for the individual sites and calculated the total number  
154 of “increasing”, “decreasing” and “no trend” occurrences for each parameter. This procedure  
155 is not strictly valid because the risk of falsely rejecting null hypotheses increases when  
156 individual results are summed. However, if each test is regarded as a Bernoulli trial with a  
157 success probability of 0.05, the total number of false rejections can still be expected to be  
158 relatively low. We therefore assume that the compilation of MKT results by region gives a  
159 good overview of trends in the data.

160 While the significance of sums of individual MKT tests are questionable from a statistical  
161 viewpoint, the slopes calculated for multiple sites within a region represent a distribution of  
162 results, which can in turn be examined and analysed for patterns. The non-parametric  
163 Wilcoxon test was used to test for different distributions of slopes (calculated with the Sen  
164 slope estimator) between two time periods of 10 years, i.e. 1990-1999 and 1999-2008 (1999 is  
165 included in both periods). The sites were grouped in the regions used for the regional trend



166 analysis (see below), and all sites that met the criteria (see above), were included in the  
167 analysis. The time intervals were chosen to minimise overlap between the time spans.

168 Regional trends in the data were assessed using the Regional Kendall Test (Helsel and Frans  
169 2006), which provides median slopes and a p-value for the trend's significance. The Regional  
170 Kendall Test has similar strengths as the MKT, and does not require normal distribution of the  
171 data.

### 172 **3. Results and discussion**

#### 173 3.1 Trends in individual sites

174 Patterns and qualitative results of the trend analyses for individual sites are summarised in  
175 Table 1. A significant decrease in  $\text{SO}_4^*$  concentration was observed at 87 % of sites; no  
176 significant increases were observed. Most sites (81 %) had no trend in  $\text{NO}_3$  concentration, but  
177 most trends for the remaining sites were negative. A decreasing trend in non-marine base  
178 cations ( $\text{Ca}+\text{Mg}$ )<sup>\*</sup> was observed at 55 % of the sites. A majority of sites did not show trends  
179 in NAR, alkalinity, ANC, DOC, or  $\text{H}^+$  concentration. However, increasing trends in NAR,  
180 alkalinity, ANC, and DOC were more common than decreasing trends, while the opposite was  
181 true for  $\text{H}^+$  concentration.

#### 182 3.2 Trends in sulphate by region

183 Concentrations of  $\text{SO}_4^*$  decreased significantly in all regions included in this analysis, except  
184 Virginia Blue Ridge in North America (Fig. 2, Tables 2 and 3). Previous trend analyses  
185 (Skjelkvåle et al. 2005; Stoddard et al. 1999) have shown similar regional patterns. In most  
186 catchments, responses of aquatic  $\text{SO}_4^*$  concentrations appear to respond rapidly to changes in  
187 atmospheric inputs of  $\text{SO}_4^*$  (Prechtel et al. 2001) because of limited capacity of the soil to  
188 adsorb  $\text{SO}_4$ . However, in the Virginia Blue Ridge region, deeply weathered soils with a large  
189 capacity to adsorb  $\text{SO}_4$  delay the response (Church et al. 1990), and the three sites follow the  
190 pattern revealed by a more comprehensive assessment of streams in the region (Stoddard et al.  
191 2003). Soils with large sulphur adsorption capacity also occur at stations from the Harz and  
192 Fichtel mountains in Germany (West and East Central European region, respectively), where  
193 again there is little evidence for reductions in surface water  $\text{SO}_4$  despite decreasing rates of

194 acidic deposition (see Alewell et al. 2001 for more detailed descriptions). A delayed response  
195 in surface waters can be caused by release of previously deposited sulphur stored in wetland  
196 and/or forest soils (see Mitchell et al. 2011 for a discussion of this and other potential  
197 confounding factors). Such release can affect surface water trends in  $\text{SO}_4^*$  as well as pH and  
198 ANC.

199 The largest rates of decline in  $\text{SO}_4^*$  concentration were observed in Europe (Table 2), and  
200 especially in South Nordic region. Trends in most regions tended to be more gradual in the  
201 second decade, but only differed significantly in Vermont/Quebec and Ontario (Table 4).  
202 Trend analyses of  $\text{SO}_4$  in precipitation have indicated substantial decreases of sulphur  
203 deposition, especially in the areas that previously received the highest loads (Tørseth et al.  
204 2012). Regional and temporal patterns in changes of  $\text{SO}_4^*$  in surface water in North America  
205 and Europe were similar to those observed in precipitation, indicating that reduced deposition  
206 of sulphur has been the main driver of decreasing  $\text{SO}_4^*$  concentrations in surface waters.

### 207 3.3 Trends in nitrate by region

208 The regional and temporal patterns in  $\text{NO}_3$  concentration were more varied than for  $\text{SO}_4^*$   
209 (Fig. 2). Even so,  $\text{NO}_3$  concentrations were found to be decreasing in 7 of the 12 regions  
210 (Tables 2 and 3). The Alps was the only region that showed increasing concentrations.  
211 However, in the Alps as well as in the North Nordic, and Maine/Atlantic Canada regions,  
212 slopes were significantly smaller for the period 1999-2008 than 1990-1999 (Table 4) and  
213 appear to have leveled out or changed from positive to negative (Fig. 2, see also Tables S1  
214 and S2 in supporting information). The results for Vermont/Quebec and possibly West  
215 Central Europe indicate that the opposite has occurred in these regions.

216 While reduced deposition of sulphur is the main driver behind the extensive decline of  
217 freshwater  $\text{SO}_4^*$ , the controls of  $\text{NO}_3$  concentration are complex as a result of the  
218 biogeochemical cycling of nitrogen in soils. Factors that have been invoked to explain trends  
219 include changes in deposition of nitrogen (Curtis and Simpson 2014; Oulehle et al. 2008;  
220 Rogora et al. 2012), progressive N saturation (Curtis et al. 2011) and changes in snow cover  
221 (Brooks et al. 1999; De Wit et al. 2008) and temperature (Brookshire et al. 2011; Monteith et  
222 al. 2000). Furthermore, insect attack on vegetation can cause large temporal variation in  $\text{NO}_3$   
223 concentration as observed in sites from Blue Ridge Mountains and East Central Europe

224 (Eshleman et al. 1998; Oulehle et al. 2013). Thus, trends in  $\text{NO}_3$  remain poorly understood  
225 but at present, declining trends are more prominent than increases.

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

### 231 3.4 Trends in non-marine base cations by region

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

235 Almost all regions showed decreasing concentrations of  $\text{Ca}^*+\text{Mg}^*$  between 1990 and 2008  
236 (Table 2, Fig. 2). However, in 6 of the regions the trend slopes were significantly less  
237 negative in the latter half of the time span (Table 4), indicating that the rate of decline is  
238 decreasing. In contrast to the other regions, and despite a significant reduction in  $\text{SO}_4^*$ , the  
239 Alps showed increasing concentrations of  $\text{Ca}^*+\text{Mg}^*$ , while the rate of increase was greater in  
240 the more recent decade. While  $\text{NO}_3$  concentrations have increased slightly, there has been an  
241 overall reduction in acid anion concentration and other mechanisms are therefore required to  
242 explain this tendency. Possible explanations for the observed recent increase in base cations in  
243 the Alps include hydrological effects (i.e., drought), increased weathering rates caused by  
244 climate change (Rogora et al. 2003), and contribution from Saharan dust deposition episodes  
245 (Rogora et al. 2004).

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

### 250 3.5 Trends in measured alkalinity and calculated ANC by region

251 Measured alkalinity and calculated charge balance ANC are widely used as indices of the  
252 extent of acidification and the susceptibility of natural waters to acidification. The steeper  
253 negative regional trends for  $\text{SO}_4^*$  relative to those for base cations, combined with the  
254 regional signal of either no change or decreasing  $\text{NO}_3$ , should result in increasing ANC and  
255 alkalinity. Indeed, all regions except Virginia Blue Ridge, the only region not to show a  
256 significant decline in  $\text{SO}_4^*$ , show positive regional trends in alkalinity and/or ANC between  
257 1990 and 2008 (Table 2, Fig. 3), indicating chemical recovery from acidification. In the South  
258 Nordic region and Vermont/Quebec, the increases in ANC were larger for 1990-1999 than  
259 1999-2008 (Table 4, Fig. 3), while in the Alps, the largest increase in ANC and alkalinity  
260 occurred in the latter time span. In the Adirondacks there was a discrepancy between trends in  
261 measured alkalinity and calculated ANC. The former indicate larger improvement for 1990-  
262 1999 than 1999-2008, while the latter suggest the opposite (Table 4). The rates of change are,  
263 however, small (Fig. 3). The discrepancy is possibly due to the influence of changes in  
264 aluminium and DOC, which are not included in the calculation of ANC, but which do  
265 influence measured (Gran) alkalinity (Driscoll et al. 1994; Waller et al. 2012).

### 266 3.6 Trends in DOC by region

267 Dissolved organic carbon (DOC) is a key component of aquatic chemistry, e.g. as an indicator  
268 of natural organic acidity (Erlandsson et al. 2011). In this respect, it has received considerable  
269 attention in recent years because of rising levels in many regions (Hruška et al. 2009;  
270 Monteith et al. 2007). The drivers of rising DOC are still debated in the scientific literature,  
271 but analysis of ICP Waters, and associated data has demonstrated that DOC trends are  
272 strongly correlated with trends in deposition chemistry and catchment acid sensitivity  
273 (Monteith et al. 2007). While changes in sulphur and seasalt deposition appear to control  
274 monotonic trends, climatic factors can exert strong influence on seasonal and interannual  
275 variations (Clark et al. 2010) and longer term climate change is therefore also likely to affect  
276 DOC trends. All regions where DOC data were available, except East Central Europe and the  
277 Appalachians, showed increasing DOC concentrations between 1990 and 2008 with median  
278 rates varying between 0.03 and 0.11 mg/L/y (Table 2). None of the regions showed a  
279 significant difference in the distribution of slopes between the first and second half of the time

280 span (Table 4), i.e. there are few indications that the rise in DOC concentrations is beginning  
281 to plateau. If the increase has mainly been driven by reduced acidification, DOC levels are  
282 likely to stabilise in the near future, because further reductions in  $\text{SO}_4^*$  concentrations are  
283 expected to be relatively slight.

284 The link between rising DOC and declining  $\text{SO}_4^*$  concentrations indicates that rising DOC  
285 concentrations may be integral to the process of chemical recovery from acidification. This  
286 partial replacement of mineral acidity by organic acidity may explain why pH and alkalinity  
287 responses are more muted than had once been anticipated and predicted by process-based  
288 models of acidification dynamics such as MAGIC (Battarbee et al. 2005; Erlandsson et al.  
289 2010).

### 290 3.7 Trends in pH by region

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

295 All regions, except the Alps, Appalachians and Virginia Blue Ridge, showed decreasing  $\text{H}^+$   
296 concentration between 1990 and 2008 (Table 2). The  $\text{H}^+$  trends in the Adirondacks were  
297 steeper between 1990 and 1999 than between 1999 and 2008 (Table 4, Fig. 2), confirming the  
298 findings of Lawrence et al. 2011. Elsewhere, however, there is little evidence that trends in  $\text{H}^+$   
299 concentrations are levelling off. The relative change is smaller in North American regions  
300 than in most European regions.

301 The trends in  $\text{H}^+$  are consistent with those observed for other parameters on a regional scale.  
302 In the European regions, the median decreases in base cations have been appreciably smaller  
303 than the equivalent declines in acid anions. Consequently, ANC, alkalinity and pH have  
304 increased here. An exception is the UK where increases in alkalinity and ANC were small and  
305 insignificant, respectively, despite significant decrease in  $\text{H}^+$ . However, trends in alkalinity  
306 over the period 1988-2008 for a wider set of UK lakes and streams than assessed here  
307 (Monteith et al. 2014) averaged  $0.63 \mu\text{Eq L}^{-1} \text{yr}^{-1}$  which is similar to the average of all  
308 European regions in this analysis. The apparent lack of response in ANC in UK may result

309 from the effect of large long-term variability in sea-salt deposition and compound analytical  
310 errors affecting the ANC calculation in waters with relatively high concentrations of sea salt  
311 (Evans et al. 2001a; b). When ANC for these UK sites is calculated using an alternative,  
312 alkalinity-based method, trends for the period 1988-2008 have been found to be statistically  
313 significant and are similar in magnitude to trends in other regions (Monteith et al. 2014). In  
314 the North American regions, the rates of decrease of base cations are closer to those observed  
315 for acid anions (see also e.g. (Driscoll et al. 2007; Stoddard et al. 2003). Changes in  
316 ANC/alkalinity are therefore relatively small and so is the decrease in  $H^+$ .

317 Inorganic monomeric aluminium ( $Al_i$ ), which is an important parameter associated with  
318 acidification, was not included in this analysis as it is not routinely measured across the ICP  
319 Waters network. The speciation of aluminium is highly dependent on pH, and decreasing  
320 trends in  $Al_i$  concentration are likely to have occurred at strongly acidified sites with  
321 decreasing  $H^+$  concentration across the ICP Waters network. The implication of these trends  
322 in hydrochemical parameters is that conditions for sensitive biota in many of these waters  
323 have improved and various communities of organisms are responding (see e.g. the articles in a  
324 recent special issue on recovery from acidification in the UK, *Ecological Indicators* 37B,  
325 2014).

#### 326 **4. Conclusions**

327 A pattern of chemical recovery from acidification of surface waters across a large number of  
328 rivers and lakes in Europe and North America is shown by trend analysis of  $SO_4^*$ , pH, ANC,  
329 and alkalinity data from 173 acid-sensitive ICP Waters monitoring sites. This recovery  
330 appears to be driven primarily by the reduction of sulphur deposition, confirming that  
331 emission control programs are having their intended effect on aquatic chemistry, even though  
332 improvements are not as universally clear, or rapid, as were once expected.

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

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

343 **Acknowledgements:**

344 We are grateful to all Focal centers that submit data to the ICP Waters programme centre,  
345 making large regional assessments of the environmental state of nutrient poor, acid sensitive  
346 lakes and rivers possible. We also thank Climate and Pollution Directorate in Norway and the  
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## Tables and figure captions

**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 neutralizing capacity (ANC),  $H^+$ , and dissolved organic carbon<sup>1</sup> (DOC)

		$SO_4^*$	$NO_3$	NAR	$Ca^*+Mg^*$	Alkalinity	ANC	$H^+$	DOC <sup>1</sup>
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

<sup>1</sup>DOC was measured as DOC or as TOC

**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 Neutralizing Capacity (ANC),  $H^+$ , and organic carbon (DOC)<sup>1</sup>.  $SO_4$  and base cations were seasalt-corrected. Significant ( $p<0.05$ ) upward trends in dark gray shade, significant downward trends in light gray shade, non-significant in white. Units:  $\mu Eq/L/yr$  for all except DOC: mg C/L/yr. nd, no data

		$SO_4^*$	$NO_3$	NAR	$Ca^*+Mg^*$	Alkalinity	ANC	$H^+$	DOC <sup>1</sup>
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

<sup>1</sup> DOC was measured as TOC or DOC

**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 gray shade, significant downward trends in light gray shade, non-significant in white. Units:  $\mu\text{eq/L/yr}$  for all except DOC: mg C/L/yr

		SO <sub>4</sub> <sup>*</sup>	NO <sub>3</sub>	Ca <sup>*</sup> +Mg <sup>*</sup>	H <sup>+</sup>	DOC <sup>1</sup>
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

<sup>1</sup> 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 <sub>4</sub> <sup>*</sup>	NO <sub>3</sub>	NAR	Ca <sup>+</sup> +Mg <sup>*</sup>	Alkalinity	ANC	DOC	H <sup>+</sup>
Europe	North Nordic		**(-)	**(-)					
	South Nordic	* (+)					**(-)		
	United Kingdom						*(-)		
	West Central Europe	* (+)	* (+)						
	East Central Europe			**(-)	**(+)				
	Alps	* (+)	**(-)	**(-)	**(+)	**(+)	**(+)	nd.	
N. America	Maine & Atlantic Canada		**(-)	**(-)	**(+)		*(-)		*(-)
	Vermont & Quebec	**(+)	**(+)	**(+)	**(+)		**(-)		
	Adirondacks				**(+)	**(-)	**(+)		**(+)
	Appalachians				nd.		nd.		
	Blue Ridge Mountains			* (+)	nd		nd.	nd	
	Ontario	**(+)		**(-)	**(+)				

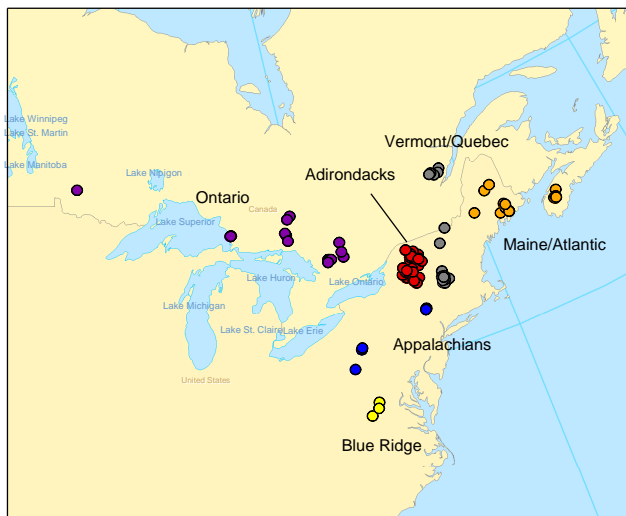
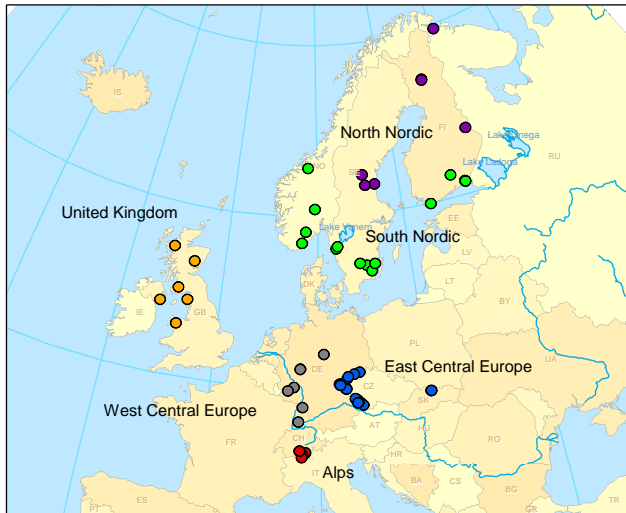
**Fig. 1** Map showing location of the monitoring stations (coloured circles). Different colouring of the circles indicates that stations belong to separate regions

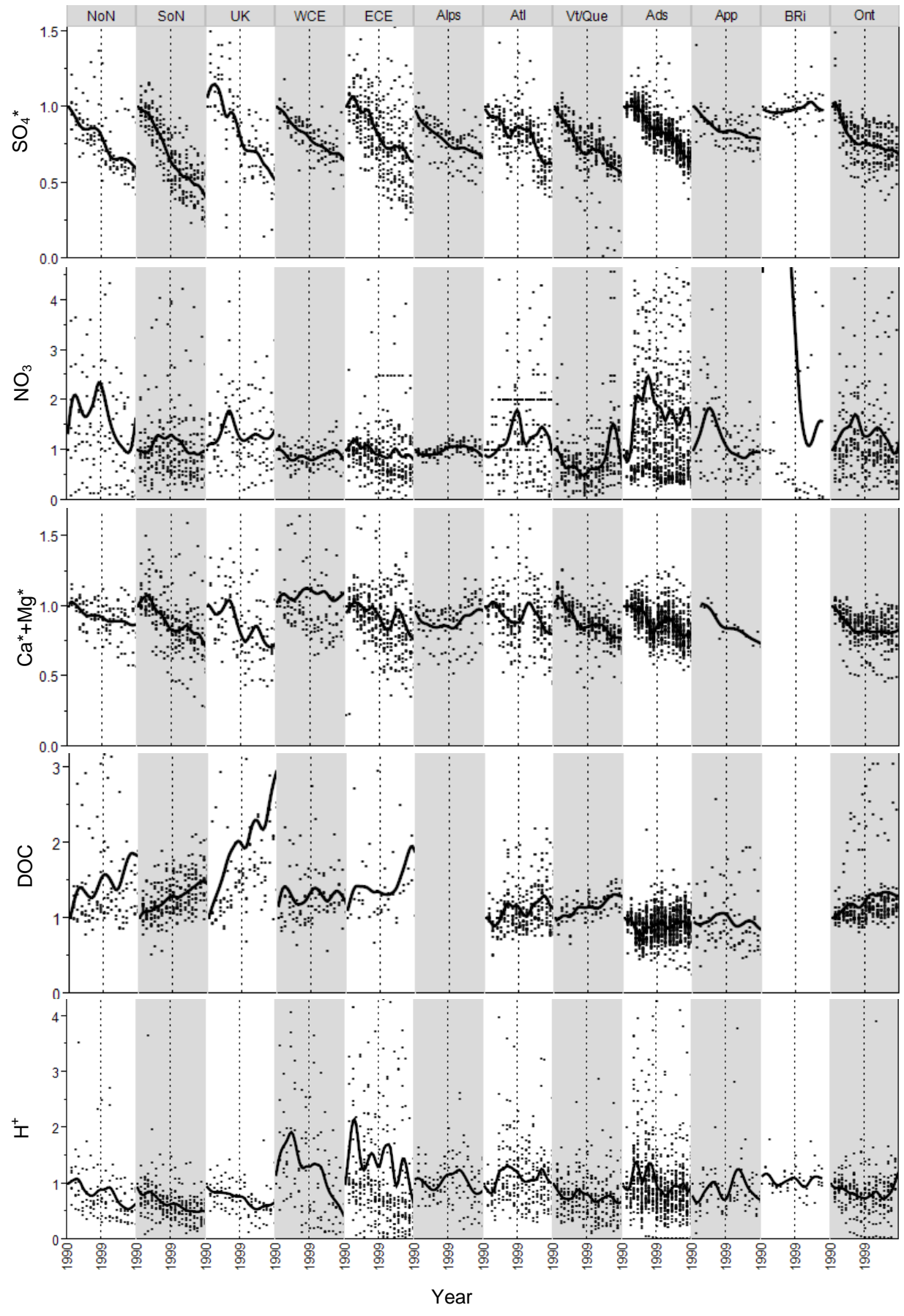
**Fig. 2** Relative change of annual means of  $SO_4^*$ ,  $NO_3$ , sum of base cations  $(Ca+Mg)^*$ ,  $H^+$ , and organic carbon  $(DOC)^l$  in regions of Europe and North America from 1990-2008. Each annual mean is divided by the first annual mean (i.e. between 1990 and 1993) of each time series. 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-Manine and Atlantic Canada, Vt/Que-Vermont and Quebec, Ads-Adirondacks, App-Appalachians, BRi-Blue Ridge Mountains, Ont-Ontario

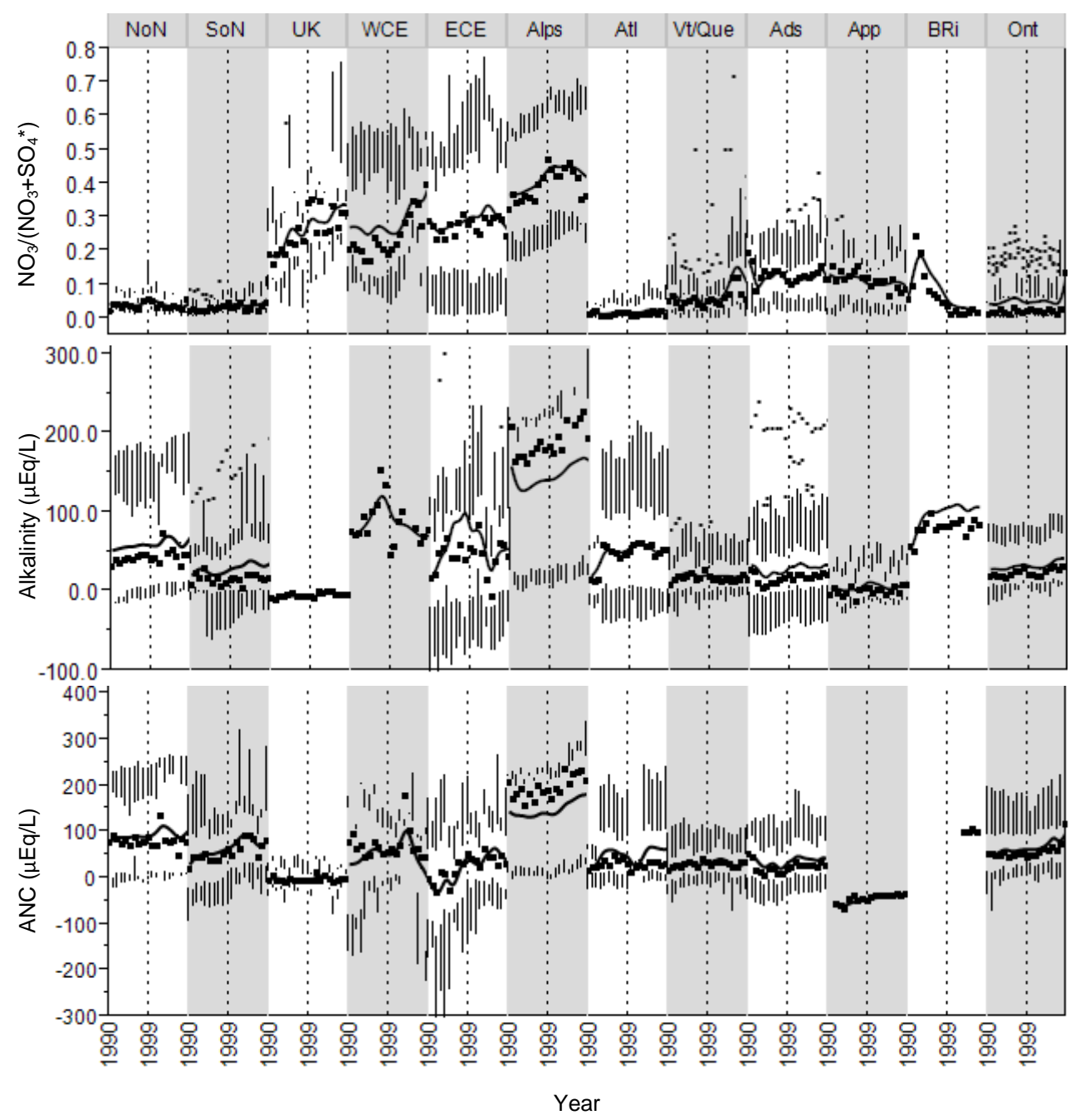
**Fig. 3** Absolute change of nitrate acidification ratio (NAR), alkalinity and ANC in regions of Europe and North America between 1990-2008. The line is a cubic spline with a lambda of 0.05. The points represent the median value and the vertical black lines extends from the 75<sup>th</sup> percentile +the interquartile range multiplied by 1.5 and the 25<sup>th</sup> percentile -the interquartile range multiplied by 1.5

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## **Supplementary material:**

### **Trends in surface water chemistry in acidified areas in Europe and North America from 1990 to 2008**

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**Table S1** Results from the Regional Kendall trend analysis for 1990 to 1999. For each region, median trend slope is shown for  $SO_4^*$ ,  $NO_3$ , Sum of base cations ( $Ca+Mg$ )\*, Acid Neutralizing Capacity (ANC),  $H^+$ , and organic carbon (DOC)<sup>1</sup>.  $SO_4$  and base cations were seasalt-corrected. Significant ( $p<0.05$ ) upward trends in dark gray shade, significant downward trends in light gray shade, non-significant in white. Units:  $\mu eq/L/yr$  for all except DOC: mg C/L/yr. nd, no data

1990-1999		$SO_4^*$	$NO_3$	$Ca^*+Mg^*$	Alkalinity	ANC	$H^+$	DOC <sup>1</sup>
Europe	North Nordic	-1.50	0.03	-0.70	1.13	1.12	-0.02	0.06
	South Nordic	-5.29	0.03	-2.72	0.48	3.23	-0.06	0.11
	United Kingdom	-1.09	0.18	-0.63	0.00	0.16	-0.16	0.13
	West Central Europe	-4.64	-1.14	-2.37	2.38	11.40	0.00	0.02
	East Central Europe	-3.39	-0.53	-1.33	-0.07	3.06	-0.16	0.13
	West Central Europe	-4.64	-1.14	-2.37	2.38	11.40	0.00	0.02
	Alps	-2.12	0.49	-1.08	1.10	0.00	0.00	
N. America	Maine & Atlantic Canada	-1.15	0.02	-1.00	-0.22	0.03	0.00	0.03
	Vermont & Quebec	-3.04	-0.24	-1.77	0.40	1.42	-0.02	0.10
	Adirondacks	-2.31	-0.18	-2.39	0.98	-0.36	-0.05	0.02
	Appalachians	-2.77	-0.28	-1.41	1.39	1.85	-0.03	0.01
	Blue Ridge Mountains	0.40	-0.96		-0.03		0.00	
	Ontario	-3.98	0.01	-3.66	0.32	0.23	-0.02	0.02

<sup>1</sup> DOC was measured as TOC or DOC

**Table S2** Results from the Regional Kendall trend analysis for 1999 to 2008. For each region, median trend slope is shown for  $SO_4^*$ ,  $NO_3$ , Sum of base cations ( $Ca+Mg$ )\*, Acid Neutralizing Capacity (ANC),  $H^+$ , and organic carbon (DOC)<sup>1</sup>.  $SO_4$  and base cations were seasalt-corrected. Significant ( $p<0.05$ ) upward trends in dark gray shade, significant downward trends in light gray shade, non-significant in white. Units:  $\mu eq/L/yr$  for all except DOC: mg C/L/yr. nd, no data

1999-2008		$SO_4^*$	$NO_3$	$Ca^*+Mg^*$	Alkalinity	ANC	$H^+$	DOC
Europe	North Nordic	-1.10	-0.11	-0.22	0.99	1.24	-0.01	0.02
	South Nordic	-2.60	-0.07	-1.43	0.21	1.09	-0.02	0.08
	United Kingdom	-0.90	0.05	-0.39	0.25	-0.43	-0.10	0.13
	West Central Europe	-1.60	1.97	-0.95	-4.81	-3.65	-0.09	0.02
	East Central Europe	-1.70	-0.16	-0.60	0.28	2.81	-0.22	0.23
	West Central Europe	-0.80	-1.13	3.49	3.29	4.86	0.00	
	Alps							
N. America	Maine & Atlantic Canada	-1.40	0.00	-0.97	-0.42	-0.67	-0.01	0.05
	Vermont & Quebec	-1.60	0.09	-1.07	0.15	-0.45	-0.02	0.07
	Adirondacks	-2.40	-0.03	-1.62	0.07	0.55	0.01	0.01
	Appalachians	-1.20	-0.12	-0.87	0.02	0.77	0.02	-0.02
	Blue Ridge Mountains	-0.30	-0.11		-0.02		0.00	
	Ontario	-1.30	-0.07	-0.50	0.96	1.20	0.01	0.02