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Trends in soil solution dissolved organic carbon (DOC) concentrations across European forests

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Abstract

Dissolved organic carbon (DOC) in soil solution is connected to DOC in surface waters through hydrological flows. Therefore, it is expected that long-term dynamics of DOC in surface waters reflect DOC trends in soil solution. However, a multitude of site-studies has failed so far to establish consistent trends in soil solution DOC, whereas increasing concentrations in European surface waters over the past decades appear to be the norm, possibly as a result from acidification recovery. The objectives of this study were therefore to understand the long-term trends of soil solution DOC from a large number of European forests (ICP Forests Level II plots) and determine their main physico-chemical and biological controls. We applied trend analysis at two levels: 1) to the entire European dataset and 2) to the individual time series and related trends with plot characteristics, i.e., soil and vegetation properties, soil solution chemistry and atmospheric deposition loads. Analyses of the entire dataset showed an overall increasing trend in DOC concentrations in the organic layers, but, at individual plots and depths, there was no clear overall trend in soil solution DOC across Europe with temporal slopes of soil solution DOC ranging between -16.8% yr^{-1} and +23% yr^{-1} (median= +0.4% yr^{-1}). The non-significant trends (40%) outnumbered the increasing (35%) and decreasing trends (25%) across the 97 ICP Forests Level II sites. By means of multivariate statistics, we found increasing DOC concentrations with increasing mean nitrate (NO_3^-) deposition and decreasing DOC concentrations with decreasing mean sulphate (SO_4^{2-}) deposition, with the magnitude of these relationships depending on plot deposition history. While the attribution of increasing trends in DOC to the reduction of SO_4^{2-} deposition could be confirmed in N-poorer forests, in agreement with observations in surface waters, this was not the case in N-richer forests. In conclusion, long-term trends of soil solution DOC reflected the interactions between controls acting at local (soil and vegetation properties) and regional (atmospheric deposition of SO_4^{2-} and inorganic N) scales.

1 Introduction

Dissolved organic carbon (DOC) in soil solution is the source of much of the terrestrially derived DOC in surface waters (Battin et al., 2009; Bianchi, 2011; Regnier et al., 2013). Soil solution DOC in forests is connected to streams through different hydrological pathways: DOC mobilized in the forest floor may be transported laterally at the interface of forest floor and mineral soil to surface waters or percolates into the mineral soil, where additional DOC can be mobilized and/or DOC is partly adsorbed on particle surfaces and mineralized thereafter. From the mineral soil DOC may be either leached laterally or vertically via groundwater into surface waters (Mcdowell and Likens, 1988). Therefore, it could be expected that long-term dynamics of DOC in ecosystem soil solutions mirror those observed in surface waters.

Drivers related to climate change (temperature increase, precipitation change, atmospheric CO_2 increase), the decrease in acidifying deposition or land use change and management may individually or jointly explain trends in surface water DOC concentrations (Evans et al., 2012; Freeman et al., 2004; Oulehle et al., 2011; Sarkkola et al., 2009; Worrall and Burt, 2004). Increasing air temperatures warm the soil, thus stimulating soil organic matter (SOM) decomposition through greater microbial activity (Davidson and Janssens, 2006; Hartley and Ineson, 2008; Kalbitz et al., 2000). Other drivers, such as increased atmospheric CO_2 and the accumulation of atmospherically deposited inorganic nitrogen are thought to increase the sources of DOC by enhancing primary plant productivity (i.e., through stimulating root exudates, litterfall) (Sucker and Krause, 2010). Changes in precipitation, land use and management (e.g. drainage of peatlands, changes in forest management or grazing systems) may alter the flux of DOC leaving the ecosystem but no consistent trends in the hydrologic regime or due to land use changes were detected in areas where increasing DOC trends have been observed (Monteith et al., 2007).

Recent focus was mainly on decreasing acidifying deposition as an explanatory factor for DOC increases in surface waters in Europe and North America by means of decreasing ionic strength (Hruška et al., 2009) and increasing the pH of soil solution, consequently increasing DOC solubility (Evans et al., 2005; Haaland et al., 2010; Monteith et al., 2007). Although the hypothesis of an increase in surface water DOC concentration due to a recovery from past acidification was confirmed in studies of soil solution DOC in the UK and Northern Belgium (Vanguelova et al., 2010; Verstraeten et al., 2014), it is not consistent with observed trends in soil solution DOC concentrations measured in Finnish, Norwegian, and Swedish forests (Löfgren and Zetterberg, 2011; Ukonmaanaho et al., 2014; Wu et al., 2010). This inconsistency between soil solution DOC and stream DOC trends could suggest that DOC in surface water and soil solution responds differently to (changes in) environmental conditions in different regions (Akselsson et al., 2013; Clark et al., 2010; Löfgren et al., 2010). Alternatively, other factors such as tree species and soil type, may be co-governing organic matter dynamics and input, generation and retention of DOC in soils.

Trends of soil solution DOC not only vary among forests but often also within the same site (Löfgren et al., 2010). Forest characteristics such as tree species composition, soil fertility, texture or sorption capacity may affect the response of soil solution DOC to environmental controls, for instance, by controlling the rate of soil acidification through soil buffering and nutrient plant uptake processes (Vanguelova et al., 2010). Within a site, DOC variability with soil depth is typically caused by different intensity of DOC production, transformation and sorption along the soil profile. Positive temporal trends in soil solution DOC (increasing concentrations over time) are frequently reported for the organic layers and shallow soils where production and decomposition processes control the DOC concentration (Löfgren and Zetterberg, 2011). However, no dominant trends are found for the mineral soil horizons, where physico-chemical processes, such as sorption, become more influential (Borken et al., 2011; Buckingham et al., 2008). Furthermore, previous studies have used different temporal and spatial scales which may have further added to the inconsistency in the DOC trends reported in the literature (Clark et al., 2010).

In this context, the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, 2010) compiled a unique dataset containing data from more than 100 intensively monitored forest plots (Level II) which allow to unravel regional trends in soil solution DOC of forests at European scale, and perform statistical analysis of the main controls behind these regional trends. Long-term measurements of soil solution DOC are available for these plots, along with information on aboveground biomass, soil properties, and atmospheric deposition of inorganic N and SO_4^{2-}, collected using a harmonized sampling protocol across Europe (Ferretti and Fischer, 2013). This dataset has previously been used to investigate the spatial variability of DOC in forests at European scale (Camino-Serrano et al., 2014), but an assessment of the temporal trends in soil solution DOC using this large dataset has not been attempted so far. The main objective of this study was to understand the long-term temporal trends of DOC concentrations in soil solution measured at the ICP Forests Level II plots across Europe. Based on the increasing DOC trends in surface water, we hypothesized that temporal trends in soil solution DOC would also be positive, but with trends varying locally depending on plot characteristics. We further investigated whether plot characteristics, specifically climate, inorganic N and SO_4^{2-} deposition loads, forest type, soil properties, and changes in soil solution chemistry can explain differences across sites in DOC trends.

2 Materials and Methods

2.1 Data description

Soil solution chemistry has been monitored within the ICP Forests Programme since the 1990s on most Level II plots. The ICP Forests data were extracted from the pan-European Forest Monitoring Database (Granke, 2013). A list of the Level II plots used for this study can be found in Supplementary material S1, Table S1. The methods for collection and analysis of soil solution used in the various countries (Switzerland: Graf Pannatier et al. (2011); Flanders: Verstraeten et al. (2012); Finland: Lindroos et al. (2000); UK: Vanguelova et al. (2010), Denmark: Hansen et al. (2007)) follow the ICP Forests manual (Nieminen, 2011). Generally, lysimeters were installed at several fixed depth intervals starting at 0 cm, defined as the interface between the surface organic layer and underlying mineral soil. These depths are typically aligned with soil “organic layer”, “mineral topsoil”, “mineral subsoil” and “deeper mineral soil” but sampling depths vary among countries and even among plots within a country. Normally, zero-tension lysimeters were installed under the surface organic layer and tension lysimeters within the mineral soil. However, in some countries zero-tension lysimeters were also used within the mineral layers and in some tension lysimeters below the organic layer. Multiple collectors (replicates) were installed per plot and per depth to assess plots spatial variability. However, in some countries, samples from these replicates were pooled before analyses or averaged prior to data transmission. The quality assurance and control procedures included the use of control charts for internal reference material to check long-term comparability within national laboratories as well as participation in periodic laboratory ring tests (e.g., Marchetto et al., 2011) to check the international comparability. Data were reported annually to the pan-European data center, checked for consistency and stored in the pan-European Forest Monitoring Database (Granke, 2013).

Soil water was usually collected fortnightly or monthly, although for some plots sampling periods with sufficient soil water for collection were scarce, especially in prolonged dry periods or in winter due to snow and ice. After collection, the samples were filtered through a 0.45 μm membrane filter, stored below 4 °C and then analyzed for DOC, together with other soil solution chemical properties (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{-2}, total dissolved Al, total dissolved Fe, pH, electrical conductivity). The precision of DOC analysis differed among the laboratories. The coefficient of variation of repeatedly measured reference material was 3.7% on average. The time span of soil solution time series used for this study ranged from 1991 to 2011, although coverage of this period varied from plot to plot (Supplementary material S1, Table S1).

Soil properties, bulk and throughfall atmospheric deposition of NO_3^-, NH_4^+ and SO_4^{2-}, meteorological variables and stem volume increment were also measured at the plots. Stem volume growth was calculated by the ICP Forests network from diameter at breast height (DBH), live tree status, and tree height which were assessed for every tree (DBH > 5 cm) within a monitoring plot approximately every five years since the early 1990. Tree stem volumes were derived from allometric relationships based on diameter and height measurements according to De Vries et al. (2003), accounting for species and regional differences. Stem volume growth (in m^3) between two consecutive inventories was calculated as the difference between stem volumes at the beginning and the end of one inventory period for living trees. Stem volume data were corrected for all trees that were lost during one inventory period, including thinning. Stem volume at the time of disappearance (assumed at half of the time of the inventory period) was estimated from functions relating stem volume of standing living trees at the end of the period *vs* volume at the beginning of the period. The methods used for collection of these data can be found in the Manuals of the ICP Forests Monitoring Programme (ICP Forests, 2010). The soil properties at the plots used for this study were derived from the ICP Forests aggregated soil database (AFSCDB.LII.2.1) (Cools and De Vos, 2014).

Since continuous precipitation measurements are not commonly available for the Level II plots, precipitation measurements for the location of the plots were extracted from the observational station data of the European Climate Assessment & Dataset (ECA&D) and the ENSEMBLES Observations (E-OBS) gridded dataset (Haylock et al., 2008). We used precipitation measurements extracted from the E-OBS gridded dataset to improve the temporal and spatial coverage and to reduce methodological differences of precipitation measurements across the plots. The E-OBS dataset contains daily values of precipitation and temperature from stations data gridded at 0.25 degrees resolution. When E-OBS data was not available, it was gap-filled with ICP Forests precipitation values gained by deposition measurements where available (open field bulk deposition or throughfall deposition).

2.2 Data preparation

We extracted data from plots with time series covering more than 10 years and including more than 60 observations of soil solution DOC concentrations of individual or groups of collectors. Outliers, defined as ± 3 interquartile range of the 25 and 75 quantiles of the time series, were removed from each time series to avoid influence of few extreme values in the long-term trend (Schwertman et al., 2004). Values under 1 mg L^{-1}, which is the detection limit for DOC in the ICP Level II plots, were replaced by 1 mg L^{-1}. After this filtering, 529 time series from 118 plots, spanning from Italy to Norway, were available for analysis. Soil solution, precipitation, and temperature were aggregated to monthly data by the median of the observations in each month and by the sum of daily values in the case of precipitation. Data of inorganic N (NH_4^+ and NO_3^-) and SO_4^{2-} canopy throughfall and open field bulk deposition measured at the plots were interpolated to monthly data (Waldner et al., 2014).

The plots were classified according to their forest type (broadleaved/coniferous dominated), soil type (World Reference Base, Reference Soil Group (WRB 2006)), their stem growth (slow, < 6 m^3 ha^{-1} yr^{-1}, intermediate, 6–12 m^3 ha^{-1} yr^{-1}; and fast, > 12 m^3 ha^{-1} yr^{-1}), and soil pH (low, <4.2, intermediate, 4.2–5, high, >5). Plots were also classified based on throughfall inorganic N (NO_3^- +NH_4^+) deposition level, defined as: high deposition (HD, >15 kg N ha^{-1} yr^{-1}), medium deposition (MD, 5–15 kg N ha^{-1} yr^{-1}), and low deposition (LD, <5 kg N ha^{-1} yr-

^{1}) and throughfall SO_4^{2-} level, defined as: high deposition (HD, >6 kg S ha^{-1} yr^{-1}), and low deposition (LD, < 6 kg S ha^{-1} yr^{-1}).

2.3 Statistical methods

The sequence of methods applied is summarized in Fig. 1. The analysis of temporal trends in soil solution DOC concentrations was carried out at two levels: 1) the European level and 2) the plot level of each individual time series. While the first analysis allows an evaluation of the overall trend in soil solution DOC at a continental scale, the second analysis indicates whether the observed large scale trends are occurring at local scales as well, and tests whether local trends in DOC can be attributed to certain driver variables.

Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution DOC concentration at the European scale (Fig. 1). For these models, the selected 529 time series were used. For the trend analysis of individual time series, however, we focused on the investigation of the potential long-term trends in soil solution DOC at European forests that show monotonicity. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010) with the time series showing breakpoints, i.e., not monotonic, being discarded (Supplementary material S2.2.) (Fig. 1). Then, monotonic trend analyses were carried out using the Seasonal Mann Kendall (SMK) test for monthly DOC concentrations (Hirsch et al., 1982; Marchetto et al., 2013). Partial Mann Kendall (PMK) tests were also used to test the influence of precipitation as a co-variable to detect if the trend might be due to a DOC dilution/concentration effect (Libiseller and Grimvall, 2002). Sen (1968) slope values were calculated for SMK and PMK. Moreover, LMMs were performed again with the filtered dataset to compare results with and without time series showing breakpoints (Fig. 1).

For this study, five depth intervals were considered: the organic layer (0 cm), topsoil (0-20 cm), intermediate (20-40 cm), subsoil (40-80 cm) and deep subsoil (> 80 cm). The slopes of each time series were standardized by dividing them by the median DOC concentration over the sampling period, aggregated to a unique plot-soil depth slope and classified by the direction of the trend as significantly positive (P, $p < 0.05$), significantly negative (N, $p < 0.05$), and non-significant (NS, $p \geq 0.05$). When there was more than one collector per depth, the median of the slopes was used when the direction of the trend (P, N, or NS) was similar. When the different trends at the same plot-soil depth combination were either P and NS, or N and NS, it was marked as “Weighted positive” and “Weighted negative” to indicate that there was potential predominant direction of the trend but with less significance. Trends for other soil solution parameters (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, total dissolved Al, total dissolved Fe, pH, electrical conductivity), precipitation and temperature were calculated using the same methodology as for DOC. Finally, two multivariate statistical analyses were performed, General Discriminant Analysis (GDA) and Structural Equation Models (SEM), to investigate the main factors explaining differences in DOC trends among the selected plots (Fig. 1). All the statistical analyses were performed in R software version 3.1.2 (R Core Team, 2014) using the “rkt” (Marchetto et al., 2013), “bfast01” (de Jong et al., 2013) and “sem” (Fox et al., 2013) packages, except for the GDA that was performed using Statistica 8.0 (StatSoft, Inc. Tule, Oklahoma, USA) and the LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA). More detailed information on the statistical methods used can be found in Supplementary material S2.

3 Results

3.1 Soil solution DOC trends at European scale

First, temporal trends in DOC were analyzed for all the European DOC data pooled together by means of LMM models to test for the presence of overall trends. A significantly increasing DOC trend ($p<0.05$) in soil solution collected with zero-tension lysimeters in the organic layer was observed mainly under coniferous forest plots (Table 1). Similarly, a significantly increasing DOC trend ($p<0.05$) in DOC for soil solution collected with tension lysimeters was found in deep mineral horizon (>80cm) for all sites, but mainly for coniferous forest sites (Table 1). By contrast, non-significant trends were found in other mineral horizons (0-20 cm, 20-40 cm, 40-80 cm) by means of the LMM models. When the same analysis was applied to the filtered European dataset, i.e., without the time series including breakpoints (see Sect. 3.2), fewer significant trends were observed: only an overall positive trend was found for DOC in the organic layer using zero-tension lysimeters, again mainly under coniferous forest sites but no statistically significant trends were found in the mineral soil (Table 1).

3.2 Soil solution DOC trend analysis of individual time series

3.2.1 Comparison of methods of individual trend analysis

We applied the BFAST analysis to select the monotonic time series in order to assure that the overall detected trends were not influenced by breakpoints in the time series. Time series with breakpoints represented more than 50% of the total time series aggregated by soil depth interval (245 out of 436). In total, 191 plot-soil depth combinations from 97 plots were analyzed after filtering out the time series showing breakpoints and 94% of the analyzed plot-depth combinations showed consistent trends among replicates collected at the same depth. In contrast, when also considering the time series with breakpoints, the trends calculated for plot-depth combinations agreed only in 75% of the cases implying that the proportion of contradictory trends within plot-depth combinations increased from 6% in the dataset without breakpoints to 25% in the entire dataset (Fig. 2). For both datasets, the majority of the trends were not statistically significant (44% and 41%, for the dataset with and without breakpoints, respectively). In other words, filtering the time series for breakpoints reduced the within-plot variability, while most of the plots showed similar aggregated trends per plot-depth combinations. For this reason, the results discussed from here on correspond only to the trends of monotonic (breakpoint filtered) time series of soil solution DOC concentrations.

There was a good agreement between results using the three methods: BFAST, SMK, and PMK (Table 2). The direction and significance of the trend agreed for 84.5% of the time series analyzed. For the majority of the remaining time series for which the trends did not agree, BFAST did not detect a trend when SMK and PMK did, thus, the latter two methods seemed more sensitive for trend detection than BFAST. Trends computed with SMK and PMK agreed well.

For virtually all plots, including precipitation as a co-variable in the PMK test gave the same result as the SMK test, which indicates that precipitation (through dilution or concentration effects) did not affect the DOC concentration trends. Dilution/concentration effect was only detected in four plots (Supplementary material S1, Table S1).

3.2.2 Soil solution DOC concentration trends using the SMK test

The individual trend analysis using the SMK test showed temporal slopes of soil solution DOC concentration ranging from -16.8% yr^{-1} to +23% yr^{-1} (median= +0.4% yr^{-1}, interquartile range = +4.3% yr^{-1}). Among all the time series analyzed, the majority were not statistically significant trends (40%, 104 time series), followed by significantly positive trends (35%, 91 time series) and significantly negative trends (24%, 63 time series) (Table 2). There was, thus, no uniform trend in soil solution DOC in forests across a large part of Europe. Although a slight tendency of increasing trends in central and decreasing trends in north and south Europe was observed (Fig. 3), the uneven number of analyzed time series for each country (few in Austria, Italy or Finland and many in Germany) made it difficult to draw firm conclusions about the spatial pattern of the trends in soil solution DOC concentrations in Europe. Furthermore, the regional trend differences were inconsistent when looking at different soil depth intervals separately (Fig. 4 and 5).

The variability in trends was high, not only at continental scale, but also at plot level (Fig. 6). We found consistent within-plot trends only for 50 out of the 97 sites. Moreover, some plots even showed different trends (P, N or NS) in DOC within the same depth interval, which was the case for 17 plot-depth combinations (16 in Germany and one in Norway), evidencing a high small-scale plot heterogeneity.

Trend directions often differed among depths. For instance, in the organic layer, we found mainly non-significant trends and, when a trend was detected, it was more often positive than negative, while positive trends were the most frequent in the subsoil (below 40 cm) (Table 2). Nevertheless, it is important to note that a statistical test of whether there was a real difference in DOC trends between depths was not possible as the set of plots differed between the different soil depth intervals. However, a visual comparison of trends for the few plots in which trends were evaluated for more than three soil depths showed that, at first sight, there was no difference in DOC trends between soil depths (Supplementary material S3, Fig. S1 and S2).

3.3 Factors explaining the direction and slopes of the soil solution DOC trends

A stratification of the forests into broadleaved and coniferous forest revealed no direct effect of forest type on the direction of the statistically significant trends in soil solution DOC (Fig. 7C). Both positive and negative trends were equally found under broadleaved and coniferous forests ($\chi^2(1, n = 97) = 0.073$, $p = 0.8$). Increasing DOC trends, however, occurred more often under forests with a mean stem growth less than 6 $m^3\ ha^{-1}\ yr^{-1}$ over the study period, whereas decreasing DOC trends were more often associated with forests with a mean stem growth between 6 and 12 $m^3\ ha^{-1}\ yr^{-1}$ ($\chi^2(2, n = 53) = 5.8$, $p = 0.05$) (Fig. 7D).

Mean annual throughfall SO_4^{2-} and inorganic N deposition both had a significant effect on the direction of the trends in soil solution DOC (Fig. 7A, 7B). Increasing trends were more frequent in forests with high or medium inorganic N deposition than in forests with low inorganic N deposition where only decreasing trends were found ($\chi^2(2, N = 57) = 9.58$, $p =$

0.008). Correspondingly, the probability of positive trends in soil solution DOC was higher at high inorganic N deposition loads (Fig. 8A). Also throughfall SO_4^{2-} deposition significantly influenced the direction of the trend in soil solution DOC, with more positive trends found for sites with high mean throughfall SO_4^{2-} deposition (> 6 kg S ha^{-1} yr^{-1}) than for sites with low SO_4^{2-} deposition ($\chi^2(1, N = 57) = 8.75$, $p = 0.003$). However, while there were also relatively more positive trends at high and medium SO_4^{2-} than at low SO_4^{2-} , this pattern is less clear than for inorganic N deposition (Fig. 8B).

Regarding the soil properties, more than half of the plots showing a consistent increasing DOC trend at all evaluated soil depth intervals were located in Cambisols, (6 out of 11 plots), which are rather fertile soils, whereas plots showing consistent negative trends covered six different soil types. Other soil properties, like clay content, cation exchange capacity or pH, did not clearly differ between sites with positive and negative DOC trends (Table 3). It is remarkable that trends in soil solution pH, Mg^{2+} and Ca^{2+} concentrations were similar across plots with both positive and negative DOC trends. Soil solution pH increased distinctly in almost all the sites, while Ca^{2+} and Mg^{2+} decreased markedly (Table 3). However, we found evidence that soil acidity controlled the SO_4^{2-} deposition effect on the trends of DOC in soil solution (Fig. 9). In very acid soils, a higher mean SO_4^{2-} deposition enhanced the temporal increase in soil solution DOC, while in less acid soils, there was no significant effect of mean SO_4^{2-} on DOC trends. Finally, no significant correlations were found between trends in temperature or precipitation and trends in soil solution DOC, with the exception of an increasing trend in temperature in the soil depth interval 20-40 cm ($r = 0.47$, $p = 0.03$).

Results from the GDA analysis showed a marginally significant separation of plot-soil depth combinations with negative and positive DOC trends (p = 0.06) (Fig. 10). Median soil solution conductivity, median soil solution NO_3^-, and median soil solution SO_4^{2-} were significant in the model and thus played an important role in the distinction between positive and negative DOC trends (Table 4). The fitted GDA model was able to predict 63.1% of the variance in DOC trends within the first axis (Fig. 10).

To test whether the influence of stem growth and soil solution chemistry was related to the effect of SO_4^{2-} and/or NO_3^- deposition on soil solution DOC, we applied SEM to determine the capacity of these variables in explaining variability in the slope of DOC trends. We evaluated the influence of both the annual mean (kg ha^{-1} yr^{-1}) and the trends (% yr^{-1}) in deposition and soil solution parameters.

3.3.1 Effects of mean deposition and soil solution parameters

Analyzing different models that could explain the DOC trends using the overall dataset indicated both direct and indirect effects of the annual mean SO_4^{2-} and NO_3^- throughfall atmospheric deposition on the slopes of DOC trends. The SEM accounted for 32.7% of the variance in DOC trend slopes (Fig. 11A). This model identified a significantly negative direct effect of SO_4^{2-} deposition on trends in soil solution DOC. On the other hand, throughfall NO_3^- deposition had a significantly positive direct effect on DOC trends (Fig. 11A).

The variables in the model that best explained temporal changes in DOC were the same for the forests with low and medium N deposition; for both groups, NO_3^- deposition and SO_4^{2-} deposition (directly, or indirectly through its influence on plant growth) influenced the trend in DOC (Fig. 11B). Mean SO_4^{2-} deposition again had a significant negative effect on DOC slopes, while NO_3^- deposition had a significantly positive effect. The percentage of variance in DOC trend slopes explained by the model was 33%. For the plots with high N deposition, however, we found no model for explaining the trends in DOC using the mean annual SO_4^{2-} and NO_3^- throughfall deposition.

3.3.2 Effects of trends in deposition and soil solution parameters

When the SEM is applied using the trends in SO_4^{2-} and NO_3^- deposition instead of the mean values, a positive significant effect of trend in NO_3^- and a negative of SO_4^{2-} deposition were also apparent, but the latter was non-significant (Supplementary material S4, Fig. S3A). However, the percentage of variance in DOC trend slopes explained by the model was now much lower (16%). The SEM applied with the trends in SO_4^{2-} and NO_3^- throughfall deposition for forests with low and medium N deposition explained 24.4% of the variance of DOC trends, and showed a significantly negative effect of trends in SO_4^{2-} deposition on trends in DOC (Supplementary material S4, Fig. S3B).

For the forests with high N deposition, the best model used the relative trends in SO_4^{2-}, NO_3^- deposition and in median soil solution conductivity (% yr^{-1}) as explaining variables (Fig. 11C). The relative trend slopes of NO_3^- were positively related to the DOC trend slopes. Also both the trend slopes of SO_4^{2-} and NO_3^- deposition affected the trend slopes of DOC indirectly through an effect on the trends of soil solution conductivity, although acting in opposite directions: while trends in NO_3^- deposition negatively affected the trends on soil solution conductivity, trends in SO_4^{2-} deposition had a marginally significant positive effect ($p=0.06$) on the trends on soil solution conductivity. The trends in conductivity, in turn, positively affected the trend slopes of DOC. The percentage of the variance in DOC trend slopes explained by the model was 25% (Fig. 11C).

In summary, long-term trends in soil solution DOC were negatively related to mean SO_4^{2-} deposition (except for sites with high N deposition, where the effects of mean and trends in SO_4^{2-} deposition were not significant, Fig. 11A and 11B versus 11C) and positively related to N deposition (Fig. 11). Also, trends in soil solution DOC were negatively correlated with trends in SO_4^{2-} deposition when the N deposition was low or intermediate (Supplementary material S4, Fig. S3).

4 Discussion

4.1 Trend analysis of soil solution DOC in Europe

4.1.1 Are the many non-significant trends real?

Non-significant trends dominated the site-level DOC concentrations across the ICP Forests network. Measurement precision, strength of the trend, and the choice of the method may all affect trend detection (Sulkava et al., 2005; Waldner et al., 2014). Evidently, strong trends are easier to detect than weak trends. To detect a weak trend, either very long time series or very accurate and precise data are needed. The quality of the data is assured within the ICP Forests by means of repeated ring tests that are required for all participating laboratories and the accuracy of the data has been improved considerably over an eight years period (Ferretti and König, 2013; König et al., 2013). However, the precision and accuracy of the dataset still varies across countries and plots. By filtering out the time series with breakpoints and removing outliers, we improved the overall quality of the data, and thus guaranteed that the detected positive and negative trends were factual at a 0.05 significance level. Nevertheless, we found a majority of non-significant trends. For these cases, we cannot state with certainty that DOC did not change over time: it might be that the trend was not strong enough to be detected, or that the data quality was insufficient for the period length available for the trend analysis (more than 9 years in all the cases). For example, the mixed-effects models detected a positive trend in the organic layer, and while many of the individual time series measured in the organic layer also showed a positive trend, most were classified as non-significant trends (Fig. 4). This probably led to an underestimation of trends that separately might not be strong enough to be detected by the individual trend analysis but combined with the other European data these sites may contribute to an overall trend of increasing DOC concentrations in soils of European forests.

The uncertainty in the interpretation of the non-significant trends was compensated by using the SMK and PMK tests applied to monthly data for the trend analysis, which can detect weaker trends (Marchetto et al., 2013; Waldner et al., 2014). In summary, while there is probability (at $p<0.05$) that the detected statistically significant trends are genuine and not influenced by artifacts in the time series, the group of non-significant trends in DOC might well contain plots with significant trends that could not (yet) be detected statistically. Nevertheless, the selected trend analysis technique is the most suitable to detect weak trends, thus reducing the chances of hidden trends within the non-significant trends category.

4.1.2 Analysis of breakpoints in the time series

Soil solution DOC time series measured with lysimeters are subject to possible interruptions of monotonicity, which is manifested by breakpoints. For instance, installation effect, collector replacement, local forest management, disturbance by small animals, or by single or repeated canopy insect infestations may disrupt DOC concentrations through abrupt soil disturbances and/or enhanced throughfall chemical input to soil (Akselsson et al., 2013; Kvaalen et al., 2002; Lange et al., 2006; Moffat et al., 2002; Pitman et al., 2010). In general, detailed information on the management history and other local disturbances was not available for the majority of Level II plots, which hinders selection of individual monotonic time series based on specific site conditions. The BFAST analysis allowed us to filter out time series affected by local disturbances (natural or artefacts) from the dataset and retain time series that represented monotonic trends. Thereby, we removed some of the within-plot variability (Fig. 2) that might be caused by local factors not directly explaining the long-term monotonic trends in DOC and thus complicating or confounding the trend analysis (Clark et al., 2010).

In view of these results, we recommend that testing for monotonicity of the individual time series is a necessary first step in this type of analyses and that the breakpoint analysis is an appropriate tool to filter large datasets prior to analyzing the long-term temporal trends in DOC concentrations. It is worth mentioning that, since our main goal was to study general monotonic trends, we did not focus on finding the direct causes of breakpoints in time series. Further work is needed to interpret the causes of these abrupt changes and verify if these are artefacts or mechanisms, since they may also contain useful information on local factors affecting DOC trends, such as forest management or extreme events (Tetzlaff et al., 2007).

4.1.3 Variability in soil solution DOC trends within plots

Even after removing sites with breakpoints in the time series, within-plot variability remained high (median within-plot range: 3.3% yr^{-1}), with different trends observed for different collectors from the same plot (Fig. 6). This high small-scale variability in soil solution DOC makes it difficult to draw conclusions about long-term DOC trends from individual site measurements, particularly in plots with heterogeneous soil and site conditions (Löfgren et al., 2010).

The trends in soil solution DOC also varied across soil depth intervals. The mixed-effect models suggested an increasing trend in soil solution DOC concentration in the organic layer, and an increasing trend in soil solution DOC concentration under 80 cm depth when the entire dataset (with breakpoints) was analyzed. The individual trend analyses seemed to confirm the increasing trend under the organic layer (Table 1), while more heterogeneous trends in the mineral soil were found, which is in line with previous findings (Borken et al., 2011; Evans et al., 2012; Hruška et al., 2009; Löfgren and Zetterberg, 2011; Vanguelova et al., 2010). This difference has been attributed to different processes affecting DOC in the organic and shallow soils and in the subsoil. External factors such as acid deposition may have a more direct effect in the organic layer where interaction between DOC and mineral phases is less important compared to deeper layers of the mineral soil (Fröberg et al., 2006). However, DOC measurements are not available for all depths at each site, complicating the comparison of trends across soil depth intervals. Hence, the depth-effect on trends in soil solution DOC cannot be consistently addressed within this study (see Supplementary material S3).

Finally, the direction of the trends in soil solution DOC concentrations did not follow a clear regional pattern across Europe (Fig. 4 and 5) and even contrasted with other soil solution parameters that showed widespread trends over Europe, such as decreasing SO_4^{2-} and increasing pH. This finding indicates that effects of environmental controls on soil solution DOC concentrations may differ depending on local factors like soil type (e.g., soil acidity) as well as site and stand characteristics (e.g., tree growth or acidification history). Thus, the trends in DOC in soil solution appear to be an outcome of interactions between controls acting at local and regional scales.

4.2 Controls on soil solution DOC temporal trends

4.2.1 Vegetation

Biological controls on DOC production and consumption, like stem growth, operating at site or catchment level, are particularly important when studying soil solution as plant-derived carbon is the main source of DOC (Harrison et al., 2008). Stem growth was available only for 53 sites as the increment between inventories carried out every five years, and as such no annual growth estimates were available. Nevertheless, our results suggest that vegetation growth is an important driver of DOC temporal dynamics in forests, as reported for peatlands (Billett et al., 2010; Dinsmore et al., 2013). Differences in DOC temporal trends across all soil depths were not related to forest type but to stem growth: more fertile plots, as indicated by higher stem volume increment, exhibited more often decreasing trends in DOC (Fig. 7 and 11), possibly in response to reduced C allocation to belowground nutrient acquisition system (Vicca et al., 2012).

It is well-established that N-enrichment favors the above-ground tissue production (as indicated by a higher stem volume increment) in forests (Janssens et al., 2010; Vicca et al., 2012) at the expense of C allocation to the root system, hence, reducing an important source of belowground DOC. On the other hand, forests with higher production would also have higher aboveground litterfall (Hansen et al., 2009), providing a higher input of labile carbon as a source for DOC leaching. Nevertheless, fertile forests may exhibit a higher microbial use efficiency, which may lead to proportionally more DOC being consumed, i.e., less DOC remaining in soil solution (Manzoni et al., 2012). Also, compared to vigorously growing forests with dense canopies, slower forest growth with less dense canopies have less interception and higher soil water input, which could stimulate litter decomposition and thus DOC production. Finally, forest growth might indirectly affect DOC trends through changes in soil solution chemistry (via cation uptake) (Vanguelova et al., 2007), but our data did not allow to test these pathways and thus the DOC response to vegetation uptake remains hypothetical.

4.2.2 Acidifying deposition

Decreased atmospheric SO_4^{2-} deposition and accumulation of atmospherically deposited N were hypothesized to increase DOC in European surface waters over the last 20 years (Evans et al., 2005; Hruška et al., 2009; Monteith et al., 2007). Sulphate and inorganic N deposition decreased in Europe over the past decades (Waldner et al., 2014) but trends in soil solution DOC concentrations varied largely, with increases, decreases, as well as steady states being observed across respectively 56, 41 and 77 time series in European forests (Fig. 4 and 5). Although we could not demonstrate a direct effect of trends in SO_4^{2-} and inorganic N deposition on the trends of soil solution DOC concentration, we observed a switch in the direction of the DOC trends according to the mean SO_4^{2-} and inorganic N deposition levels (Fig. 7 and 8), with increasing soil solution DOC trends occurring more often in plots with high N and, to a lesser extent, SO_4^{2-} deposition. This suggests an interaction between the deposition load and the mechanisms underlying the temporal change of soil solution DOC.

Inorganic nitrogen

Our results suggest that at sites with lower N deposition and lower soil NO_3^-, DOC concentration in the soil solution is predominantly decreasing (Fig. 8A and 10) and in these forests, we showed that decreasing trends in SO_4^{2-} deposition coincided with increasing trends in soil solution DOC (Fig. S3). The role of atmospheric N deposition in increasing DOC leaching from soils has been well documented (Bragazza et al., 2006; Pregitzer et al., 2004; Rosemond et al., 2015). The mechanisms behind this relationship are either physico-chemical or biological. Chemical changes in soil solution through the increase of NO_3^- ions can trigger desorption of DOC (Pregitzer et al., 2004), and biotic forest responses to N deposition, namely, enhanced photosynthesis, altered carbon allocation, and reduced soil microbial activity (Bragazza et al., 2006; de Vries et al., 2009; Janssens et al., 2010), can affect the final amount of DOC in the soil. One proposed mechanism is incomplete lignin degradation and greater production of DOC in response to increased soil NH_4^+ (Pregitzer et al., 2004; Zech et al., 1994). Alternatively, N-induced reductions of forest heterotrophic respiration (Janssens et al., 2010) may lead to greater accumulation of DOC.

Sulphate

Similar to our observation for soil solution DOC, decreasing SO_4^{2-} deposition has been linked to increasing surface water DOC (Evans et al., 2006; Monteith et al., 2007; Oulehle and Hruska, 2009). Sulphate deposition triggers soil acidification and a subsequent release of Al^{3+} in acid soils. The amount of Al^{3+} is negatively related to soil solution DOC due to two plausible mechanisms: 1) The released Al^{3+} can build complexes with organic molecules, enhancing DOC precipitation and, in turn, suppress DOC solubility, therefore decreasing DOC concentrations in soil solution (de Wit et al., 2001; Tipping and Woof, 1991;

Vanguelova et al., 2010), and 2) at higher levels of soil solution Al^{3+} in combination with low pH, DOC production through SOM decomposition decreases due to toxicity of Al^{3+} to soil organisms (Mulder et al., 2001). Consequently, when SO_4^{2-} deposition is lower, increases of soil solution DOC concentration could be expected (Fig. 11A, B). Finally, an indirect effect of plant response to nutrient-limited acidified soil could also contribute to the trend in soil solution DOC by changes to plant belowground C allocation (Vicca et al., 2012) (see Sect. 4.2.1.).

The SO_4^{2-} deposition effect on the trends of DOC in soil solution depended on the soil acidity (Fig. 9). Moreover, the soil chemical characteristics, more specifically the soil solution conductivity (which is an indirect measure of ionic strength (Griffin and Jurinak, 1973)), and the soil solution NO_3^- and SO_4^{2-} concentrations, were the most important factors determining whether DOC concentrations increased or decreased over time (Fig. 10).

Ultimately, internal soil processes control the final concentration of DOC in the soil solution. The solubility and biological production and consumption of DOC are regulated by pH, ionic strength of the soil solution and the presence of Al^{3+} and Fe (Bolan et al., 2011; De Wit et al., 2007; Schwesig et al., 2003). These conditions are modulated by changes in atmospheric deposition but not uniformly across sites: soils differ in acid-buffering capacity (Tian and Niu, 2015), and the response of DOC concentrations to changes in SO_4^{2-} deposition will thus be a function of the initial soil acidification and buffer range (Fig. 9 and 11). Finally, modifications of soil properties induced by changes in atmospheric deposition are probably an order of magnitude lower than the spatial variation of these soil properties across sites, making it difficult to isolate controlling factors on the final observed response of soil solution DOC at continental scale (Clark et al., 2010).

In conclusion, the response of DOC to changes in atmospheric deposition seems to be controlled by the past and present N deposition loads and acidification of soils (Clark et al., 2010; Evans et al., 2012; Tian and Niu, 2015). It suggests that the mechanisms of recovery from SO_4^{2-}deposition and acidification take place only in non-N-saturated forests, as it has been observed for N deposition effects (de Vries et al., 2009). In high N deposition areas, it is likely that impacts of N-induced acidification on forest health and soil condition lead to more DOC leaching, even though SO_4^{2-} deposition has been decreasing. Therefore, soil solution DOC concentrations responded as expected to changes in acid deposition, particularly in non N-saturated sites but the hypothesis of recovery from acidity cannot fully explain overall trends in Europe, as was also previously suggested in local or national studies of long-term trends in soil solution DOC (Löfgren et al., 2010; Stutter et al., 2011; Ukonmaanaho et al., 2014; Verstraeten et al., 2014).

Finally, our results confirm the long-term monotonic trends of DOC in soil solution as a consequence of the interactions between local (soil properties, forest growth), and regional (atmospheric deposition) controls acting at different temporal scales. However, further work is needed to quantify the role of each mechanism underlying the final response of soil solution DOC to environmental controls. We recommend that particular attention should be paid to the biological controls (e.g., net primary production, stem growth, root exudates or litterfall and canopy infestations) on long-term trends in soil solution DOC, which remains poorly understood.

4.3 Link between DOC trends in soil and streams

An underlying question is how DOC trends in soil solution relate to DOC trends in stream waters. Several studies have pointed out recovery from acidification as a cause for increasing trends in DOC concentrations in surface waters (Dawson et al., 2009; Evans et al., 2012; Monteith et al., 2007; Skjelkvåle et al., 2003). Overall, our results point to a noticeable increasing trend in DOC in the organic layer of forest soils, which is qualitatively consistent with the increasing trends found in stream waters and in line with positive DOC trends reported for the soil organic layer or at maximum 10 cm depth of the mineral soil in Europe (Borken et al., 2011; Hruška et al., 2009; Vanguelova et al., 2010). On the other hand, while there was also evidence of increasing trends in the deep mineral horizon (> 80 cm), trends at different soil horizons along the mineral soil were more variable and responded to other soil internal processes.

Hence, the results from the trend analysis for the overall European dataset points out to a link between the long-term dynamics in surface and deep soil and surface water DOC. However, the individual trend analysis reflects a high heterogeneity in the long-term response of soil DOC to environmental controls. In fact, it is currently difficult to link long-term dynamics in soil and surface water DOC. Large scale processes become more important than local factors when looking at DOC trends in surface waters (Lepistö et al., 2014), while the opposite seems to apply for soil solution DOC trends. Furthermore, stream water DOC mainly reflects the processes occurring in areas with a high hydraulic connectivity in the catchment, such as peat soils or floodplains, which normally yield most of the DOC (Löfgren and Zetterberg, 2011). Further monitoring studies in forest soils with high hydraulic connectivity to streams are needed to be able to link dynamics of DOC in forest soil with dynamics of DOC in stream waters.

5 Conclusions

Different monotonic long-term trends of soil solution DOC have been found across European forests at plot scale, with the majority of the trends for specific plots and depths not being statistically significant (40%), followed by significantly positive (35%) and significantly negative trends (25%). The distribution of the trends did not follow a specific regional pattern. There was evidence that an overall increasing trend occurred in the organic layers and, to a lesser extent, in the deep mineral soil**,** however, there is less agreement on the trends found in different soil horizons along the mineral soils.

A multivariate analysis revealed a negative relation between long-term trends in soil solution DOC and mean SO_4^{2-} deposition and a positive relation to mean NO_3^- deposition. While the hypothesis of increasing trends of DOC due to reductions of SO_4^{2-} deposition could be confirmed in more N-limited forests, there was no significant relationship with SO_4^{2-} deposition in more N-enriched forests. We found evidence that soil pH determines the response of trends of DOC in soil solution to SO_4^{2-} deposition, indicating that internal soil processes control the final response of DOC in soil solution. Although correlative, our results suggest that there is no single mechanism responsible for soil solution DOC trends operating at large scale across Europe but that interactions between controls operating at local (soil properties, site and stand characteristics) and regional (atmospheric deposition changes) scales are taking place at the same time.

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Table 1. Temporal trends of DOC concentrations obtained with the linear mixed models (LMM) built for different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints) and the Seasonal Mann Kendal tests (SMK). The table shows the relative slope (rslope in % yr-1), the number of observations (n) and the p value. For the SMK tests, the number of time series showing significant negative (N), non-significant (NS) and significant positive (P) trends are shown. LMMs for which no statistically significant trend was detected (p>0.1) are represented in grey and the LMMs for which a significant trend (p<0.05) was detected are in bold. (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm/ TL: tension lysimeter, ZTL: zero-tension lysimeter/ n.s.: no significant.)

In broadleaved and coniferous forests:

Collector type	Layer	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
		n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	3133	6.75	*0.0782*	1168	-0.30	n.s.	-1.03 (±1.65)	1	3	1
	M02	19311	0.10	n.s.	8917	-1.06	n.s.	0.16 (±4.78)	17	29	21
	M24	7700	2.69	n.s.	3404	3.66	n.s.	0.6 (±9.03)	11	12	11
	M48	24614	0.95	n.s.	11065	0.80	n.s.	0.67 (±4.76)	22	30	32
	M8	9378	**6.78**	**0.0036**	3394	3.41	n.s.	1.007 (±8.79)	8	9	16
ZTL	O	8136	**3.75**	**<0.001**	4659	1.63	*0.0939*	**1.7** **(±4.28)**	3	16	8
	M02	3389	-0.54	n.s.	445	0.17	n.s.	-0.7 (±1.85)		3	1
	M24	739	0.36	n.s.							

	M48	654	-3.37	n.s.	336	1.05	n.s.	1.07 (±3.08)	1	2	1
	M8	118	1.39	n.s.							

In broadleaved forests:

Collector type	Layer	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
		n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	637	-5.96	n.s.	475	-0.17	n.s.	-0.3 (±0.9)	0	2	0
	M02	8397	3.07	*0.0764*	3104	0.51	n.s.	0.89 (±5.94)	4	7	10
	M24	2584	-0.05	n.s.	928	6.01	n.s.	1.03 (±11.31)	3	5	4
	M48	10635	-0.93	n.s.	4634	2.46	n.s.	1.51 (±5.31)	11	8	16
	M8	4354	-6.85	*0.0672*	1797	-0.10	n.s.	0.3 (±6.28)	4	5	6
ZTL	O	4057	0.37	n.s.	1956	-0.90	n.s.	0.96 (±5.47)	2	7	3
	M02	608	0.26	n.s.	192	1.88	n.s.	2.72			1
	M24	94	**11.80**	**0.026**							
	M48	427	-2.84	n.s.				0		1	
	M8	34	**-36.18**	**<0.001**							

In coniferous forests:

Collector type	Layer	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
		n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	2496	8.15	*0.0633*	693	1.33	n.s.	-1.06	1	1	1

								(±2.25)			
	M02	10914	-0.97	n.s.	5813	-1.60	n.s.	-0.04 (±3.98)	13	22	11
	M24	5116	2.71	n.s.	2476	3.66	n.s.	-0.3 (±7.82)	7	7	8
	M48	13979	1.24	n.s.	6431	0.05	n.s.	0.3 (±4.32)	16	22	11
	M8	5024	**9.93**	**<0.001**	1597	7.58	n.s.	2.89 (±10.28)	4	4	10
ZTL	O	4079	**3.59**	**0.0018**	2703	**3.09**	**0.0045**	**1.85** **(±2.88)**	1	9	5
	M02	2781	-0.60	n.s.	253	-1.44	n.s.	-0.83 (±0.4)	0	3	0
	M24	645	0.23	n.s.							
	M48	227	-0.39	n.s.	251	-0.55	n.s.	2.14 (±3.66)	1	1	1
	M8	84	13.87	*0.0995*							

Table 2. Median relative trend (rslope in % yr^{-1}) of DOC concentrations and interquartile range of rslope and number of time series with statistically significant ($p < 0.05$) positive (P) and negative (N) trends and with non-significant (NS) trends of DOC using the seasonal Mann-Kendall test (SMK), the partial Mann-Kendall test (PMK) and the Breaks For Additive Seasonal and Trend test (BFAST). (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm.)

Soil depth	**SMK**				**PMK**				**BFAST**			
	rslope	**N**	**NS**	**P**	**rslope**	**N**	**NS**	**P**	**rslope**	**N**	**NS**	**P**
O	1.18 (±3.37)	4	19	9	1.0 (±3.44)	4	18	9	1.15 (±3.47)	5	18	9
M02	0.04 (±3.41)	17	32	22	0.10 (±3.29)	16	33	21	-0.40 (±3.56)	19	34	18
M24	0.61 (±8.62)	11	12	11	-0.03 (±8.97)	10	11	11	0.83 (±9.31)	10	11	13
M48	1.01 (±4.79)	23	32	33	0.77 (±4.75)	22	31	33	0.59 (±6.32)	23	33	32
M8	1.18 (±9.39)	8	9	16	1.01 (±8.48)	8	11	14	1.75 (±9.59)	7	9	17

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Table 3. Site properties for the 13 plots showing consistent negative trends (N) of DOC concentrations and for the 12 plots showing consistent positive trends (P) of DOC concentrations. Soil properties (clay percentage, C/N ratio, pH($CaCl_2$), cation exchange capacity (CEC)) are for the soil depth interval 0-20 cm. Mean atmospheric deposition (inorganic N and SO_4^{2-}) is throughfall deposition. When throughfall deposition was not available, bulk deposition is presented with an asterisk. Trends in soil solution pH, Ca^{2+} and Mg^{2+} concentrations were calculated using the seasonal Mann-Kendall test.

Code Plot	Trend	Soil Type (WRB)	Clay (%)	C/N	pH	CEC ($cmol_+ kg^{-1}$)	MAP (mm)	MAT (°C)	N depos. (kg N $ha^{-1} yr^{-1}$)	SO_4^{2-} deposition (kg S $ha^{-1} yr^{-1}$)	slope pH (%yr^{-1})	slope Ca^{2+} (% yr^{-1})	slope Mg^{2+} (% yr^{-1})
France (code = 1)													
30	N	Cambic Podzol	3.79	16.8	3.96	1.55	567	11.9	7.28	4.25	0.10	-0.90	-1.00
41	N	Mollic Andosol	23.9	16.6	4.23	7.47	842	10.6	4.43	4.15	0.00	-1.10	-1.30
84	N	Cambic Podzol	4.09	22.8	3.39	4.07	774	10.5	7.66	3.77*	0.50	2.00	1.00
Belgium (code =2)													
11	P	Dystric Cambisol	3.54	17.7	2.81	6.22	805	11.0	18.7	13.2	0.40	-11.0	-8.00
21	P	Dystric Podzo-luvisol	11.2	15.4	3.59	2.41	804	10.3	16.8	13.2	0.00	-9.00	-5.00
Germany (code:= 4)													
303	N	Haplic Podzol	17.3	16.5	3.05	8.77	1180	9.10	17.5		0.40	-5.00	-2.00
304	N	Dystric Cambisol	21.3	17.7	3.63	6.14	1110	6.20	16.4		0.00	-3.00	-0.40
308	N	Albic	3.80	16.5	3.41	1.63	816	9.20	14.2*		0.00	-5.00	-2.00

Code Plot	Trend	Soil Type (WRB)	Clay (%)	C/N	pH	CEC (cmol$_+$ kg^{-1})	MAP (mm)	MAT (°C)	N depos. (kg N ha^{-1} yr^{-1})	SO_4^{2-} deposition (kg S ha^{-1} yr^{-1})	slope pH (%yr^{-1})	slope Ca^{2+} (% yr^{-1})	slope Mg^{2+} (% yr^{-1})
		Arenosol											
802	N	Cambic Podzol	6.00	25.7	3.35	4.33	836	11.9	25.2	13.2	0.50	-2.40	-1.50
1502	N	Haplic Arenosol	4.40	23.8	3.78	2.35	593	9.40	9.79	5.66		-16.0	-14.0
306	P	Haplic Calcisol					782	10.2	13.9		0.50	2.00	2.00
707	P	Dystric Cambisol					704	10.7	18.3	8.49	0.00	-10.0	-2.00
806	P	Dystric Cambisol					1349	8.30	23.0	6.81	0.30	-7.00	-6.00
903	P	Dystric Cambisol					905	9.60			0.20	-5.00	-3.00
920	P	Dystric Cambisol					908	8.90			-1.00	-6.00	-0.50
1402	P	Haplic Podzol	8.65	26.2	3.24	9.04	805	6.90	13.5	24.3	1.20	-6.00	9.00
1406	P	Eutric Gleysol	15.9	23.1	3.59	6.67	670	8.80	15.3	6.23	1.11	-4.00	-3.00
Italy (code = 5)													
1	N	Humic Acrisol	3.14	12.2	5.32	31.6	670	23.3			-0.30	-10.0	-10.0
United Kingdom (code = 6)													
922	P	Umbric Gleysol	34.8	15.6	3.31	10.8	1355	9.50			0.40	-9.00	2.00
Austria (code = 14)													

Code Plot	Trend	Soil Type (WRB)	Clay (%)	C/N	pH	CEC (cmol+ kg^{-1})	MAP (mm)	MAT (°C)	N depos. (kg N ha^{-1} yr^{-1})	SO_4^{2-} deposition (kg S ha^{-1} yr^{-1})	slope pH (%yr^{-1})	slope Ca^{2+} (% yr^{-1})	slope Mg^{2+} (% yr^{-1})
9	N	Eutric Cambisol	20.1	12.8	5.26	25.9	679	10.8		3.80*	0.40	-1.50	-0.60
Switzerland (code = 50)													
15	N	Dystric Planosol	17.6	14.7	3.73	7.76	1201	8.90	15.1	4.67	-0.10	-13.0	-4.00
2	P	Haplic Podzol	14.7	18.3	3.17	3.59	1473	4.40			-0.80	-5.00	-3.00
Norway (code =55)													
14	N	Cambic Arenosol	9.83	25.4	3.46				14.7	21.9	0.10	-1.70	-3.30
19	N		10.5	18.7	3.79		836	4.60	1.54	2.61	0.50	-7.00	-4.00
18	P		3.05	29.5	3.69		1175	0.35		2.40	-0.90	0.00	0.00

Table 4. Statistics (Wilks' Lambda and p value) of the General Discriminant Analysis among groups of plot-soil depth combinations with different trend in DOC during the last years conducted with 10 different soil solution and deposition variables as independent continuous variables and soil depth as categorical independent variable. Bold type indicates a significant effect of the variable in the model ($p < 0.05$)

Independent variables	**Wilks' Lambda**	***p* value**
pH	0.913	0.158
log(NH_4^+_TF)	0.973	0.575
log(NO_3^-_BD)	0.944	0.308
log(SO_4^{2-}_BD)	0.920	0.182
log(SO_4^{2-}_SS)	0.857	**0.042**
log(NO_3^-_SS)	0.814	**0.015**
log(NH_4^+_SS)	0.947	0.331
log(AL_SS)	0.961	0.434
log(FE_SS)	0.930	0.224
log(CONDUCTIVITY_SS)	0.807	**0.012**

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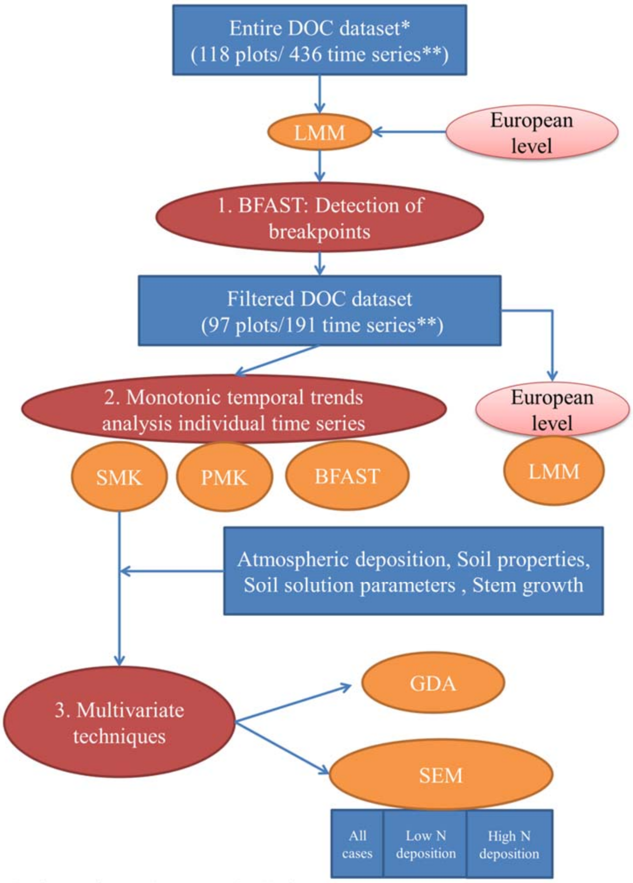

* Time series > 10 years and > 60 obs.
* Time series aggregated per soil depth

Acronym	**Model**	**Type of analysis**
LMM	Linear mixed-effects models	Temporal trends
BFAST	Breaks For Additive Seasonal and Trend	Analysis of breakpoints in time series
SMK	Seasonal Mann Kendall test	Monotonic temporal trends
PMK	Partial Mann Kendall test	Monotonic temporal trends
GDA	General Discriminant Analysis	Multivariate analysis
SEM	Structural equation Model	Multivariate analysis (direct/indirect effects)

Figure 1. Flow-diagram of the sequence of methods applied for analysis of temporal trends of soil solution DOC and their drivers.

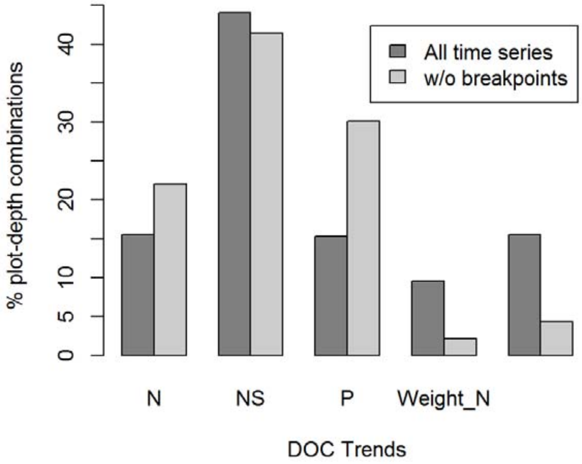

Figure 2. Percentage of plot-soil depth combinations for which negative (N), non-significant (NS), positive (P), negative and non-significant (Weight_N) and positive and non-significant (Weight_P) trends of DOC concentrations were found using SMK (seasonal Mann-Kendall) tests when 1) all the 436 time series were used, 2) only 191 time series without breakpoints (detected using the BFAST (*Breaks For Additive Seasonal and Trend*) analysis) were used.

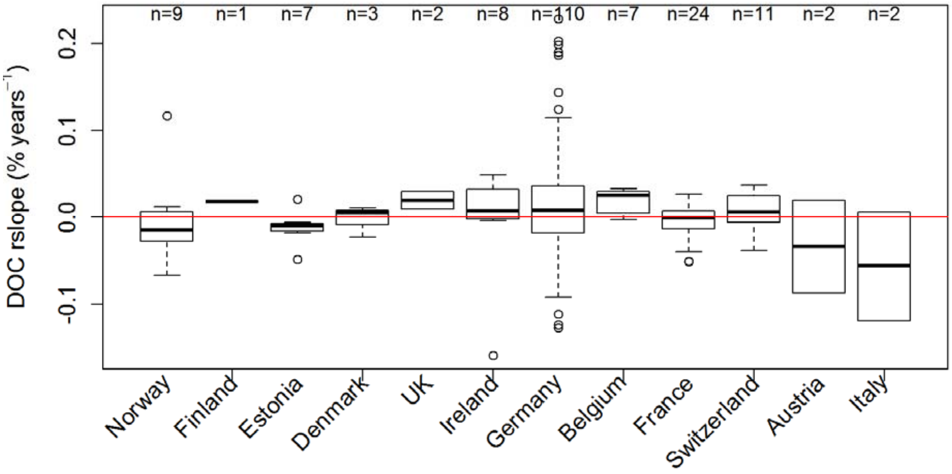

Figure 3. Relative trend slope of DOC trends calculated using the seasonal Mann-Kendall test (SMK) for time series with more than 10 years of measurements and no breakpoints in 12 European countries, ranked from north to south.

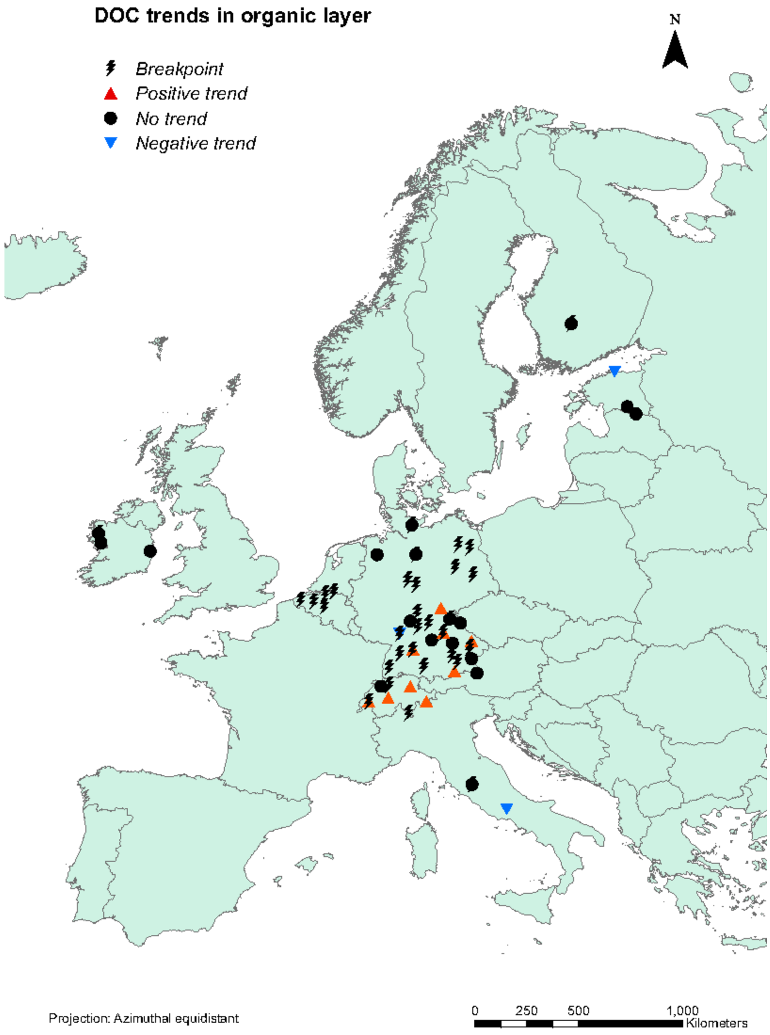

Figure 4. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the seasonal Mann-Kendall test. Data span from 1991 to 2011.

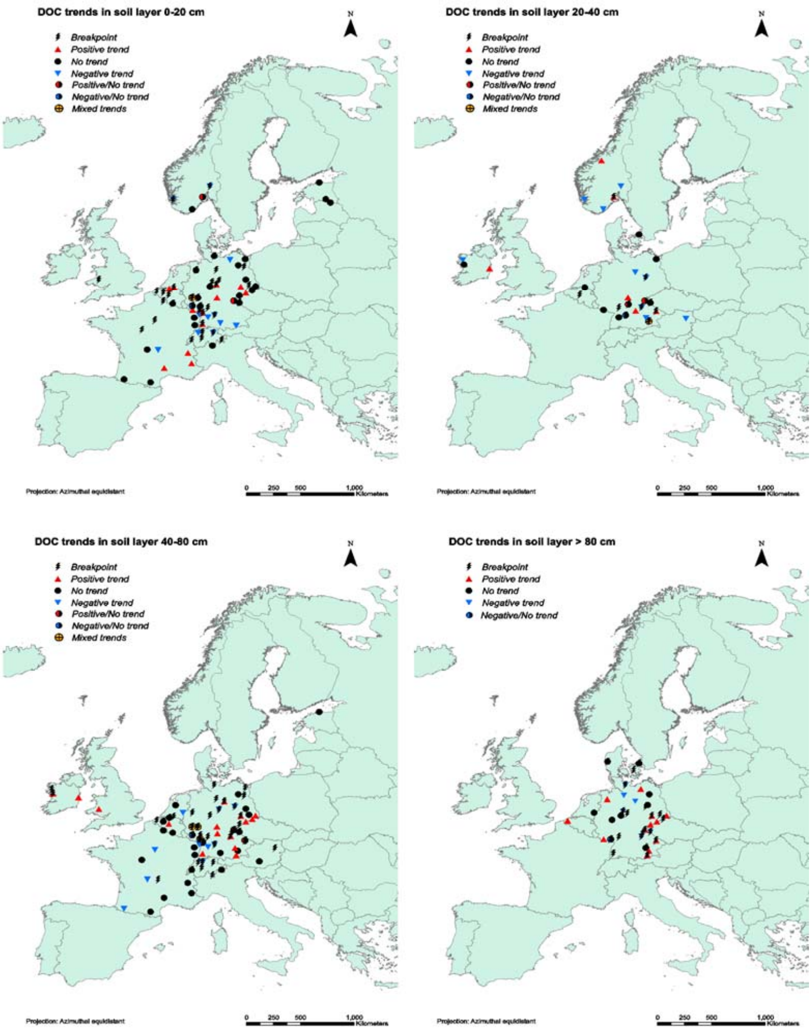

Figure 5. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0–20 cm), b) intermediate (20–40 cm), c) subsoil (40–80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the seasonal Mann-Kendall test. Data span from 1991 to 2011.

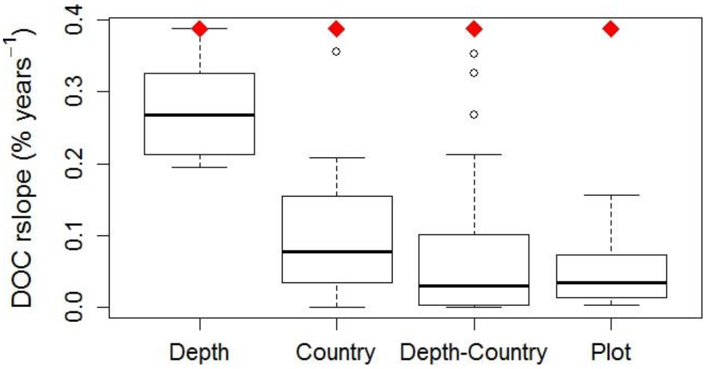

Figure 6. Range of relative trend slopes (max-min) for trends of DOC concentration in soil solution within each 1) depth interval, 2) country, 3) depth interval per country, and 4) plot. The boxplots show the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers) and higher values (circles). The red diamond marks the maximum range of slopes in soil solution trends in the entire dataset.

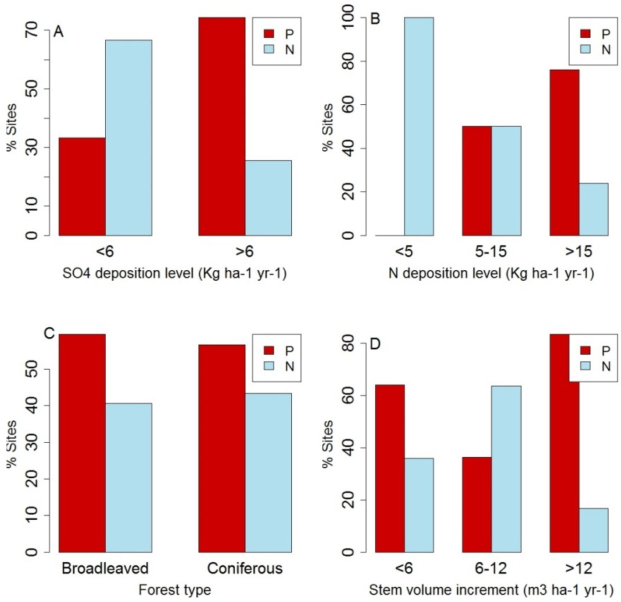

Figure 7. Percentage of occurrence of positive and negative trends in soil solution separated by A) throughfall SO_4^{2-} deposition level (kg S ha^{-1} yr^{-1}), B) throughfall inorganic N deposition level (kg N ha^{-1} yr^{-1}), C) forest type and D) stem volume increment (m^3 ha^{-1} yr^{-1}).

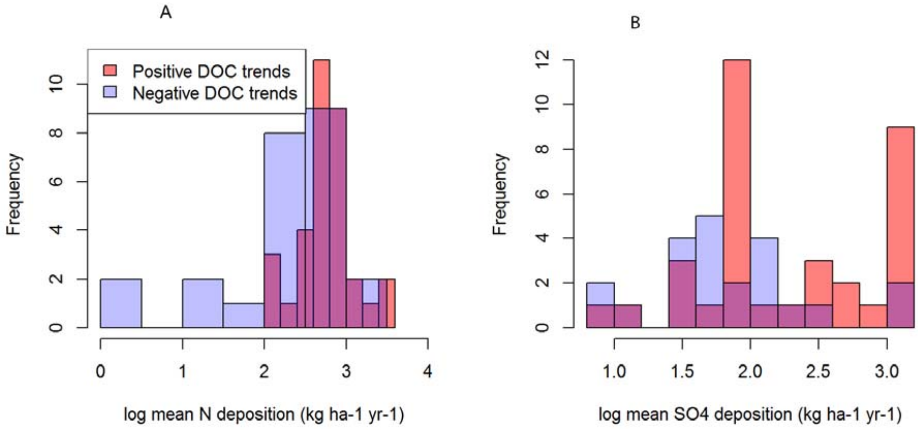

Figure 8. Histograms for natural log-transformed mean throughfall SO_4^{2-} deposition (A) and for log-transformed mean throughfall inorganic N deposition (B) for positive and negative trends of DOC.

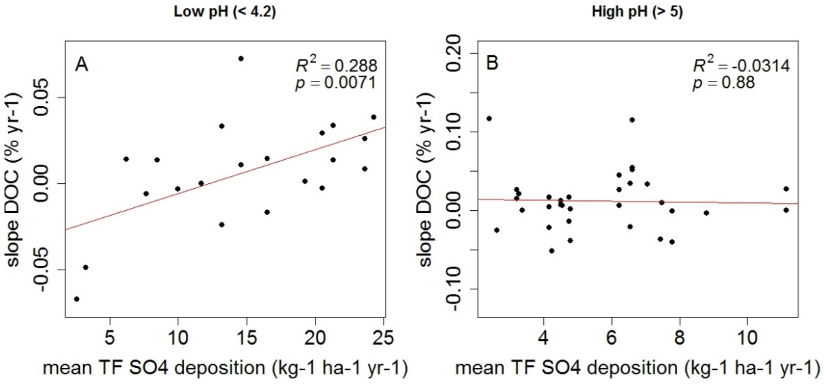

Figure 9. Relationship between mean throughfall SO_4^{2-} deposition and relative slopes of DOC for very acid soils (pH in soil solution < 4.2) (left) and non-acid soils (pH in soil solution > 5) (right).

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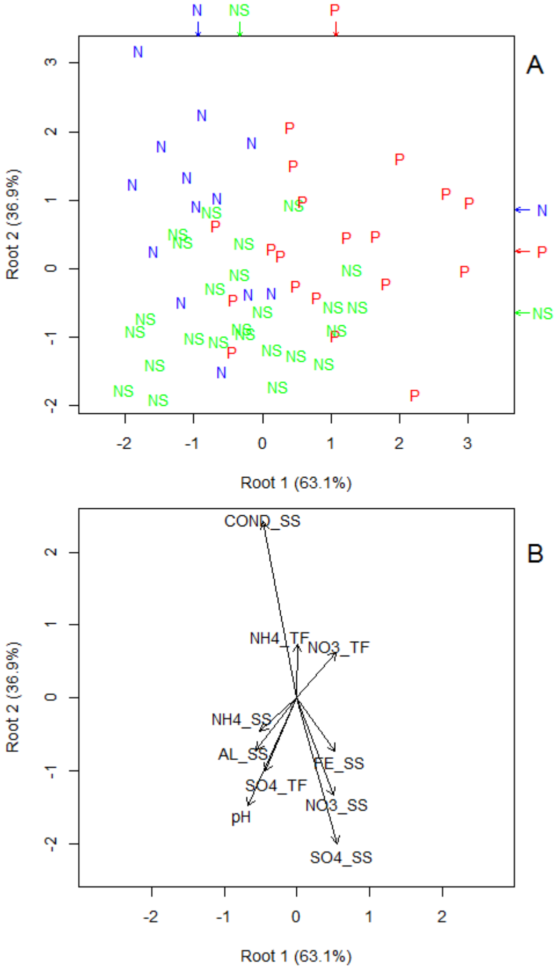

Figure 10. Biplot representing the scores for the single plot-soil depth combinations for the two roots of the General Discriminant Analysis (GDA). (B) Biplot representing the standardized canonical discriminate function coefficients for the two roots of this GDA. The GDA is generated to explain the variance among groups of plot-soil depth combinations with different trend in soil solution DOC (N for negative trends, P for positive trends and NS for non-significant trends) during the last years conducted with 7 soil solution variables (pH, NH4_SS, NO3_SS, FE_SS, SO4_SS, COND_SS, AL_SS) and three throughfall deposition variables (NH4_TF, NO3_TF, SO4_TF) as independent continuous variables and different soil layers as categorical independent variable.

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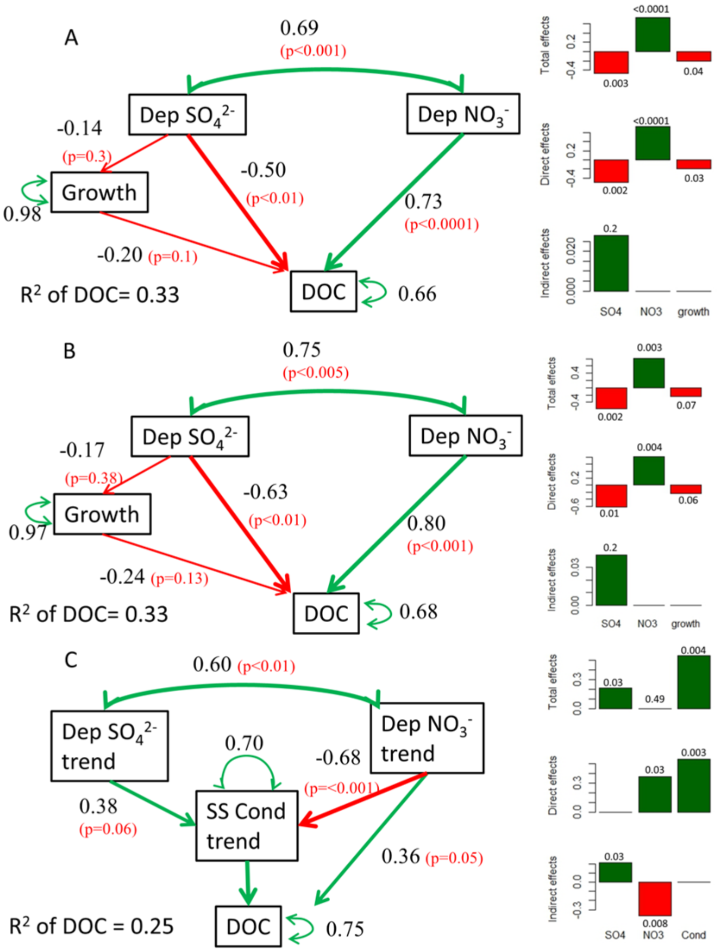

Figure 11. Diagrams of the structural equation models (SEM) that best explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium throughfall inorganic N deposition (> 15 kg N ha^{-1} yr^{-1}), and C) cases with high throughfall inorganic N deposition with mean or trends in annual SO_4^{2-} and NO_3^- deposition (kg N ha^{-1} yr^{-1}) with direct and indirect effects through effects on soil solution parameters (trends of conductivity in µS/cm) and mean annual stem volume increment (growth) in m^3 ha^{-1} yr^{-1}). p-values of the significance of the corresponding effect are between brackets. Green arrows indicate positive effects and red arrows indicate negative effects. Side bar graphs indicate the magnitude of the total, direct and indirect effects and their p-value.