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The response of soil solution chemistry in European forests to decreasing acid deposition

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Abstract

Acid deposition arising from sulphur (S) and nitrogen (N) emissions from fossil fuel combustion and agriculture has contributed to the acidification of terrestrial ecosystems in many regions globally. However, in Europe and North America, S deposition has greatly decreased in recent decades due to emissions controls. In this study we assessed the response of soil solution chemistry in mineral horizons of European forests to these changes. Trends in pH, acid neutralising capacity (ANC), major ions, total aluminium (Al_{tot}), and dissolved organic carbon (DOC) were determined for the period 1995-2012. Plots with at least 10 years of observations from the ICP Forests monitoring network were used. Trends were assessed for the upper mineral soil (10-20 cm, 104 plots) and subsoil (40-80 cm, 162 plots). There was a large decrease in the concentration of sulphate (SO_4^{2-}) in soil solution; over a ten-year period (2000-2010), SO_4^{2-} decreased by 52% at 10-20 cm and 40% at 40-80 cm. Nitrate was unchanged at 10-20 cm but decreased at 40-80 cm. The decrease in acid anions was accompanied by a large and significant decrease in the concentration of the nutrient base cations, calcium, magnesium and potassium ($Bc = Ca^{2+} + Mg^{2+} + K^+$) and Al_{tot} over the entire dataset. The response of soil solution acidity was non-uniform. At 10-20 cm, ANC increased in acid-sensitive soils (base saturation ≤10%) indicating a recovery, but ANC decreased in soils with base saturation >10%. At 40-80 cm ANC remained unchanged in acid-sensitive soils (base saturation ≤20%, pH_{CaCl_2}≤4.5) and decreased

in better-buffered soils (base saturation >20%, pH_{CaCl_2}>4.5). In addition, the molar ratio of Bc to Al_{tot} either did not change or decreased. The results suggest a long-time lag between emission abatement and changes in soil solution acidity and underline the importance of long-term monitoring in evaluating ecosystem response to decreases in deposition.

Introduction

Air pollution can impact forest health directly, through foliar damage, and indirectly, through soil-mediated effects on nutrient availability and root functioning which in turn can exacerbate natural stress factors such as drought and pest outbreaks (De Vries *et al*., 2000). Acid deposition arising from emissions of sulphur (S) and nitrogen (N) from fossil fuel combustion and agriculture has contributed to the acidification of terrestrial ecosystems in many regions globally (Bouwman *et al*., 2002). Acid deposition increases the concentration of protons (H^+) and strong acid anions (AA), including sulphate (SO_4^{2-}), nitrate (NO_3^-) and chloride (Cl⁻), in soils, which increases the rate of base cation leaching ($Ca^{2+}, Mg^{2+}, K^+, Na^+$) and associated soil acidification. In forest soils, acid deposition is primarily buffered by Bc released from mineral weathering (Ulrich, 1983). However, when the rate of proton deposition exceeds Bc weathering, soil solution becomes more acidic, with a decrease in pH and acid neutralizing capacity (ANC) - the difference between Bc and AA (ANC = $(Ca^{2+} + Mg^{2+} + K^+ + Na^+) - (SO_4^{2-} + NO_3^- + Cl^-)$). This in turn can bring potentially toxic forms of aluminium (Al) and other metals into solution (Reuss and Johnson, 1986). In addition, soil exchangeable Bc pools are depleted and base saturation (BSat) the proportion of Bc on the soil cation exchange complex, decreases. As a result, in poorly buffered soils (BSat<20%), acid deposition results in elevated inorganic Al and H^+ in soil solution and drainage waters (Driscoll *et al*., 2001).

Ecological impacts on forests have been widely documented. Acid deposition has resulted in a decline of sugar maple and red spruce stands in eastern North America due to soil Ca^{2+} depletion (DeHayes *et al*., 1999; Sullivan *et al*., 2013; Battles *et al*., 2014). In Europe, high levels of Al in soil solution have reduced Mg^{2+} nutrition in Norway spruce (de Wit *et al*., 2010; Lomský *et al*., 2012). High inorganic Al in soil solution can also impact tree fine root growth and functioning (Godbold *et al*., 2003; Vanguelova *et al*., 2007a). Acid deposition also significantly altered carbon (C) and N cycling in soil organic horizons of Norway spruce forests in the Czech Republic (Oulehle *et al*., 2011). In China, acid deposition has resulted in significant acidification of subtropical forest soils (Liu *et al*., 2010; Larssen *et al*., 2011; Liu *et al*., 2011; Zhu *et al*., 2016).

In recent decades, air pollution reduction policies, such as the Convention on Long-Range Transboundary Air Pollution (CLRTAP) (UNECE, 1979) in Europe and the Clean Air Act Amendments in North America have resulted in large decreases in S emissions. Nitrogen emissions also decreased but not to the same extent (EEA, 2016). As a result, there has been a large decrease in atmospheric S deposition. In Europe, precipitation SO_4^{2-} decreased by 73% between 1990-2012 (Colette *et al*., 2016). Meanwhile, NO_3^- in precipitation decreased by 33% for the same period (Colette *et al*., 2016). In many parts of the world however, acid deposition is increasing due to rapid economic expansion (Dentener *et al*., 2006) such that many forests will experience acid deposition in the future (Posch *et al*., 2015). For example, in industrialized and agriculturally intensive areas of China, rates of inorganic N deposition are like peak levels in northwestern Europe in the 1980s (Liu *et al*., 2013). Evaluating responses to changes in acid deposition is thus key to supporting worldwide effective emissions controls and recovery of impacted ecosystems.

There has been much focus on the response of sensitive soils and surface waters in Europe and North America to acid deposition. In surface waters, there has been an almost universal decrease in SO_4^{2-} often accompanied by increasing pH and ANC (Stoddard *et al*., 1999; Skjelkvåle *et al*., 2007; Garmo

et al., 2014; Driscoll *et al.,* 2016). The response varies regionally with delayed recovery of pH and ANC in some areas (Strock *et al.,* 2014) due to desorption of SO_4^{2-} accumulated in soils and depletion of soil Bc pools (Alewell *et al*., 2000a; Futter *et al.*, 2014; Fakhraei *et al.*, 2016; Watmough *et al*., 2016).

Monitoring of the effects of air pollution on forest health has been carried out in Europe by ICP Forests (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests) under the CLRTAP. Soil solution has been monitored at the intensive monitoring Level II plots in the ICP Forests network since the early 1990s (De Vries *et al*., 2003). The chemistry of soil solution provides an indication of nutrient availability, potential acid stress to fine roots and mycorrhizae (Binkley and Fisher, 2012) as well as potential exceedance of deposition critical loads. The molar ratio of nutrient cations (Bc = Ca^{2+} + Mg^{2+}+K^+), to total aluminium, Bc:Al_{tot} or the Ca^{2+} to Al_{tot} ratio (Ca:Al_{tot}) are often used as indicators of toxic effects of Al on plant roots (Cronan *et al.,* 1989; Sverdrup and Warfvinge, 1993). They are also used as the chemical criteria in calculating critical loads of acidity in forests; a Bc:Al_{tot} threshold of between 0.6 and 1.2 is applied depending on tree species (CLRTAP, 2017).

In contrast to surface waters, there have been relatively few regional assessments of changes in soil solution in response to decreasing acid deposition. Iost *et al.* (2012) found no change in the soil solution Bc:Al_{tot} molar ratio or inorganic N at ICP Forests plots with at least 5 years of data up to the mid-2000s. However, changes in S, pH, ANC and other parameters have yet to be assessed.

The soil solution data collected at intensively monitored plots in the ICP Forests network represent a unique long-term dataset to assess the response of soil solution acidity to decreasing SO_4^{2-} and inorganic N deposition in recent decades. The data have been collected using harmonised methods for sampling and analysis, making it possible to assess changes at the European scale. Specific objectives

were to characterise the chemistry of soil solution with respect to acidity (pH, ANC, $Bc:Al_{tot}$), major ions and dissolved organic carbon (DOC) and to assess the temporal changes in these parameters since the mid-1990s. It was expected that the decrease in SO_4^{2-} and inorganic N deposition would result in less SO_4^{2-} and NO_3^- in soil solution. This in turn was expected to result in an increase in ANC, $Bc:Al_{tot}$ and pH in poorly buffered soils and a decrease in soil solution Bc in better-buffered soils. As such, trends were stratified by soil buffering capacity. Soil solution chemistry also varies biogeographically (Garmo *et al*., 2014), between forest types (Kristensen *et al*., 2004) and by the magnitude of atmospheric deposition. A second objective was to assess the influence of these factors on soil solution trends.

Materials and methods

Sample collection and analysis

Soil solution, throughfall deposition and soil chemistry data from the ICP Forests Level II monitoring network were used (Lorenz, 2010). Deposition data were processed by the ICP Forests Expert Panel on Deposition as described by Waldner *et al*. (2014). Throughfall and soil solution data used for the 42 Swedish plots were collected within the SWETHRO network (Pihl Karlsson *et al*., 2011). Soil pH_{CaCl_2} and BSat, from a soil survey in the mid 1990s, were provided by the Forest Soil Coordinating Centre (FSCC) of ICP Forests. Methods for soil solution collection, analysis and quality control have been harmonized since 1995 and are described in the ICP Forests manual on soil solution collection and analysis (Nieminen *et al*., 2016). The number of lysimeters varied among plots and depth intervals and was generally reported as a single value either from analysis of a pooled sample or the average of individual samples. A mandatory minimum of three lysimeters per depth interval was required (Nieminen *et al*., 2016). Sampling took place weekly, fortnightly or monthly. After sample collection, a subsample was taken for determination of pH and conductivity. The remaining sample was passed through a 0.45 µm membrane filter and analysed for major ions ($Ca^{2+}, Mg^{2+}, K^+, Na^+$,

NH_4^+, SO_4^{2-}, NO_3^-, Cl^-), DOC and Al_{tot}. Laboratories in ICP Forests network participating countries carried out the analyses. Sample collection and analysis were subject to quality assurance and quality control checks including the use of control charts for internal reference, charge balance and participation in laboratory ring tests (König *et al*., 2013; Marchetto *et al*., 2009). Sampling below canopy throughfall and of open field bulk precipitation was carried out at the plots, and on a nearby opening, respectively, following the ICP Forests manual on sampling and analysis of deposition (Clarke *et al*., 2016). In general, between 3 and 20 replicate collectors were used and samples collected at weekly, fortnightly or monthly intervals.

Time series selection

Temporal changes were tested for plots that had at least 10 years of data between 1995 and 2012. Time series with gaps of 5 years or more were excluded. Soil solution was sampled using a range of lysimeters; the most common was the tension (suction-cup) lysimeter. To avoid artifacts due to sampler type, the analysis was applied for tension lysimeters only. In addition, data from organic soils (Histosols) were excluded, as they would be expected to respond differently than mineral soils to changes in deposition. Sampling depths ranged from just below the forest floor (0 cm) down to 4 m, with 90% of the lysimeters located between 0 and 80 cm. In general, lysimeters were installed in the upper mineral soil corresponding to the rooting zone and at a deeper depth, considered to be below the rooting zone. The time series were grouped into two depth intervals: upper mineral soil: 10-20 cm representing the upper, more organic rich rooting zone and lower mineral soil: 40-80 cm representing a deeper, more mineral horizon where water was draining from the soil profile. Where more than one depth was sampled in an interval, the depth closest to the median of all the plots was selected; either 20 cm (for 10-20 cm interval) or 50 cm (40-80 cm interval).

Site and soil description

A total of 171 plots were included. Of these, 104 had soil solution data at 10-20 cm, 162 at 40-80 cm (Fig. 1) and 95 at both depth intervals. Of the 171 plots, 120 were primarily coniferous stands and 51 were dominated by deciduous trees. The most common tree species were *Picea abies* (L.) Karst. (67), *Pinus sylvestris* L. (35) and *Fagus sylvatica* L. (31). Median soil pH_{CaCl_2} was 3.9 in the 10-20 cm depth interval and 4.4 at 40-80 cm (Table 1). The number of plots with pH_{CaCl_2} <5 was 93 (of 100) in the upper depth interval and 124 (of 145) in the lower depth interval. The majority were acid soils and buffered via silicate weathering, cation exchange and, at lower pH, the dissolution of aluminium oxides and hydroxides (Ulrich, 1983). Base saturation was low, median values being 11% and 20% in the two depth intervals, respectively. A BSat of 20% was observed as a threshold at which acid deposition resulted in the mobilisation of Al and H^+ to surface waters (Driscoll *et al.*, 2001). The ranges of soil pH_{CaCl_2} and BSat were representative of those reported from the ICP Forests Level I network (Cools and de Vos, 2011).

Data pre-treatment

Values reported as below quantification limit were replaced either by a value submitted by individual countries to represent the quantification limit over the time (10 countries), or by the limit of detection values submitted to the ICP Forests database in 2010 (3 countries). Secondly, the precision of data (number of decimal places) submitted to the database changed over the study period. Levene's test (Levene, 1960) was used to test for homogeneity of variance in the data at different levels of precision and there were no significant differences so that trend analysis could be applied across the whole-time series. At some plots, data from individual lysimeters were reported in the database, in which case the median value was used. Soil solution data were aggregated to monthly time intervals by taking the median of multiple observations per month, where present. Trends in pH, major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-), DOC, Al_{tot} and the molar $Bc:Al_{tot}$ ratio were tested. $Bc:Al_{tot}$ trends were

also tested for soils with pH_{CaCl2} <5.0, where the ratio is closer to the critical limit. In addition, trends were tested for AA, Bc and ANC. Ammonium in soil solution was close to or below detection limit for most plots and was not analysed for trends. The normality of soil solution data was evaluated for skewness and kurtosis (Pearson's kurtosis, R) using the 'moments' package in R. Except for pH and ANC, the data were heavily skewed. Hence, a log-transformation was applied to improve normality for all the other parameters ($Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-$, DOC, Al_{tot}, AA, Bc, $Bc{:}Al_{tot}$). Deposition consisted of monthly fluxes of throughfall and open field bulk precipitation. Details of data preparation and checks are described in Waldner *et al.* (2014).

Trends at the European scale

A linear mixed-effects model was used to detect temporal changes in soil solution at the European scale, like that applied by Jonard *et al.* (2015). The intercept and slope of the model contained both fixed and random effects. For the intercept, the fixed parameter 'a' corresponded to solute concentration in the year 2000 and 'month' to the monthly intercept (Eqn. 1). As the intercept of the linear model would correspond to the concentration in the year 0, the data were centred on the year 2000 by subtracting 2000 from the sampling year. Another random factor $ctry_{int}$ was used to account for country effects (e.g. due to differences in sample collection or analysis among countries) and a random factor $plot_{int}$ was used to account for plot effects. Another random factor ($year_{int}$) was included to account for the non-linear interannual variability.

For the slope, parameter b is the fixed part describing the slope over time—the long-term change. Random coefficients ($ctry_{slp}$) and plots ($plot_{slp}$) were included to account for individual country and plot changes (Eqn. 1).

solute var. $= \left[a + \text{month} + \text{ctry}_{\text{int}}\left(0, \sigma_{\text{ci}}^2\right) + \text{plot}_{\text{int}}\left(0, \sigma_{\text{pi}}^2\right) + \text{year}_{\text{int}}\left(0, \sigma_{\text{yi}}^2\right)\right]$

$$+ \left[b + \text{ctry}_{\text{slp}}\left(0, \sigma_{\text{cs}}^2\right) + \text{plot}_{\text{slp}}\left(0, \sigma_{\text{ps}}^2\right)\right] \cdot (\text{year} - 2000) + \varepsilon(0, \sigma^2) \quad (1)$$

where σ_{ci}^2 is the variance of the intercept (i) due to random factor country, σ_{pi}^2 the variance of the intercept (i) due to plot factor and σ_{yi}^2 the intercept variance due to random factor year. σ_{cs}^2 is the variance of the slope (s) due to random factor country and σ_{ps}^2 random slope variance due to plot effects.

Several covariance structures were tested to test if accounting for serial autocorrelation would improve the model. The structures tested were autoregressive (AR), Toeplitz, autoregressive moving average (ARMA) and three forms of spatial covariance (exponential, linear and power). The tests were carried out on a subset of data and evaluated by comparing the information criteria (AIC, BIC) of the fitted model. The best fit was given by the autoregressive moving average (ARMA), which then was used in the full dataset.

For log-transformed data, the fitted values of the fixed parameters were used to report the change relative to the intercept over 10 years according to:

$$\text{relative 10 year change (\%)} = \frac{10^{a+5 \cdot b} - 10^{a-5 \cdot b}}{10^a} \cdot 100 \quad (2)$$

For untransformed data the relative change was described by:

$$\text{relative 10 year change (\%)} = \frac{b \cdot 10}{a} \cdot 100 \quad (3)$$

The fitting of the linear model was carried out with the MIXED procedure of the SAS software (version 9.3; SAS institute Inc., Cary, NC, USA).

Trends at individual plots

The linear mixed-effects model was run at individual plots with 'year' and 'month' as fixed factors and 'year' as a random factor. At each plot, the intercept in the year 2000 gave the concentration for that year. These values were used to calculate summary statistics for soil solution in the year 2000. The linear model was run for throughfall chemical changes at individual plots and the relative change was calculated as above. The plots were then assigned to two categories of throughfall and included in the analysis by environmental factors.

Stratification by environmental factors

To assess the influence of environmental factors on soil solution trends, additional models were run with these factors included as fixed factors. The models tested whether temporal trends differed among levels of the factor. Factors were limited to two or three levels to avoid fragmenting the data into too many small subsets of plots making the detection of trends difficult. The variables were region, forest type, soil acidity, and trends in throughfall deposition.

The factor region was included to reflect regional changes in deposition, as well as biogeography and climatic influences on soil acidity trends. Countries were assigned to three regions as follows: North (Norway, Sweden, Finland), West (Belgium, Denmark, France, Ireland, United Kingdom) and Central (Austria, Germany, Switzerland). Plots in Spain (1) and Italy (2) were not included as there were not enough to form a category for southern Europe.

Soil solution trends could differ between deciduous and coniferous plots due to differences in nutrient cycling, deposition magnitude and trends as well as soil fertility. For example, it has been shown that there was a greater response in soil solution NO_3^- to atmospheric inputs at broadleaf forests in Europe, as they are usually located on more fertile soils (Kristensen *et al.*, 2004).

Soil acidity is an important determinant of soil solution chemistry and would be expected to moderate the response to deposition changes. In more acidic soils, decreased acid input should result in less inorganic Al and H^+ in soil solution, whereas Bc response should be more evident in less acidic soils. We divided the plots into two categories of soil pH_{CaCl_2} and BSat using their median values. The values differed with depth interval, as the upper layer was more acidic.

For SO_4^{2-}, throughfall provides an indication of the total deposition (Clarke *et al*., 2016). Plots were divided into groups based on the change in flux for a ten-year period relative to the year 2000. For throughfall SO_4^{2-}, the plots were divided into two categories based on the median, e.g. for SO_4^{2-} the median trend was a 60% decrease over ten years, so plots were grouped into those with a greater decrease and those with a smaller (Table 2). Soil solution trends were tested between levels of throughfall Bc, inorganic N ($NO_3^- + NH_4^+$) and potential acidity (Ac_{pot}), which was used to account for the potential acidifying effect due to nitrification of NH_4^+ deposition. Potential acidity is the sum of total deposition of non-marine AA plus + NH_4^+ minus non-marine Bc ($Ac_{pot} = nmSO_4^{2-} + nmCl^- + NO_3^- + NH_4^+ - nmBCnmBCc$) (CLRTAP, 2017). The non-marine fraction was calculated assuming all Na^+ was of marine origin and then using the ratio of Na^+ to other ions in seawater to calculate their marine and non-marine fractions.

Results

Soil solution statistics

Soil solution was acidic at most plots with median ANC values of −47 and −26 µeq L^{-1} in the year 2000, at 10-20 cm and 40-80 cm depth respectively (Table 3, Fig. 2, Fig. 3). Soil solution pH was lower at 10-20 cm than at 40-80 cm; 5th and 95th percentiles were 3.7 and 7.0 at 10-20 cm, and 4.1 and 7.7 at 40-80 cm (Table 3). At 10-20 cm, Ca^{2+} made the greatest contribution to Bc, followed by Na^+, Mg^{2+} and K^+. At 40-80 cm, Na^+ was the most abundant Bc followed by Ca^{2+}, Mg^{2+} and K^+.

The difference between depths was likely due to the inclusion of 42 plots from Sweden at 40-80 cm. These plots had a higher Na^+ concentration due to marine deposition. Median $Bc:Al_{tot}$ ratio was 1.4 and 1.5 in both depth intervals, respectively. The concentration of DOC decreased with depth, with median values of 12 mg L^{-1} at 10-20 cm and 6.8 mg L^{-1} at 40-80 cm (Table 3, Fig. 2, Fig. 3).

Sulphate was the anion in highest concentration in soil solution, and it increased markedly from shallow to deeper soil depths (Table 3). Chloride concentrations were also relatively high; median values were 94 and 106 µeq L^{-1} at 10-20 cm and 40-80 cm. Median NO_3^- was 16 and 7.2 µeq L^{-1} (0.23 and 0.10 mg N L^{-1}) at 10-20 cm and 40-80 cm, respectively. However, there were considerable regional differences in NO_3^- with some areas having concentrations close to detection limit, while others had elevated NO_3^-. At 10-20 cm, 46 plots (44%) had median concentrations greater than 1 mg N L^{-1} (71 µeq L^{-1}), a proposed threshold for critical N leaching and saturation (Gundersen *et al*., 2006; Stoddard, 1994). At 40-80 cm, the number of plots with median higher than 1 mg N L^{-1} was 51 (31%).

Trends in soil solution: global model

There was a large and significant decrease in the concentrations of SO_4^{2-}, Bc and Al_{tot} at both soil depths over the monitoring period (Table 4, Fig. 2, Fig. 3). Sulphate decreased by 52% and 40% at 10-20 cm and 40-80 cm respectively over a ten-year period, a change in concentration of −61 and −69 µeq L^{-1}, respectively. Concentrations of Ca^{2+} decreased by −57 and −68 µeq L^{-1} over a ten-year period, while Mg^{2+} decreased by −24 and −18 µeq L^{-1} and K^+ by −7.1 and −3.5 µeq L^{-1} at the two depths (Table 4). Nitrate was unchanged at 10-20 cm but showed a relative decrease of 30% at 40-80 cm. There was no change in Na^+ or Cl^-. Overall, Bc decreased by 47% and 26% over a ten-year period. These decreases offset the decrease in AA such that ANC did not change (Table 4, Fig. 2, Fig. 3). In addition, there were no significant trends in soil solution pH. Total Al declined at both depths; relative decreases were 19% at 10-20 cm and 17% at 40-80 cm over ten years. Despite the decrease in

Al_{tot}, the $Bc:Al_{tot}$ ratio of acidic soils (pH_{CaCl_2}<5.0) showed no change. The concentration of DOC showed a small but significant decrease (17%) at 40-80 cm but no change at 10-20 cm (Table 4, Fig. 2, Fig. 3).

With the exceptions of DOC and NO_3^-, trends were similar between soil depths (Table 4). The significance, direction and magnitude were similar when the analysis was carried out on the forest plots common to both soil depths (Supporting Information; Table S1). The only differences were for NO_3^-, which no longer was significant at 40-80 cm, and Na^+, which showed a small but significant decrease at 10-20 cm.

There were also similarities between trends in soil solution and deposition. Significant decreasing trends were found for SO_4^{2-}, inorganic N and Bc in throughfall at the plots (Supporting Information; Table S2). Throughfall SO_4^{2-} decreased by 60% over a ten-year period, a change in concentration of −35 µeq L^{-1} (Table S2). Throughfall inorganic N decreased by 33% over ten years relative to 2000 and by a concentration of −17 µeq L^{-1}. Trends were significant for both NO_3^- and NH_4^+ in throughfall deposition. Base cation deposition in throughfall also decreased but not to the same extent as AA. The relative ten-year change in Bc was −14%. As a result, ANC increased in throughfall, by +27 µeq L^{-1} over ten years. ANC was unchanged in bulk precipitation, which suggests that dry deposition of S and/or internal cycling of Bc influenced ANC in throughfall. pH increased significantly in both bulk precipitation and throughfall (Supporting Information; Table S2). The difference in ANC and pH trends in bulk precipitation was likely due to a difference in the datasets used, ANC was not available at all plots, while other plots were missing pH in some years.

Trends in soil solution, stratified by environmental factors

There was a non-uniform response of soil solution acidity when stratified by soil buffering capacity. At 40-80 cm, decreases in deposition resulted in greater changes in soil solution concentrations of Bc in better-buffered soils (pH_{CaCl_2}>4.5, BSat>20%). This was due to the larger decrease in Ca^{2+} in soil solution in these soils as might be expected due to their buffering capacity (Table 5). However, the decrease in AA did not match that of Bc and ANC decreased in these soils as a result (Table 5). In contrast, in soils with pH_{CaCl_2}≤ 4.5, there was a greater decrease in SO_4^{2-} and NO_3^-, but there was no trend in ANC in these soils. Aluminium decreased significantly in both groups, but more in the more acidic one (pH_{CaCl_2}≤4.5, BSat≤20%). When sites were classified according to BSat, the trends were similar; soils with BSat>20% experienced greater decrease in Bc and decreasing ANC trend compared to those with BSat≤20% (Supporting Information; Table S3). As such, at 40-80 cm, soil solution acidity was unchanged in the more acidic soil group but continued to increase in better-buffered soils.

At 10-20 cm there was no difference in trends between soils classified by soil pH_{CaCl_2} (Table 5); however, soils with BSat≤10% showed a significant increase in ANC, whereas those with BSat>10% had significantly decreasing ANC (Supporting Information; Table S3).

Forest type (coniferous/deciduous) had a significant influence on soil solution Bc trends. At both soil depths, Ca^{2+} decreased more under deciduous plots while K^+ decreased more under coniferous plots (Table 5). Magnesium, Na^+ and Bc decreased significantly more in deciduous plots at 40-80 cm. The relative change in these ions was generally higher in coniferous plots where concentrations were lower. At 40-80 cm, there was a significant increase in ANC at coniferous plots and a decrease at deciduous plots. At 10-20 cm, Al_{tot} decreased significantly at coniferous plots. The trends for forest type were somewhat like those for soil pH and BSat. This was due to covariance between factors; coniferous plots had lower BSat and greater decreases in throughfall SO_4^{2-} than deciduous plots (Supporting Information; Table S4).

There were few regional differences in soil solution trends (Table 5). At 10-20 cm, the only difference was for Mg^{2+}, which decreased more in the Central region compared to the North and West Europe. At 40-80 cm, Al_{tot} decreased more in the Central and West regions than in northern Europe and a significant decrease in DOC was evident in the Central and Western regions but not in the North (Table 5).

There were few differences in soil solution trends when plots were grouped by changes in throughfall SO_4^{2-}, Ac_{pot}, Bc or inorganic N. At 10-20 cm, SO_4^{2-} showed a response to throughfall; soil solution SO_4^{2-} decreased more at plots with larger decreases in throughfall SO_4^{2-} (Table 5). In contrast, at 40-80 cm, Al_{tot} decreased more in plots where throughfall SO_4^{2-} decreased by less than 60% but ANC declined significantly at these plots. Overall, there were few significant trends, or few consistent trends between depth intervals or among throughfall SO_4^{2-}, Ac_{pot}, Bc or inorganic N categories (Supporting Information; Table S3).

Discussion

Large decrease in soil solution SO_4^{2-}

The large decrease in deposition and soil solution SO_4^{2-} at the European scale was similar to observations from individual forest plots (Brumme *et al.*, 2009; Vanguelova *et al.*, 2010; Pihl Karlsson *et al.*, 2011; Verstraeten *et al.*, 2012; Waldner *et al.*, 2014) and surface waters (Prechtel *et al.*, 2001; Kvaalen *et al.*, 2002; Garmo *et al.*, 2014; Driscoll *et al.*, 2016) and consistent with the large decrease in SO_2 emissions in Europe and North America (EEA, 2016). Trends in soil solution SO_4^{2-} at 10-20 cm were similar in magnitude to changes in throughfall. Larger changes were observed at plots with larger decreases in throughfall SO_4^{2-}, suggesting that the upper soil layer responded rapidly to changes in inputs. However, the

magnitude of the soil solution decrease at 40-80 cm was lower than at 10-20 cm. Many studies have reported a lag in response of SO_4^{2-} in soil solution and surface waters to decreasing SO_4^{2-} deposition (Oulehle *et al*., 2006; Meesenburg *et al*., 2016). This has been attributed to desorption of previously deposited SO_4^{2-} from soils (Sokolova and Alekseeva, 2008; Fakhraei *et al*., 2016), dissolution of Al-hydroxy-sulphates (Khanna *et al*., 1987) or climate induced changes in S cycling (Mitchell and Likens, 2011). Release of SO_4^{2-} from soils is generally higher in areas with historically high deposition (Oulehle *et al*., 2006), and SO_4^{2-} desorption isotherms suggest it can take decades for soil solution to reach a steady state with current inputs (Alewell *et al*., 2000a).

Decreasing Bc in soil solution

The strong temporal decline in soil solution SO_4^{2-} (and overall AA) was partly balanced by a significant decrease in Bc. The comparable magnitudes of AA and Bc trends suggest that the changes in strong acid anions drove trends in Bc and as such, that Bc weathering and release were the primary buffering mechanism for acid deposition. Throughfall Ca^{2+} and Mg^+ also decreased significantly and likely contributed to decreasing Bc in soil solution. Where soil exchangeable Bc pools and weathering rates were small, Bc deposition can influence soil solution cations (Watmough *et al*., 2005). Several studies have pointed to Bc deposition as a factor in temporal soil solution changes (Alewell *et al*., 2000a; Fölster *et al*., 2003; Vanguelova *et al*., 2010; Ukonmaanaho *et al*., 2014). Tree uptake of Bc is an important flux, but it is unlikely to have caused the large decrease in soil solution. Although forest growth has increased in Europe (Ciais *et al*., 2008), the rate of Bc uptake has not kept pace. Observations of foliar Bc nutrition at Level II plots indicate that there has been a progressive deterioration of the foliar Bc nutrition of European beech and common oak, while no overall

change in foliar Bc nutrition has been observed for conifer plots (Jonard *et al*., 2015). Conversely, it is not evident that changes in soil solution Bc and Al$_{tot}$ have influenced foliar nutrition in European forests. The changes observed in foliar Bc of broadleaved plots were rather due to a dilution effect associated with an increased growth rate (Jonard *et al*., 2015). In addition, in the ICP Forests network, most plots have normal foliar Bc levels. Berger *et al*. (2016) similarly found adequate Bc nutrition in beech stands in Austria and declining foliar Bc trends despite increasing soil exchangeable cations.

Trends in soil solution pH and ANC

The results indicate a non-uniform response to decreases in acid deposition. In the upper soil, poorly buffered soils (BSat<10%) showed a significant increase in ANC as expected. However, at 40-80 cm, ANC decreased in better-buffered soils (BSat >20%), which was not expected. In some respects, these trends reflect those reported by individual studies. At some sites soil solution pH and ANC increased (Vanguelova *et al*., 2010; Johnson *et al*., 2013; Fuss *et al.*, 2015); however, in others acidity remained unchanged or aggravated (Graf Pannatier *et al*., 2011; Verstraeten *et al*., 2012; Meesenburg *et al*., 2016). Trends in acidity appear to be spatially variable, and dependent on factors including soil conditions, forest type, deposition levels and climate. For example, in Sweden, sites in the south, which historically received the highest deposition, showed a recovery in pH, ANC and inorganic Al, while sites in other parts of the country did not (Pihl-Karlsson *et al*., 2011). In the UK, trends of acidity (pH, ANC) were variable among 10 plots, with the greatest response occurring at sandy soil sites with the largest deposition reductions (Vanguelova *et al*., 2010). When aggregated at the European scale, it could be that opposing trends cancel each other out, as was the likely case here.

ANC decreased in better-buffered soils at 40-80 cm because SO_4^{2-} and NO_3^- did not decrease as much as Bc. Ongoing acidification has been attributed to release of previously adsorbed S (Meesenburg *et al.*, 2016; Oulehle *et al.*, 2006) as well as decreasing Bc deposition (Ukonmaanaho *et al.*, 2014; Verstraeten *et al.*, 2012; Fölster *et al.*, 2003; Alewell *et al.*, 2000a) mentioned above. In addition, forests in parts of Europe (Switzerland, Denmark, Belgium, Germany) are characterised by high N deposition and NO_3^- in soil solution, which contributes to soil acidification (Hansen *et al.*, 2007; Graf Pannatier *et al.*, 2011; Verstraeten *et al.*, 2012; Waldner *et al.*, 2014). The response has also been hampered by mobilisation of acid cations (H^+, Al) due to marine ion deposition in Atlantic coastal areas, which could have influenced the trends (Akselsson *et al.*, 2013; Löfgren *et al.*, 2011). Another source of noise in the data arises from the nature of the suction cup lysimeters. In these samples, it is not possible to determine how long the sample has had to equilibrate with the soil, which could vary among collection periods making the detection of trends more difficult.

The differing acidification trends reflect the results of some repeat soil surveys. In a comparison of soil pH and BSat between two soil surveys 12 years apart, Cools and De Vos (2011) found a recovery of BSat in more acidic soils ($pH_{CaCl_2} < 4.0$, BSat <20%) but a decrease in less acidic soils ($pH_{CaCl_2} > 4.0$, BSat >20%). Lawrence *et al.* (2015) reported an initial recovery in the O horizon at sites in northeastern US and eastern Canada, but BSat continued to decline in the B-horizon at a third of the same sites. This suggests that the rate of S and inorganic N deposition might still exceed buffering capacity in these soils and/or that the lag between deposition reductions and soil response is longer than expected.

For deeper soils, ANC showed no change in poorly buffered soils. Recovery in these soils could be limited by decreases in soil solution Bc due to historic depletion of soil exchangeable Bc pools (Houle *et al.*, 2006; Warby *et al.*, 2005; van der Heijden et al., 2011). At one of the best-documented sites of soil acidification, at Solling in Germany, soil exchangeable Bc pools were depleted by as much as

60% (Meesenburg *et al*., 2016). Weathering rates were low in these soils, and exchangeable pools could take decades to recover (Reinds *et al*., 2009). Repeated soil surveys over 50 years in Germany indicate that the rates of Bc and BSat loss from mineral soils have levelled off at many forest plots, with some showing an increase in BSat (Wellbrock *et al*., 2016). Overall, the decrease in soil solution Bc concentration indicates that the rate of Bc depletion has slowed. Soil exchangeable pools could recover if the rates of Bc weathering were sufficient to balance the Bc loss. Further research should focus on the magnitude and direction of Bc budgets at the plots to determine the potential for recovery in poorly buffered soils.

Trends in soil solution Al_{tot}

Aluminium decreased in soil solution across the whole dataset and at 40-80 cm it decreased more in acidic soils. This was expected given that Al dissolution is a buffering mechanism in acidic soils. However, the $Bc:Al_{tot}$ ratio did not increase in these soils. There are more reasons for this. Data for Al_{tot} were used, which includes both the inorganic and organic Al fractions (Fakhraei *et al.*, 2015), of which the organic can be significant (Brumme *et al.*, 2009). For example, in Norway, Lange *et al*. (2006) found that the proportion of organically bound Al in soil solution was 39% and 26% at 15 and 40 cm, respectively, while in the UK, Vanguelova *et al*. (2007b) found the proportion to be 30-40% in podzols. There were no changes in DOC at 10-20 cm and a relative decrease of 17% for a ten-year period at 40-80 cm. The small changes in DOC would have maintained the organic fraction of Al in solution, potentially dampening the trends. However, organically bound Al is less toxic to biota and a shift in favour of this fraction could support the recovery of drainage waters.

A second point relates to ionic strength of soil solution and cation exchange. Matschonat and Vogt (1998) found that a decrease in cation concentration resulted in the preferential adsorption of trivalent cations on the soil exchange complex relative to di- and mono-valent cations. It would thus be expected that there would be more of a decrease in Al relative to other cations, and an increase in ANC. However, this was not the case. A possible explanation is that the dissolution and precipitation of Al oxides and hydroxides are strongly pH dependent (Reuss and Johnson, 1986) and, as the pH of soil solution did not change, ionic forms of Al remained soluble.

No change in DOC in the upper mineral soil

DOC showed no change (10-20 cm) or decreased (40-80 cm) in soil solution. National studies show non-uniform results; some forest plots previously impacted by acid deposition show increasing DOC concentrations (Hruška *et al*., 2009; Verstraeten *et al*., 2014), whereas no changes are evident in others (Ukonmaanaho *et al*., 2014). In addition, surface horizons often show increasing DOC while mineral horizons show no changes, or decreases (Borken *et al*., 2011; Sawicka *et al*., 2016). The results at 10-20 cm are like those observed by Camino-Serrano *et al*. (2016) who previously examined DOC time changes at 84 ICP Forests plots. They reported no consistent DOC concentration changes in the mineral soil. Our result of decreasing DOC at a depth of 40-80 cm may have arisen due to differences in the number of plots and spatial coverage; a larger proportion of plots were included from Fennoscandia in this study, where DOC decreased or showed no changes (Clarke and Lindroos, 2010; Wu *et al*., 2010; Löfgren and Zetterberg, 2011). Many studies attribute changes in DOC to climate effects (Worrall and Burt, 2009), reduced ionic strength (Hruška *et al*., 2009; Haaland *et al*., 2010) or acidity (de Wit *et al*., 2007; Monteith *et al*., 2007). As climate is less of an influence on DOC in deeper mineral soils, possible explanations include increased adsorption by mineral surfaces due to desorption of SO_4^{2-}, or changes in DOC stability as complexation with Al is decreased, leading to faster DOC decay (Borken *et al*., 2011).

For both DOC and acidity, the trends here contrast with those of surface waters reported widely in Europe and North America (e.g. Monteith *et al*., 2007; Garmo *et al*., 2014). One reason for the difference is the spatial coverage of the sites. The dataset here includes many forest plots from central Europe not included in studies of acid sensitive surface waters e.g. France, Switzerland, Germany, Italy, Austria, Belgium. It has previously been reported that surface waters in Central Europe had not recovered from acidification to the extent as for other parts of Europe (Alewell *et al*., 2000b). Secondly, the processes controlling acidity in soil solution and surface waters are different. Soil solution is naturally more acidic due to higher dissolved CO_2 and DOC (Reuss and Johnson, 1986). In addition, surface water chemistry is not determined by soil solution leachate alone but integrates contributions from direct runoff, e.g. snow melt and storm events, groundwater and riparian water (Shand *et al.*, 2005; Fuss *et al*., 2015). The contribution of these components to surface waters varies spatially within catchments and seasonally (Michalzik *et al*., 2003; James and Roulet *et al.* 2006; Casson *et al.,* 2014; Fuss *et al*., 2015). In addition, surface water DOC has been shown to be a function of landscape features such as wetlands and riparian zones, as well as of catchment connectivity and hydrology (Laudon *et al*., 2011; Knorr, 2013). Organic soils of upper horizons and near-stream zones are considered to be the main sources of dissolved organic matter in headwater catchments (e.g. Brooks *et al*., 1999; Billett *et al*., 2006; Evans *et al*., 2007; Winterdahl *et al.*, 2011) where trends in DOC have been observed in comparison to the mineral soils studied here.

Decline in NO_3^- in the lower mineral soil

Another important result was the decrease in NO_3^- at 40-80 cm depth. This most likely reflects the N status of many plots in Western Europe as inorganic N deposition has decreased. Many plots in Germany, Denmark, Belgium and the UK have elevated NO_3^- in soil solution and as such are considered N saturated. Numerous studies have shown that decreases in N deposition have decreased soil solution NO_3^- (e.g. Boxman *et al*., 2008; Vanguelova *et al*., 2010; Verstraeten *et al*., 2012; Meesenburg *et al*., 2016). In contrast to Iost *et al*. (2012) where no changes were found at most plots,

the decreasing concentrations here potentially indicate an initial recovery from N saturation; however, N critical loads are still exceeded in many areas in Europe (Waldner *et al*., 2015), a situation that is likely to persist for several decades (Posch *et al*., 2015). This study was not focused specifically on assessing changes in N status, and included plots that were strongly N limited, with NO_3^- concentrations close to or below detection limit. As such, a more in-depth examination of N saturated forests is necessary to evaluate their status.

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Tables

Table 1 Soil pH_{CaCl_2} and base saturation (BSat) summary statistics of soil survey (1990-2000).

Layer	Variable	Min.	Median	Mean	Max.	n	no data
10-20 cm	pH_{CaCl_2}	2.7	3.9	4.0	7.2	100	4
	BSat (%)	2	11	23	100	98	6
40-80 cm	pH_{CaCl_2}	3.3	4.4	4.6	7.6	145	17
	BSat (%)	2	20	34	100	136	26

Table 2 Environmental factors included as stratifying factors in the linear mixed-effects model. The model tested if soil solution trends were different between factor levels.

Factor	Soil depth	Levels
Region		West, Central, North
Forest type		Deciduous, Coniferous

Soil Chemistry

Factor	Soil depth	Levels
pH ($CaCl_2$)	10-20 cm	$\leq 4.0, >4.0$
	40-80 cm	$\leq 4.5, >4.5$
BSat (%)	10-20 cm	$\leq 10, >10$
	40-80 cm	$\leq 20, >20$

Throughfall trend

	Relative change for a ten-year period %	Absolute change for ten years ($\mu eq\ L^{-1}$)
SO_4^{2-}	$<, \geq -60$	$<, \geq -40$
Bc	$<, \geq -11$	$<, \geq -10$
N inorg	$<, \geq -22$	$<, \geq -13$
Ac_{pot}		$<, \geq -46$

Table 3 Summary statistics (5th, median, 95th percentile) of the intercept of the linear model applied to individual plots. The intercept represents the value in the year 2000. $Bc:Al_{tot}$ is the molar ratio of nutrient base cations ($Ca^{2+} + Mg^{2+} + K^+$) to total Al.

		10-20 cm			40-80 cm		
		5th	Median	95th	5th	Median	95th
pH		3.7	4.6	7.0	4.1	4.8	7.7
Ca^{2+}		10	96	720	11	74	2039
Mg^{2+}		12	59	245	9	61	464
K^+		2	12	73	2	11	69
Na^+	$\mu eq\ L^{-1}$	20	84	373	22	123	631
Cl^-		14	94	541	13	106	702
NO_3^-		2	16	441	1	7.2	583
SO_4^{2-}		41	131	464	37	212	739
ANC		−531	−47	489	−569	−26	2414
Al_{tot}	$mg\ L^{-1}$	0.03	1.00	4.2	0.02	0.8	5.7
DOC		1.4	12	42	1.2	5.8	29
$Bc:Al_{tot}$		0.2	1.4	105	0.2	1.5	785

Table 4 Temporal trends in soil solution at the European scale. The change in concentration for a ten-year period is shown relative to the year 2000 and as absolute value. $Bc:Al_{tot}$ trends are shown for soils with soil pH_{CaCl_2}<5.0. $Bc = \Sigma(Ca^{2+} + Mg^{2+} + K^+)$, $AA = \Sigma(SO_4^{2-} + NO_3^- + Cl^-)$. Note: trends in Bc, AA or ANC differ from the sum of individual ions as not all-time series had complete ions for all months and years.

Variable	Unit	10-20 cm			40-80 cm		
			Ten year change			Ten year change	
		Significance	Relative to 2000 (%)	Absolute	Significance	Relative to 2000 (%)	Absolute
pH		ns	+1.0	+0.05	ns	+1.2	+0.07
Ca^{2+}		***	−55	−57	***	−58	−68
Mg^{2+}		**	−35	−24	*	−28	−18
K^+		**	−57	−7.1	**	−32	−3.5
Na^+		ns	−9	−8.4	ns	−6	−7.5
SO_4^{2-}		**	−52	−61	***	−40	−69
NO_3^-	$\mu eq\ L^{-1}$	ns	−14	−2.3	(*)	−30	−4.2
Cl^-		ns	−9	−8.8	ns	−5	−6.1
$Bc+Na^+$		***	−31	−110	*	−30	−143
AA		***	−34	−110	***	−28	−116
ANC		ns	−5	−19	ns	−19	−36
Al_{tot}	mg L^{-1}	**	−19	−0.13	*	−17	−0.08
DOC		ns	−4	−0.44	*	−17	−1.14
$Bc:Al_{tot}$ (soil pH_{CaCl_2}<5.0)		ns	−18	−0.30	ns	−11	−0.23

*** p<0.001, **p<0.01, *p<0.05, (*) p<0.1, ns = not significant

Table 5 Trends in soil solution stratified by environmental factors. Only trends that were significantly different between factor levels are shown. For throughfall SO_4^{2-}, the magnitude of the change is for a ten-year period. Significance for each factor level is indicated as follows: ***$p<0.001$, **$p<0.01$, *$p<0.05$, (*) $p<0.1$, ns = not significant

Variable	Factor / Level / Layer	Soil pH_{CaCl_2} ≤4.0/>4.0 10–20 cm	≤4.5/>4.5 40–80 cm	Forest type Coniferous/Deciduous 10–20 cm	40–80 cm	Region Central /North/West 10–20 cm	40–80 cm	Decrease in throughfall SO_4^{2-} ≥60%/<60% 10–20 cm	40-80 cm
Ca^{2+}	Significance		***/***	(*)/**	*/**				
	Change (%)		−66/−33	−66/−46	−67/−47				
	Change (µeq L^{-1})		−49/−71	−51/−73	−54/−104				
Mg^{2+}	Significance		***/***		(*)/ns	C*/N/W(*)			
	Change (%)		−39/−18		−29/−15	−47/−26/−19			
	Change (µeq L^{-1})		−24/−15		−14/−16	−29/−6/−14			
K^+	Significance		**/*	*/*	(*)/(*)				
	Change (%)		−41/−16	−75/−43	−39/−20				
	Change (µeq L^{-1})		−5.2/−1.5	−8.6/−6.4	−4.8/−1.8				
Na^+	Significance				*/(*)				
	Change (%)				−1.3/−12				
	Change (µeq L^{-1})				−1.6/−19				
Cl^-	Significance						C**/N/W		
	Change (%)						−17/+1.4/+6.5		
	Change (µeq L^{-1})						−6.6/+0.9/+19		
SO_4^{2-}	Significance		***/*					***/(*)	
	Change (%)		−45/−32					−61/−48	
	Change (µeq L^{-1})		−94/−44					−82/−57	

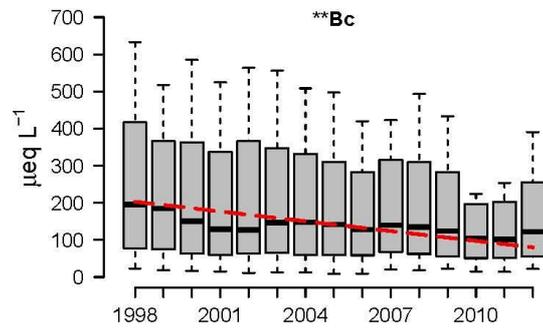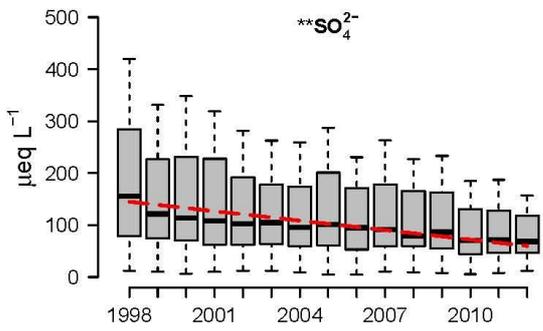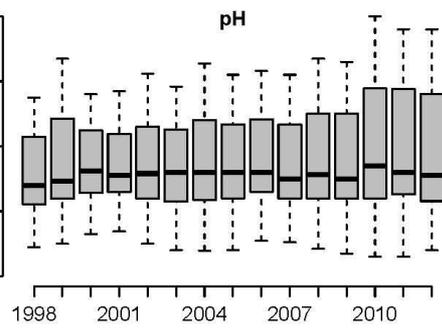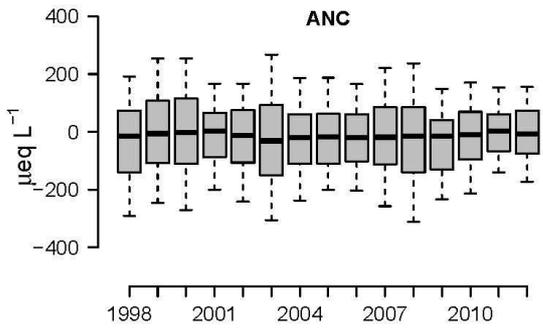|					
NO_3^-	Significance	*/*			
	Change (%)	−50/−1.6			
	Change (μeq L^{-1})	−6.1/−0.2			
Al_{tot}	Significance	***/***	**/ns	C**/N(*)/W*	ns/(*)
	Change (%)	−34/−2	−29/−3	−43/+0.3/−20	−28/−12
	Change (mg L^{-1})	−0.4/−0.003	−0.28/−0.01	−0.15/+0.001/−0.07	−0.22/−0.04
pH	Significance				
	Change (%)				
	Change (pH unit)				
DOC	Significance			C**/N/W**	
	Change (%)			−4.8/−15/−27	
	Change (mg L^{-1})			−0.2/−0.8/−2.9	
Bc	Significance	***/***	(*)/**		
	Change (%)	−53/−27	−45/−32		
	Change (μeq L^{-1})	−92/−106	−80/−133		
AA	Significance	***/*			
	Change (%)	−32/−19			
	Change (μeq L^{-1})	−149/−67			
Bc:Al$_{tot}$	Significance				
	Change (%)				
	Change (absolute)				
ANC	Significance	ns/**	**/(*)		ns/*
	Change (%)	+23/−16	+40/−29		+179/−29
	Change (μeq L^{-1})	+40/−118	+14/−165		+10/−119

Figure Captions

Fig. 1 Location of the Level II ICP Forests plots included in the study, left plots at 10-20 cm soil depth and right at 40-80 cm soil depth.

Fig. 2 Median concentrations at 10-20 cm for selected variables with the trend from the linear model superimposed. The model was run for the period 1995-2012, but to be consistent, the period displayed is for years that had at least 75 plots. Significance is indicated as: ***$p<0.001$, **$p<0.01$, *$p<0.05$, (*) $p<0.1$. Boxplot whiskers represent 0.75 times the interquartile range.

Fig. 3 Median concentrations at 40-80 cm for selected variables with the trend from the linear model superimposed. The model was run for the period 1995-2012, but to be consistent, the period displayed is for years that had at least 120 plots. Significance is indicated as: ***$p<0.001$, **$p<0.01$, *$p<0.05$, (*) $p<0.1$. Boxplot whiskers represent 0.75 times the interquartile range

N

0   500   1,000   2,000 Kilometers

Projection: Lambert-Azimuthal

10−20 cm

40−80 cm