Answers to Referee 1

The authors have provided a detailed response to my comments. However, they have not taken into account in their manuscript two important points I raised:

1) a conceptual figure summarizing the main processes and factors that may control the DOC concentrations or fluxes. This article is aimed at a large audience (ecologists, biogeochemists, terrestrial and aquatic communities...) and thereby must accessible to this large audience and not to specialists only.

A general conceptual figure showing the factors and processes affecting DOC has been added to the manuscript (Figure 1). We refer to it in the introduction, when we present the potential drivers of DOC changes.

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2) I would like to see a discussion on the possible bias linked to the fact you correlate DOC in surface water to DOC concentrations in soil and not to the amount of DOC flowing out of ecosystems.

The final section *4.3. Link between DOC trends in soil and streams* has been modified and a new paragraph has been added at the end (lines 634-643 in revised manuscript). In this new paragraph, we discuss the potential implications of the fact that information on the hydrology of the site was not available for this study to calculate the fluxes. We also propose that future studies on DOC controls at large scales should take into account the hydrology.

Answers to Referee 2

I agree with reviewer #2 that the authors have responded to most of the reviewers comments and that overall the manuscript has been improved. I also agree that the two unanswered points should be answered in the revised version. In addition, and unless I've missed this, however, there has been no analysis as to the extent of the spatial correlation between the decreasing trends in SO4 and the increasing trend in NOx at low to medium levels, which strikes me as important. I assume that the statistical methods should have taken care of the interdependency, but I think that the readers should be also informed about any potenential co-variation and likely effects on the outcome of the study.

Indeed, the Structural Equation Models accounted for the co-variance between deposition of SO_4^{2-} and NO_3^- (it is represented by the arrow between Dep SO_4^{2-} and Dep NO_3^- in Figure 7 in the revised manuscript).
However, to inform the readers about the spatial correlation between SO_4^{2-} and NO_3^- deposition, and the DOC trends, a map showing the spatial variation of the SO_4^{2-} and NO_3^- deposition trends has been added (Figure 8). This map is now used in the results and discussion section to discuss the potential effect of co-variation between SO_4^{2-} and NO_3^- deposition trends on our results (lines 362-365 and 587-594 in the revised version of the manuscript).

Minor comments:
remove line 534 and 559, or make new, numbered subheadings

Lines 534 and 559 has been removed.

Most relevant changes made in the manuscript

1. A new conceptual figure (Figure 1) has been added to the manuscript.

2. A final paragraph has been added to the discussion "4.3. Link between DOC trends in soil and streams" (lines 634-643).

3. A map with the spatial variation in SO_4^{2-} and NO_3^- trends has been added (Figure 8).

4. The potential effect of covariation between SO_4^{2-} and NO_3^- is now discussed in lines 362-365 and 587-594.

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

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Abstract

Dissolved organic carbon (DOC) in surface waters is connected to DOC in soil solution through hydrological pathways. 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 of recovery from acidification. 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. The rate change of soil solution DOC ranged between -16.8% yr^{-1} and +23% yr^{-1} (median= +0.4% yr^{-1}) across Europe. 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 trends in DOC concentrations with increasing mean nitrate (NO_3^-) deposition and increasing trends in 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 low to medium N deposition areas, in agreement with observations in surface waters, this was not the case in high N deposition areas. 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 (Fig. 1). 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 surface waters mirror those observed in ecosystem soil solutions.

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 or, increased litterfall) (de Vries et al., 2014; Ferretti et al., 2014; 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 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 (De Wit et al., 2007; 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 (Sawicka et al., 2016; Vanguelova et al., 2010; Verstraeten et al., 2014), it is not consistent with trends in soil solution DOC concentrations reported from 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-drivers of 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 (Borken et al., 2011; 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 (Fig. 1). Positive temporal trends in soil solution DOC (increasing concentrations over time) were 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 a 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 is 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 waters, we hypothesize that temporal trends in soil solution DOC will 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, 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 depths 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, Mg, NH_4^+, SO_4^{-2}, total dissolved Al, total dissolved Fe, pH, electrical conductivity). Information on the soil solution chemistry at the studied plots can be found in Supplementary material (Table S4-S11). 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, Table S1).

Soil properties, open field bulk deposition and throughfall deposition of NO_3^-, NH_4^+, and SO_4^{2-}, are measured at the same plots as well as stem volume increment. The atmospheric deposition of NO_3^-, NH_4^+ and SO_4^{2-} data covers the period 1999-2010 (Waldner et al., 2014). 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 1990s. 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 were not available, they were gap-filled with ICP Forests precipitation values gained by deposition measurements where available.

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-} 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, (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 solution pH (low, <4.2, intermediate, 4.2–5, high, >5). Plots were also classified based on mean 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 mean throughfall SO_4^{2-} deposition 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

Time series can typically decomposed into random noise, seasonal, and trend components (Verbesselt et al., 2010). In this paper, we used methods to detect the actual trend (change in time) after removing the seasonal and random noise components. The sequence of methods applied is summarized in Fig. 2~~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. 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. 2~~1~~). For these models, the selected 529 time series were used. For the trend analysis of individual time series, however, we focused on the 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; Vicca et al., 2016) with the time series showing breakpoints, i.e., not monotonic, being discarded (see Description of the statistical methods in Supplementary material). In total, 258 monotonic time series from 97 plots were used for our analysis after filtering (Fig. 2~~1~~). Then, monotonic trend analyses were carried out from the filtered dataset 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. 2~~1~~).

For this study, five soil 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 (relative trend slope), aggregated to a unique plot-soil depth slope and classified by the direction of the trend as significantly positive, i.e., increasing DOC over time (P, $p < 0.05$), significantly negative, i.e., decreasing DOC over time (N, $p < 0.05$), and non-significant, i.e., no significant change in DOC over time (NS, $p \geq 0.05$). When there was more than one collector per depth interval, the median of the slopes was used when the direction of the trend (P, N, or NS) was similar. After aggregation per plot-depth combination, 191 trend slopes from 97 plots were available for analysis (Supplementary Material, Table S2). 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. Since the resulting standardized Sen slope in % yr^{-1} (relative trend slope) was used for all the statistical analysis, from here on we will use the general term “trend slope” in order to simplify.

Finally, Structural Equation Models (SEM) were performed to determine the capacity of the several factors (SO_4^{2-} and/or NO_3^- deposition, stem growth and soil solution chemistry) in explaining variability in the slope of DOC trends among the selected plots (Fig. 2~~1~~). 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.. 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 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.

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 soil solution collected with tension lysimeters was found in deep mineral soil (> 80 cm) for all sites, mainly for coniferous forest sites (Table 1), but this trend is based on a limited number of plots which are not especially well distributed in Europe (75 % of German plots). By contrast, non-significant trends were found in the other mineral soil depth intervals (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 showing breakpoints, fewer significant trends were observed: only an overall positive trend ($p < 0.05$) 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 concentration trend analysis of individual time series

We applied the BFAST analysis to select the monotonic time series in order to assure that the 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).

The individual trend analysis using the SMK test showed trend 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 1). There was, thus, no uniform trend in soil solution DOC in forests across a large part of Europe. Furthermore, the regional trend differences were inconsistent when looking at different soil depth intervals separately (Fig. 32 and 43), which made it difficult to draw firm conclusions about the spatial pattern of the trends in soil solution DOC concentrations in European forests.

The variability in trends was high, not only at continental scale, but also at plot level (Fig. 54). 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 (P, N or NS) often differed among depths. For instance, in the organic layer, we found mainly non-significant trends and, if 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 1). 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 there was no apparent difference in DOC trends between soil depths (Supplementary material, Fig. S1 and S2).

Finally, 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, Table S1).

3.3 Factors explaining the soil solution DOC trends

3.3.1 Effects of vegetation, soil and climate

There was no direct effect of forest type (broadleaved vs. coniferous) on the direction of the statistically significant trends in soil solution DOC (Fig. 65A). 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 increment below 6 $m^3\ ha^{-1}\ yr^{-1}$ over the study period, whereas decreasing DOC trends were more common in forests with a mean stem growth increment between 6 and 12 $m^3\ ha^{-1}\ yr^{-1}$ ($\chi^2(2, n = 53) = 5.8$, $p = 0.05$) (Fig. 65B). Only six forests with a mean stem growth above 12 $m^3\ ha^{-1}\ yr^{-1}$ were available for this study (five showing increasing DOC trends and one showing a decreasing DOC trend) and, thus, there is not enough information to draw conclusions about the relationship between stem growth and soil solution DOC trends for forests with very high stem growth (> 12 $m^3\ ha^{-1}\ yr^{-1}$).

The DOC trends also varied among soil types, 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 2). It is remarkable that trends in soil solution pH, Mg and Ca concentrations were similar across plots with both positive and negative DOC trends. Soil solution pH increased distinctly in almost all the sites, while Ca and Mg decreased markedly (Table 2).

Finally, no significant correlations were found between trends in temperature or precipitation and trends in soil solution DOC, with the exception of a positive correlation between trends in soil solution DOC in the soil depth interval 20-40 cm and the trend in temperature (r = 0.47, p = 0.03).

3.3.2 Effects of mean and trends in atmospheric 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 trend slopes of DOC. The Structural Equation Model accounted for 32.7% of the variance in DOC trend slopes (Fig. 7~~6~~A). According to this model, lower mean throughfall SO_4^{2-} deposition resulted in increasing trend slopes of DOC in soil solution and~~. On the other hand,~~ higher mean throughfall NO_3^- deposition resulted in increasing trend slopes of DOC (Fig. 7~~6~~A). When considering trends in SO_4^{2-} and NO_3^- deposition, there was no apparent spatial correlation with soil solution DOC trends, with deposition mainly decreasing or not changing over time (Fig. 8) and the DOC trends varying greatly across Europe (Fig. 3 and 4). However, w~~W~~hen SEM was run using the trend slopes in SO_4^{2-} and NO_3^- deposition instead of the mean values, we found that trend slopes of DOC significantly increased with increasing trend in NO_3^- and decreased with increasing trend in SO_4^{2-} deposition, but the latter was a non-significant relationship (Supplementary Material, Fig. S3). However, the percentage of variance in DOC trend slopes explained by the model was much twice lower (16%).

Sites with low and medium N deposition

The variables in the model that best explained the 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. 76B). Lower mean SO_4^{2-} deposition again resulted in a significant increase in trend slopes, while increasing NO_3^- deposition resulted in increasing DOC trend slopes. The percentage of variance in DOC trend slopes explained by the model was 33%. The SEM run 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 in DOC trends, and showed a significant increase of trend slopes of DOC with decreasing trend in SO_4^{2-} deposition (Supplementary Material, Fig. S3).

Sites with high N deposition

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. In contrast, the best model included the relative trend slopes in SO_4^{2-} and NO_3^- deposition as well as in median soil solution conductivity (% yr^{-1}) as explaining variables (Fig. 76C). Increasing the relative trend slopes of NO_3^- deposition resulted in increasing 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 in soil solution conductivity, although acting in opposite directions: while increasing NO_3^- deposition led to decreasing soil solution conductivity, increasing SO_4^{2-} deposition resulted in increasing trends in soil solution conductivity, but the latter relationship was only marginally significant ($p=0.06$). Increasing trends in conductivity, in turn, resulted in increasing trend slopes of DOC. The percentage of the variance in DOC trend slopes explained by the model was 25% (Fig. 76C). Nevertheless, trends in soil solution DOC were not directly affected by trends in SO_4^{2-} deposition in forests with high N deposition.

4 Discussion

4.1 Trend analysis of soil solution DOC in Europe

4.1.1 Evaluation of the trend analysis techniques

A substantial proportion (40%) of times series did not indicate any significant trend in 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 datasets 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. We enhanced the probability of trend detection by the SMK, PMK, and BFAST tests by removing time series with breakpoints caused by artifacts (such as installation effects).

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 (Table 1; Fig. 32). 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. Nevertheless, the selected trend analysis techniques (SMK and PMK) are the most suitable to detect weak trends (Marchetto et al., 2013; Waldner et al., 2014), thus reducing the chances of hidden trends within the non-significant trends category.

On the other hand, evaluating hundreds of time series may introduce random effects that may cause the detection of false significant trends. This multiple testing effect was controlled by evaluating the trends at a 0.01 significance level: Increasing the significance level hardly changed the number of detected significant trends (positive trends: 91 ($p<0.05$) vs. 70 ($p<0.01$); negative trends: 63 ($p<0.05$) versus 50 ($p<0.01$)). Since the detected trends at 0.01 significance level outnumbered those expected just by chance at the 0.05 level (13 out of 258 cases), it is guaranteed that the detected positive and negative trends were real and not a result of a multiple testing effect.

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 input from the canopy to the 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 lacking for the majority of Level II plots, which hinders assigning observed breakpoints to specific site conditions. The BFAST analysis allowed us to filter out time series affected by local disturbances (natural or artefacts) from the dataset and to solely retain time series with monotonic trends. By applying the breakpoint analysis, we reduced the within-plot trend variability, while most of the plots showed similar aggregated trends per plot-depth combinations (Supplementary material, Fig. S4). Thereby, we removed some of the within-plot variability 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, by selecting monotonic trends, we selected a subset of the trends for which it is more likely to relate the observed trends to environmental changes. A focus on monotonic trends does not imply that the trends with breakpoints are not interesting, 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). This level of detail is, however, not yet available for the ICP Forests Level II plots.

4.1.3 Variability in soil solution DOC trends within plots

Even after removing sites with breakpoints in the time series, within-plot trend variability remained high (median within-plot range: 3.3% yr^{-1}), with different trends observed for different collectors from the same plot (Fig. 45). 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 only when the entire dataset (with breakpoints) was analyzed. The individual trend analyses confirmed 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; Sawicka et al., 2016; Vanguelova et al., 2010). This difference has been attributed to different processes affecting DOC in the organic layer and top mineral soil 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, Fig. S1, Fig. S2).

Finally, the direction of the trends in soil solution DOC concentrations did not follow a clear regional pattern across Europe (Fig. 3~~2~~ and 4~~3~~) 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, texture) 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.

In order to compare soil solution DOC trends among sites, trends of DOC concentrations are always expressed in relative trends (% yr^{-1}). By using the relative trends, we removed the effect of the median DOC concentration at the "plot-depth" combination and, consequently, the results do not reflect the actual magnitude of the trend, but their importance in relation with the median DOC concentration at the "plot-depth" combination. It implies that the interpretation of our results was done only in relative terms (see Supplementary Material, Table S3, Fig S5).

4.2 Controls on soil solution DOC temporal trends

4.2.1 Vegetation

Biological controls on DOC production and consumption, like net primary production (NPP), 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 as a proxy for NPP only for 53 sites and was calculated as the increment between inventories carried out every five years. Similarly to what has been found for peatlands (Billett et al., 2010; Dinsmore et al., 2013), the results suggest that vegetation growth is an important driver of DOC temporal dynamics in forests.. Differences in DOC temporal trends across all soil depths were strongly related to stem growth, with more productive plots, as indicated by higher stem volume increment (6-12 m^3 ha^{-1} yr^{-1}), more often exhibiting decreasing trends in DOC (Fig. 6~~5~~ and 7~~6~~). .

The drivers of variation in forest productivity and its relationship with trends in DOC concentrations are yet unclear. Forest productivity might indirectly affect DOC trends through changes in soil solution chemistry (via cation uptake) (Vanguelova et al., 2007), but the available data do not allow to test this. Alternatively, variation in plant carbon allocation and therefore in the relationship between aboveground productivity and belowground C inputs can strongly influence the relationship between forest productivity and DOC trends. For example, nutrient availability strongly influences plant C allocation (Poorter et al., 2012; Vicca et al., 2012), with plants in nutrient rich soils investing more in aboveground tissue at the expense of belowground C allocation. Assuming that more productive forests are located in more fertile plots, the decreasing trends in DOC concentrations may result from reduced C allocation to the belowground nutrient acquisition system (Vicca et al., 2012), hence, reducing an important source of belowground DOC.

Further research assessing nutrient availability and determining the drivers of variation in forest productivity, allocation and DOC is needed to verify the role of nutrients and other factors (e.g., climate, stand age, management) in DOC trends and disentangle the mechanisms behind the effect of forest productivity on soil solution DOC trends.

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 greatly, with increases, decreases, as well as steady states being observed across respectively 56, 41 and 77 time series in European forests (Fig. 32, and 34 and 8). 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, the multivariate analysis suggested that the hypothesis of increased DOC soil solution concentration as a result of decreasing SO_4^{2-} deposition may apply only at sites with low or medium mean N deposition over the last decades.

Inorganic nitrogen

Our results show that DOC concentrations in the soil solution are positively linked to inorganic N deposition loads at sites with low or medium inorganic N deposition, and to N deposition trends at sites with high inorganic N deposition (Fig. 76). The role of atmospheric inorganic N deposition in increasing DOC leaching from soils has been well documented (Bragazza et al., 2006; Liu and Greaver, 2010; Pregitzer et al., 2004; Rosemond et al., 2015). The mechanisms behind this positive 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 inorganic 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; Liu and Greaver, 2010), can increase the final amount of DOC in the soil. As the most consistent trends are found in organic layers, where production/decomposition control DOC concentration (Löfgren and Zetterberg, 2011), effects of inorganic N deposition through increase of primary productivity (de Vries et al., 2014; de Vries et al., 2009; Ferretti et al., 2014) are likely drivers of increasing DOC trends. 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) and reduced microbial decomposition (Liu and Greaver, 2010) may lead to greater accumulation of DOC.

Moreover, our results suggested that only at sites with lower and medium inorganic N deposition, decreasing trends in SO_4^{2-} deposition coincided with increasing trends in soil solution DOC (Supplementary Material, Fig. S3), as previously hypothesized for surface waters, indicating an interaction between the inorganic N deposition loads and the mechanisms underlying the temporal change of soil solution 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, suppressing DOC solubility, thereby 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. 7~~6~~A, 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.).

Nevertheless, increasing DOC soil solution concentration as a result of decreasing SO_4^{2-} deposition occurred only at sites with low or medium mean N deposition. Therefore, our results indicate that the response of DOC to changes in atmospheric deposition seems to be controlled by the past and present inorganic N deposition loads (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 low and medium N deposition areas, as has been observed for inorganic N deposition effects (de Vries et al., 2009). In high inorganic 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, the hypothesis of recovery from acidity cannot fully explain overall soil solution DOC 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). Collinearity between SO_4^{2-} deposition and inorganic N deposition was low (variance inflation factor <3) for both the mean values and temporal trends. We therefore assumed that the proposed response of DOC to the decline in SO_4^{2-} deposition in low to medium N areas is not confounded by simultaneous changes in SO_4^{2-} and

NO_3^- deposition, even more so because the statistical models account for the covariation in SO_4^{2-} and NO_3^- deposition (Figure 7). Nonetheless, as SO_4^{2-} and NO_3^- deposition are generally decreasing across Europe (Figure 8), concomitant changes in NO_3^- deposition may still have somewhat confounded the attribution of DOC changes solely to SO_4^{2-} deposition.

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. 76). 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; Stutter et al., 2011).

In conclusion, our results confirm the long-term 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, 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). DOC from the organic layer may be transferred to surface waters via hydrologic shortcuts during storm events, when shallow lateral flow paths are activated. On the other hand, trends in different soil layers along the mineral soil were more variable and responded to other soil internal processes.

~~The results from the trend analysis for the overall European dataset revealed that the long-term trends in surface and deep soil were positive as trends reported for surface water DOC. However, the individual trend analysis reflects a high heterogeneity in the long-term response of soil DOC to environmental controls.~~ 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 (Ledesma et al., 2016; 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.

Finally, stream water DOC trends are dominantly controlled by catchment hydrology (Sebestyen et al., 2009; Stutter et al., 2011; Tranvik and Jansson, 2002), since an increase in DOC concentration does not necessarily result in increased DOC transport, which is the product of DOC concentration and discharge. Differences in hydrology among sites may (partly) explain the inconsistent patterns found in soil solution DOC concentration trends at different sites and depths, as previously proposed ~~(Sebestyen et al., 2009; Stutter et al., 2011; Tranvik and Jansson, 2002)~~(Stutter et al., 2011), but data to verify this statement are currently not available. Hence, while this study of controls on trends in DOC concentrations in soil provides key information for predictions of future C losses to stream waters, future studies at larger scale that include catchment hydrology (precipitation, runoff and drainage) are crucial to relate soil and stream DOC trends.

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. 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 low to medium N deposition areas, there was no significant relationship with SO_4^{2-} deposition in high N deposition areas. There was evidence that an overall increasing trend of DOC concentrations occurred in the organic layers and, to a lesser extent, in the deep mineral soil. However, trends in the different mineral soil horizons were highly heterogeneous, 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.

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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 median DOC concentrations in mg L^{-1} ([DOC]), relative trend 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 and the interquartile range of the rslope is between brackets. LMMs for which no statistically significant trend was detected (p>0.1) are represented in grey, the LMMs for which a significant trend is detected are in bold (p<0.05) and in italics (0.05<p<0.1). (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	[DOC]	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
			n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	47.3	3133	6.75	*0.078*	1168	-0.30	n.s.	-1.03 (±1.65)	1	3	1
	M02	12.9	19311	0.10	n.s.	8917	-1.06	n.s.	0.16 (±4.78)	17	29	21
	M24	4.93	7700	2.69	n.s.	3404	3.66	n.s.	0.6 (±9.03)	11	12	11
	M48	3.66	24614	0.95	n.s.	11065	0.80	n.s.	0.67 (±4.76)	22	30	32
	M8	3.27	9378	**6.78**	**0.0036**	3394	3.41	n.s.	1.007 (±8.79)	8	9	16
ZTL	O	37.9	8136	**3.75**	**<0.001**	4659	1.63	*0.0939*	**1.7 (±4.28)**	3	16	8
	M02	30.7	3389	-0.54	n.s.	445	0.17	n.s.	-0.7 (±1.85)	0	3	1
	M24	17.3	739	0.36	n.s.					0	0	0

	M48	4.73	654	-3.37	n.s.	336	1.05	n.s.	1.07 (±3.08)	1	2	1
	M8	3.7	118	1.39	n.s.					0	0	0

In broadleaved forests:

Collector type	Layer	[DOC]	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
			n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	41.4	637	-5.96	n.s.	475	-0.17	n.s.	-0.3 (±0.9)	0	2	0
	M02	8.80	8397	3.07	*0.0764*	3104	0.51	n.s.	0.89 (±5.94)	4	7	10
	M24	3.78	2584	-0.05	n.s.	928	6.01	n.s.	1.03 (±11.31)	3	5	4
	M48	2.60	10635	-0.93	n.s.	4634	2.46	n.s.	1.51 (±5.31)	11	8	16
	M8	2.60	4354	-6.85	*0.0672*	1797	-0.10	n.s.	0.3 (±6.28)	4	5	6
ZTL	O	33.3	4057	0.37	n.s.	1956	-0.90	n.s.	0.96 (±5.47)	2	7	3
	M02	4.26	608	0.26	n.s.	192	1.88	n.s.	2.72	0	0	1
	M24	20.4	94	**11.80**	**0.026**					0	0	0
	M48	3.42	427	-2.84	n.s.				0	0	1	0
	M8	2.42	34	**-36.18**	**<0.001**					0	0	0

In coniferous forests:

Collector type	Layer	[DOC]	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
			n	rslope	p value	n	rslope	p value	rslope	N	NS	P
TL	O	49.0	2496	8.15	*0.0633*	693	1.33	n.s.	-1.06 (±2.25)	1	1	1
	M02	15.7	10914	-0.97	n.s.	5813	-1.60	n.s.	-0.04	13	22	11

									(±3.98)			
	M24	5.72	5116	2.71	n.s.	2476	3.66	n.s.	-0.3 (±7.82)	7	7	8
	M48	4.44	13979	1.24	n.s.	6431	0.05	n.s.	0.3 (±4.32)	16	22	11
	M8	3.70	5024	**9.93**	**<0.001**	1597	7.58	n.s.	2.89 (±10.28)	4	4	10
ZTL	O	42.9	4079	**3.59**	**0.0018**	2703	**3.09**	**0.0045**	**1.85 (±2.88)**	1	9	5
	M02	36.9	2781	-0.60	n.s.	253	-1.44	n.s.	-0.83 (±0.4)	0	3	0
	M24	16.3	645	0.23	n.s.					0	0	0
	M48	44.0	227	-0.39	n.s.	251	-0.55	n.s.	2.14 (±3.66)	1	1	1
	M8	4.14	84	13.87	*0.0995*					0	0	0

Table 2. 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 from 1999 to 2010. When throughfall deposition was not available, bulk deposition is presented with an asterisk. Relative trend slopes (rslope) 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})	rslope pH (%yr^{-1})	rslope Ca^{2+} (% yr^{-1})	rslope 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	21.3	17.7	3.63	6.14	1110	6.20	16.4		0.00	-3.00	-0.40

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 ($kg S ha^{-1} yr^{-1}$)	rslope pH ($\% yr^{-1}$)	rslope Ca^{2+} ($\% yr^{-1}$)	rslope Mg^{2+} ($\% yr^{-1}$)
		Cambisol											
308	N	Albic Arenosol	3.80	16.5	3.41	1.63	816	9.20	14.2*		0.00	-5.00	-2.00
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

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})	rslope pH (%yr^{-1})	rslope Ca^{2+} (% yr^{-1})	rslope Mg^{2+} (% yr^{-1})
Austria (code = 14)													
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

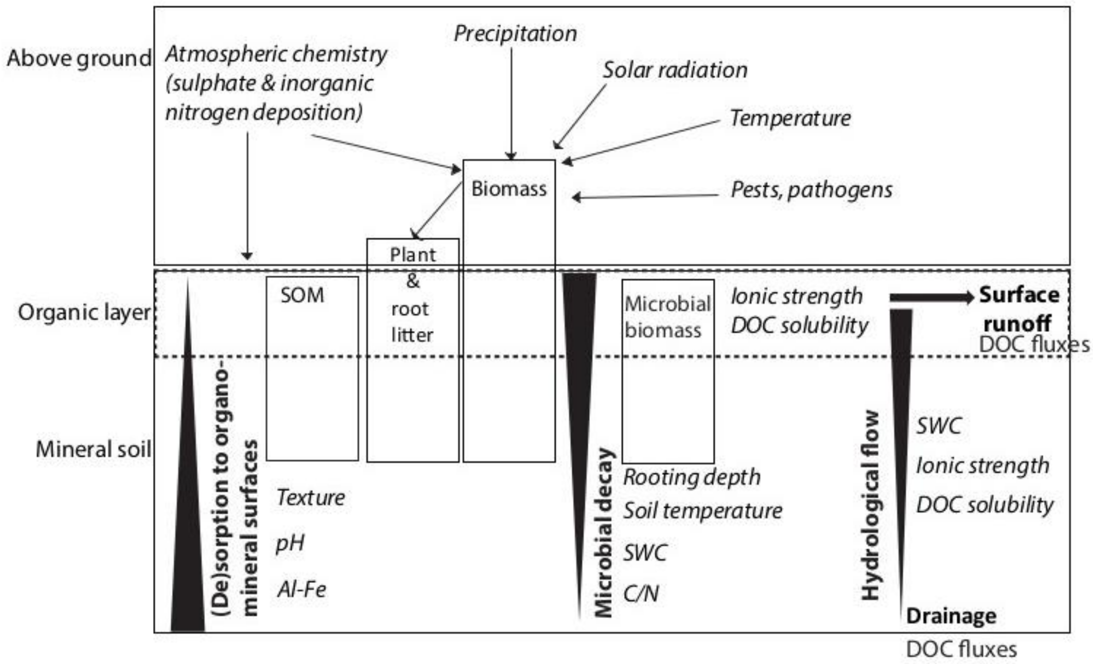
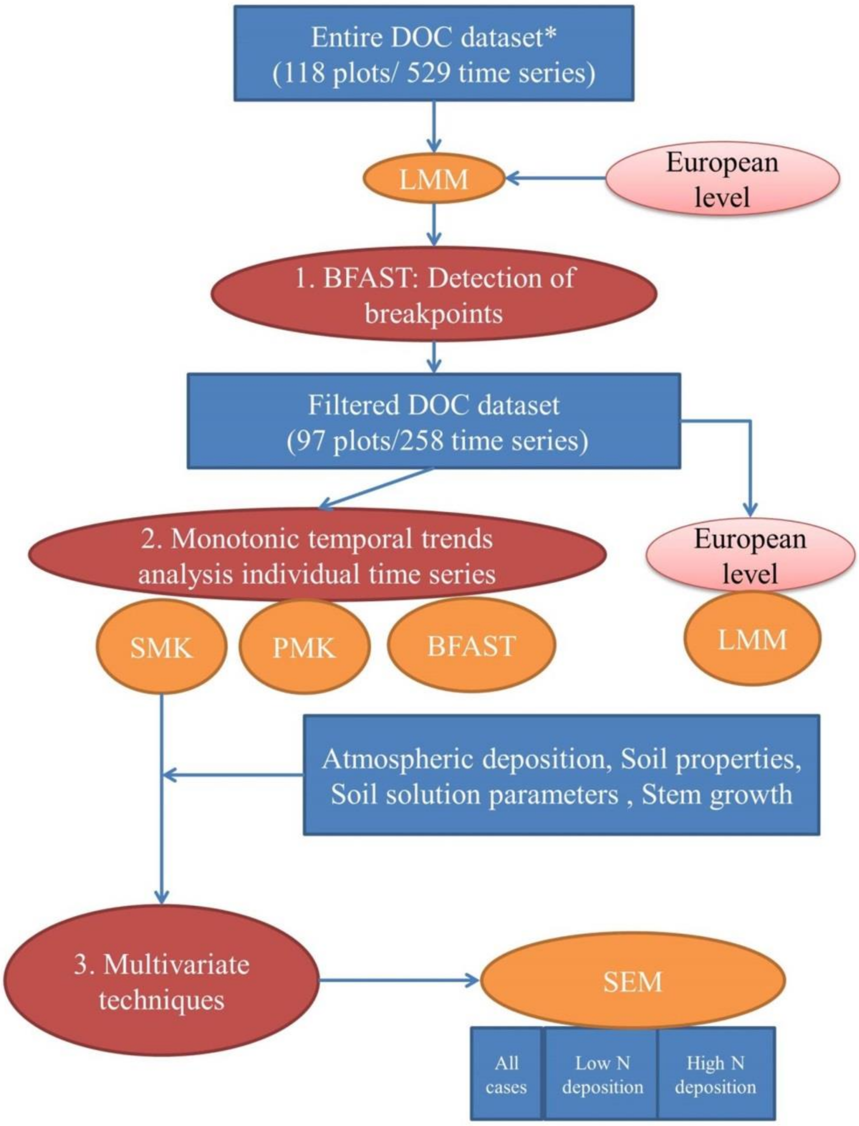


Figure 1. Schematic diagram illustrating the main sources (in boxes) of dissolved organic carbon (DOC) and the main processes (in bold) and factors (in italics) controlling DOC.



* Time series > 10 years and > 60 obs.

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
SEM	Structural equation Model	Multivariate analysis (direct/indirect effects)

Figure ~~1~~2. Flow-diagram of the sequence of methods applied for analysis of temporal trends of soil solution DOC and their drivers.

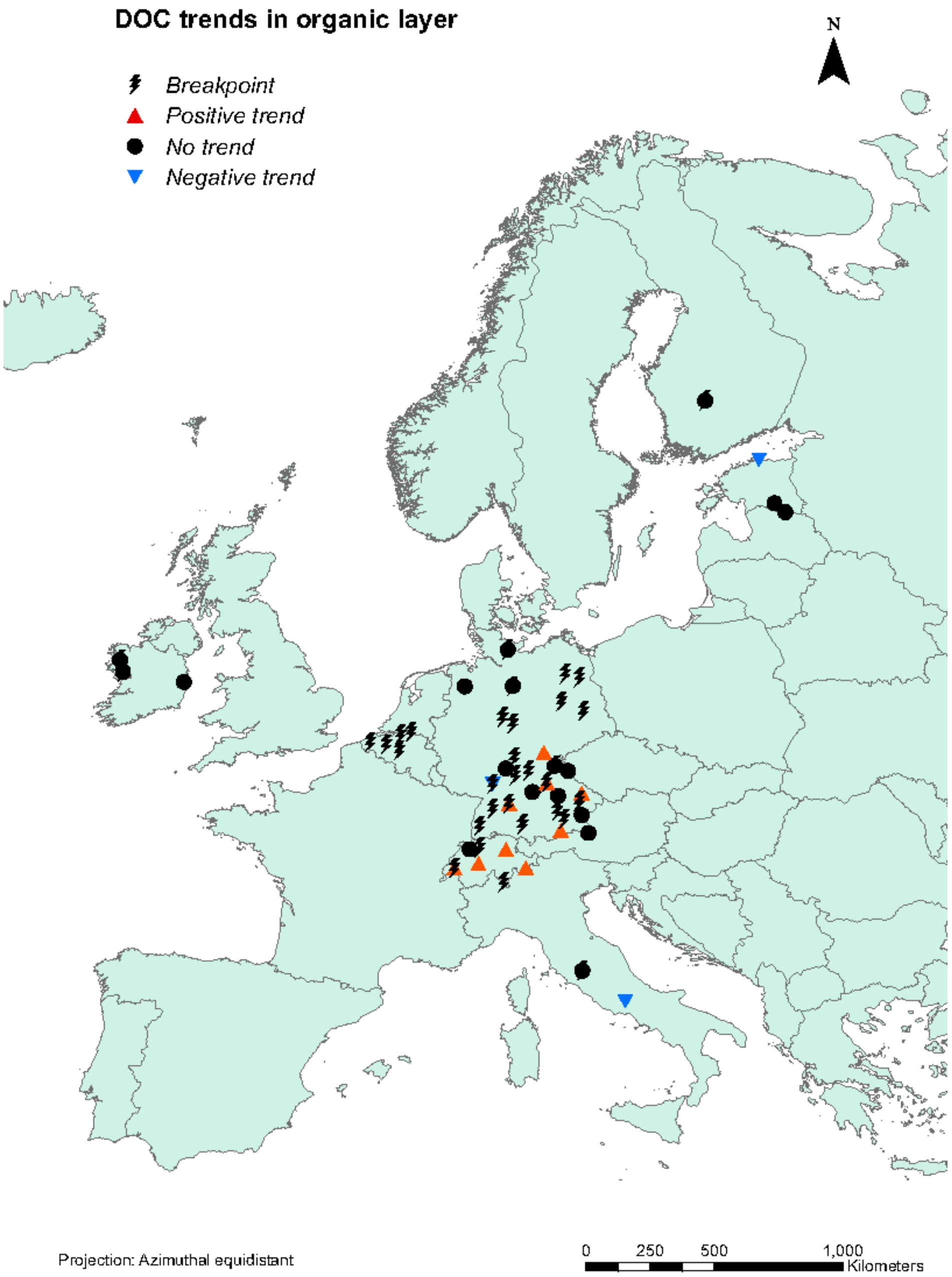


Figure 3~~2~~. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

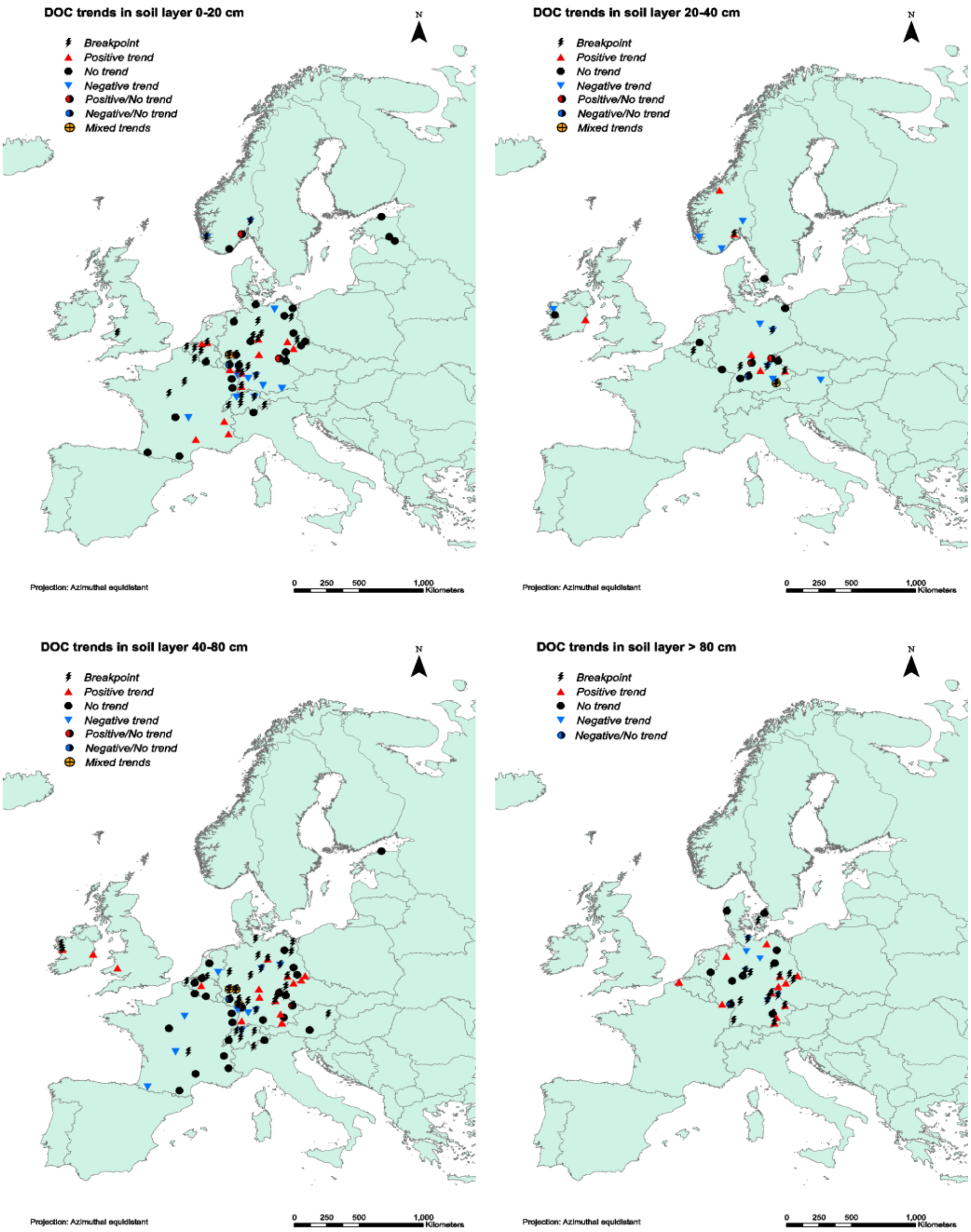


Figure 43. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0–20 cm), b) intermediate (20–40 cm), c) subsoil (40–80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

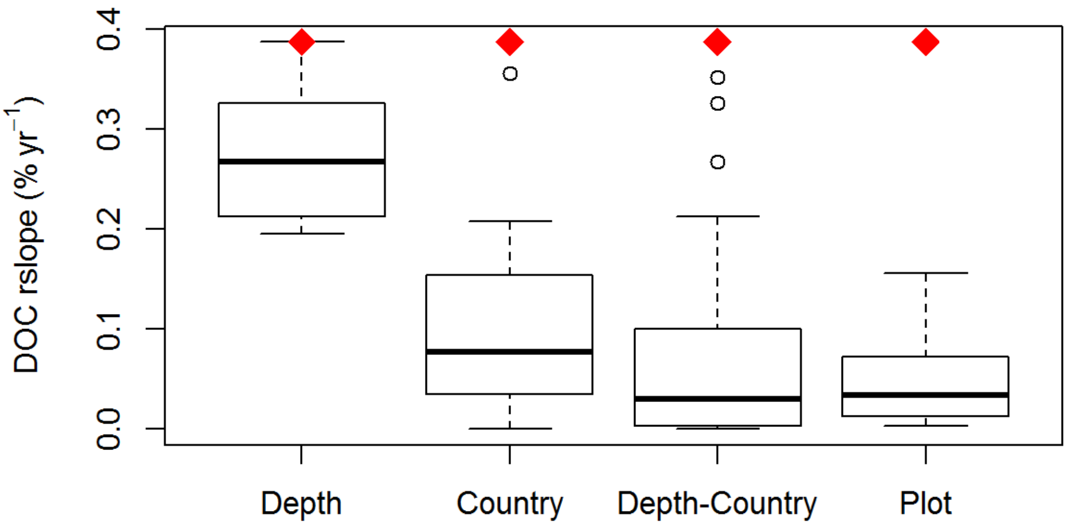


Figure 54. Range of relative trend slopes (max-min) for trends of DOC concentration in soil solution within each 1) depth interval, 2) country, 3) depth interval per country, and 4) plot. The boxplots show the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers) and higher values (circles). The red diamond marks the maximum range of slopes in soil solution DOC trends in the entire dataset.

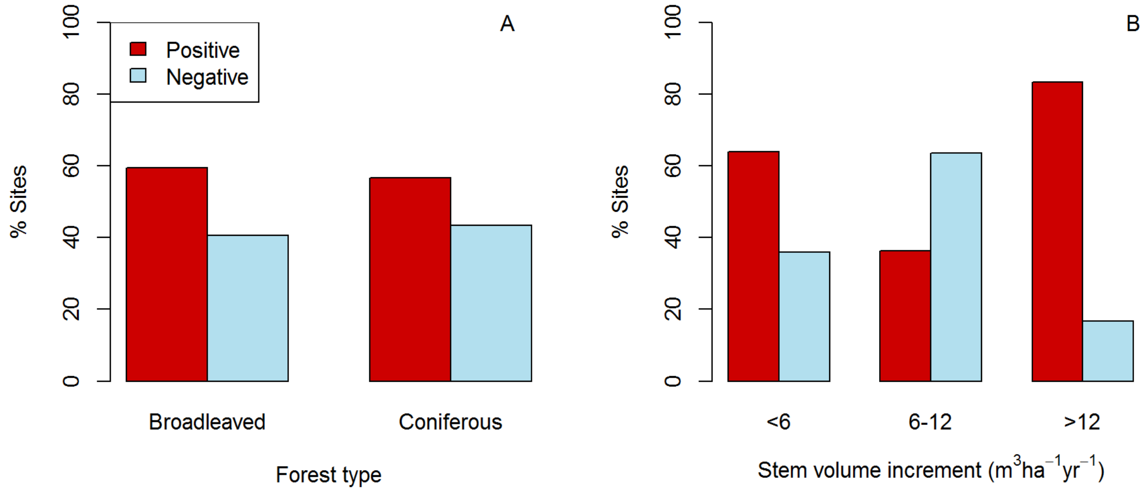


Figure 65. Percentage of occurrence of positive and negative trends of DOC concentration in soil solution separated by A) forest type and B) stem volume increment (m^3 ha^{-1} yr^{-1}).

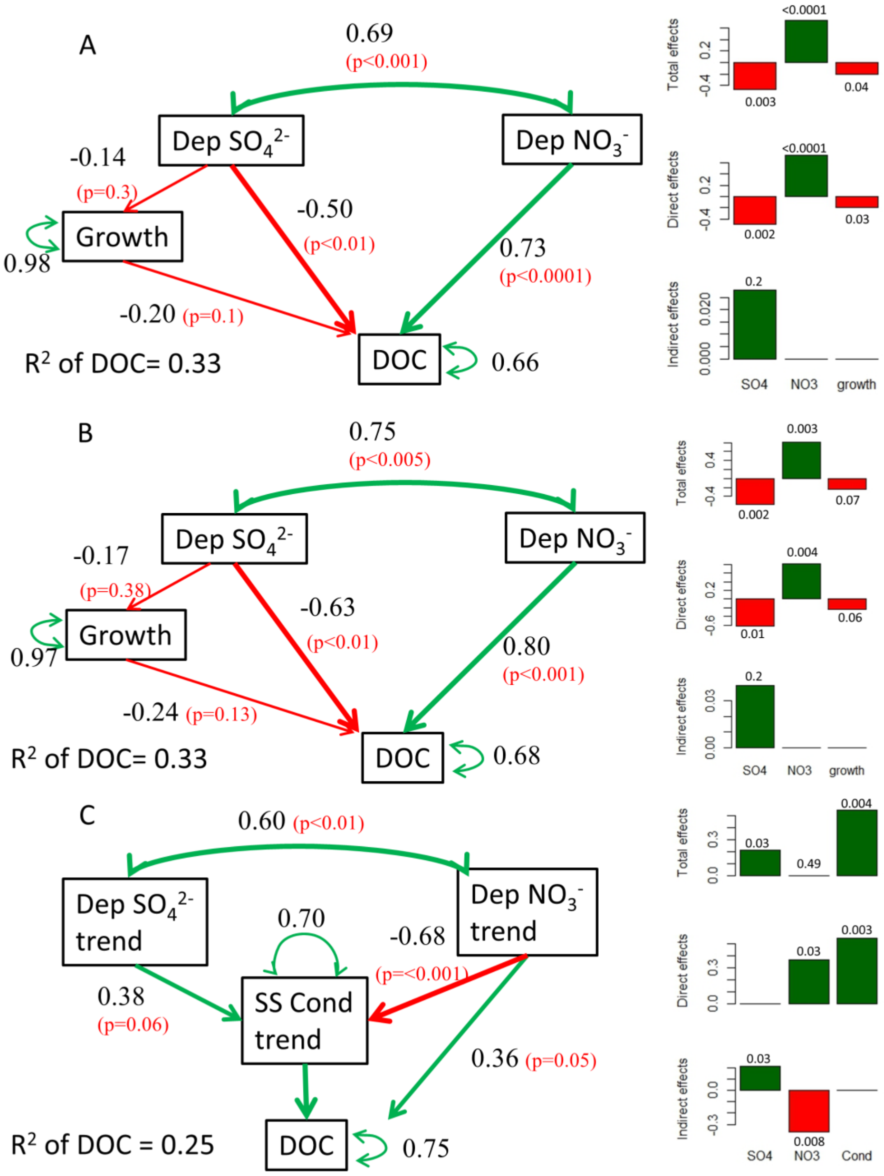


Figure 7~~6~~. Diagrams of the structural equation models (SEM) that best explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium throughfall inorganic N deposition (< 15 kg N ha^{-1} yr^{-1}), and C) cases with high throughfall inorganic N deposition (>15 kg N ha^{-1} yr^{-1}) 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^{-1}) 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-values.

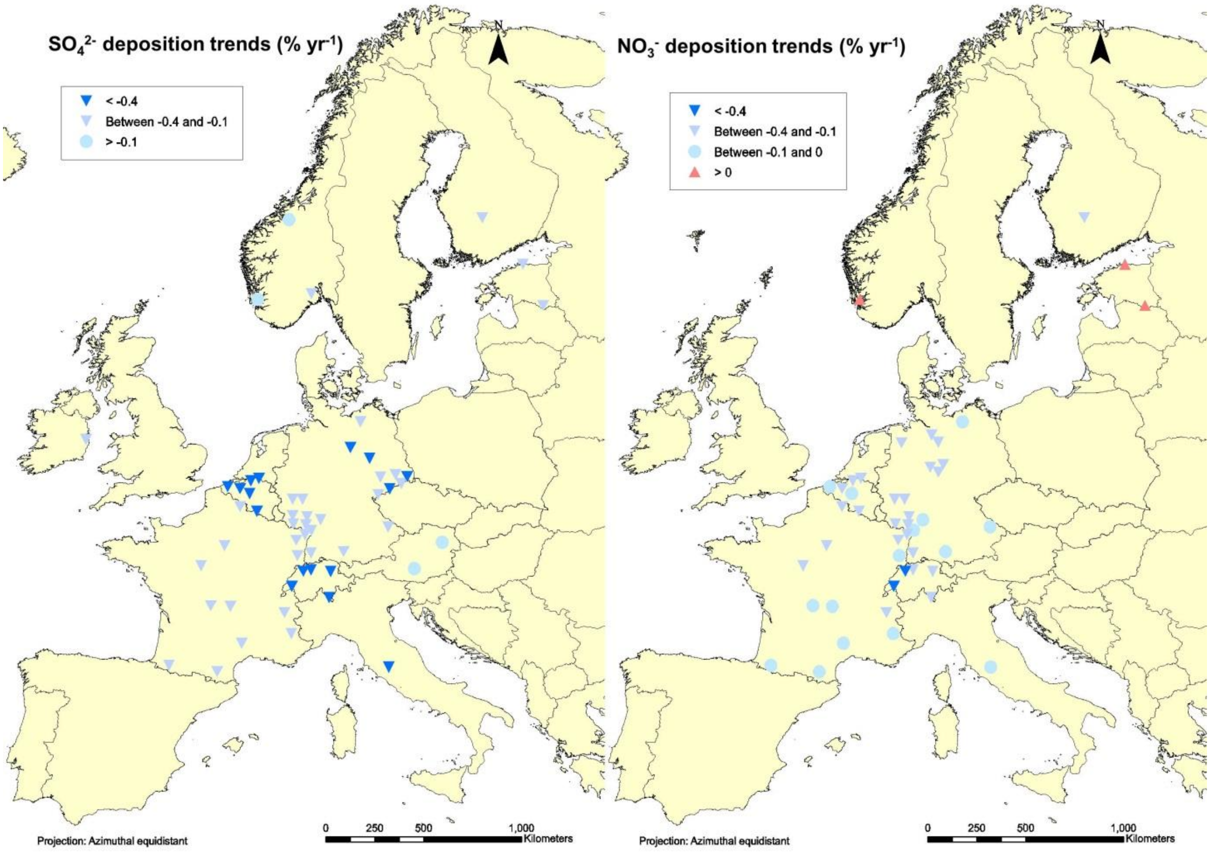


Figure 8. Temporal trends in a) throughfall SO_4^{2-} deposition and b) throughfall NO_3^- deposition at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1999 to 2010.

Supplementary material for

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

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ICP Forests Level II plots data used for the trend analysis

Table S1. List of ICP Forests Level II plots used for the trend analysis and their dominant forest species and resulting trend calculated using the Seasonal Mann-Kendall test (NS; non-significant, P: positive, N: negative). Rows in green correspond to the plots where at least one time series has been used for the individual trend analysis after filtering out the breakpoints. Rows in red correspond to the plots with measurements of DOC in soil solution that have not been used for the individual trend analysis because there was not enough data (Lack data) or breakpoints were detected (BP). Collector types are tension lysimeters (TL) or zero-tension lysimeters (ZTL).

Country	Code plot	Start year	End year	Collector type	Tree species	Trend	Dilution effect
France	1_6	1998	2011	TL	*Quercus robur*	NS	
France	1_17	1998	2011	TL	*Quercus petraea*	NS	
France	1_30	1998	2011	TL	*Quercus petraea*	N	
France	1_37	1998	2011	TL	*Picea abies*	NS	
France	1_41	1998	2011	TL	*Picea abies*	N	
France	1_46	1998	2011	TL	*Picea abies*	NS/N	
France	1_57	1998	2011	ZTL	*Fagus sylvatica*	P/NS	
France	1_63	1998	2011	TL	*Fagus sylvatica*	NS/N	
France	1_84	1998	2011	TL	*Pinus sylvestris*	N	
France	1_90	1998	2011	TL	*Abies alba*	NS/P	depth= -0.2, coll=1
France	1_93	1998	2011	TL	*Abies alba*	NS	
France	1_96	1998	2011	TL	*Abies alba*	P/NS	
France	1_98	1998	2011	TL	*Abies alba*	NS	
France	1_100	1998	2011	TL	*Abies alba*	NS	
Belgium	2_1	2000	2005		*Picea abies*	Lack data	
Belgium	2_8				*Quercus petraea*	Lack data	
Belgium	2_11	1999	2011	ZTL/TL	*Fagus sylvatica*	P	
Belgium	2_14	1999	2011	ZTL/TL	*Pinus nigra*	NS/P	
Belgium	2_15	1999	2011	ZTL/TL	*Pinus sylvestris*	NS/P	
Belgium	2_16	1999	2011	ZTL/TL	*Quercus robur*	NS	

Belgium	2_21	1999	2011	ZTL/TL	*Fagus sylvatica*	P	
Germany	4_101	1996	2011	TL	*Fagus sylvatica*	NS/N	
Germany	4_301	1997	2011	TL	*Fagus sylvatica*	NS	
Germany	4_302	1997	2011		*Picea abies*	BP	
Germany	4_303	1998	2011	TL	*Picea abies*	N	
Germany	4_304	1998	2011	TL	*Fagus sylvatica*	N	
Germany	4_305	1998	2011		*Picea abies*	BP	
Germany	4_306	1996	2011	TL	*Fagus sylvatica*	P	
Germany	4_307	1996	2011	TL	*Pinus sylvestris*	NS/P	depth=-2.5, coll=3
Germany	4_308	1993	2011	TL	*Quercus robur*	N	
Germany	4_502	1998	2011	TL	*Quercus robur*	N/NS	
Germany	4_503	1997	2011		*Fagus sylvatica*	BP	
Germany	4_506	1997	2011	TL	*Picea abies*	NS	
Germany	4_603	1998	2005		*Fagus sylvatica*	Lack data	
Germany	4_604	1998	2001		*Fagus sylvatica*	Lack data	
Germany	4_605	1998	2005		*Fagus sylvatica*	Lack data	
Germany	4_606	1996	2011	TL	*Fagus sylvatica*	NS	
Germany	4_607	1998	2010		*Fagus sylvatica*	Lack data	
Germany	4_701	1996	2011	TL	*Picea abies*	Weight_	
Germany	4_702	1996	2011	TL	*Picea abies*		
Germany	4_703	1996	2011	TL	*Fagus sylvatica*	NS/P	
Germany	4_704	1996	2011	TL	*Fagus sylvatica*	Weight_P	
Germany	4_705	1996	2011	TL	*Quercus petraea*	N/Weight_N	
Germany	4_706	1996	2011	TL	*Quercus robur*	P/Weight_P	
Germany	4_707	1996	2011	TL	*Pinus sylvestris*	P	
Germany	4_802	1997	2011	TL	*Picea abies*	N	
Germany	4_806	1997	2011	TL	*Picea abies*	P	
Germany	4_808	1997	2011	TL	*Picea abies*	N/NS	
Germany	4_809	1997	2010	TL	*Picea abies*	N/NS	

Germany	4_812	1997	2011	TL	*Picea abies*	P/N/Weight_N	
Germany	4_901	1996	2011	ZTL/TL	*Pinus sylvestris*	P/N	
Germany	4_902	1996	2011	ZTL/TL	*Picea abies*	NS	
Germany	4_903	1998	2011	ZTL/TL	*Fagus sylvatica*	P	
Germany	4_904	1996	2011	ZTL/TL	*Larix decidua*	NS	
Germany	4_905	1996	2011	ZTL/TL	*Pinus sylvestris*	P/NS	
Germany	4_906	1996	2011	ZTL/TL	*Picea abies*	NS/P	
Germany	4_907	1996	2006		*Fagus sylvatica*	Lack data/BP	
Germany	4_908	1996	2011	ZTL/TL	*Picea abies*	NS/N	
Germany	4_909	1996	2011	ZTL/TL	*Picea abies*	NS/Weight_P/P	depth=-1.2, coll=15
Germany	4_910	1996	2006		*Quercus robur*	Lack data/BP	
Germany	4_911	1996	2011	ZTL/TL	*Fagus sylvatica*	P/Weight_P	
Germany	4_912	1996	2006		*Pinus sylvestris*	Lack data/BP	
Germany	4_913	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4_914	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4_915	1996	2006		*Fagus sylvatica*	Lack data	
Germany	4_916	1996	2006		*Picea abies*	Lack data	
Germany	4_917	1996	2006		*Picea abies*	Lack data	
Germany	4_918	1996	2006		*Pinus sylvestris*	Lack data	
Germany	4_919	1996	2011	ZTL/TL	*Fagus sylvatica*	N/P/NS	
Germany	4_920	1998	2011	ZTL/TL	*Picea abies*	P	
Germany	4_921	1997	2011	ZTL/TL	*Quercus petraea*	P/Weight_P	
Germany	4_922	1997	2011	ZTL/TL	*Picea abies*	P/N	depth=-0.5, coll=6
Germany	4_1001	1998	2011	TL	*Quercus robur*	P/NS	
Germany	4_1201	2001	2007		*Pinus sylvestris*	Lack data	
Germany	4_1202	2001	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1203	2000	2011		*Pinus sylvestris*	BP	

Germany	4_1204	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1205	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1206	2000	2007		*Pinus sylvestris*	Lack data	
Germany	4_1302	1998	2011	TL	*Fagus sylvatica*	N/P	
Germany	4_1303	1997	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1401	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1402	1996	2012	TL	*Picea abies*	P	
Germany	4_1403	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1404	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1405	1996	2012	TL	*Pinus sylvestris*	NS	
Germany	4_1406	1996	2011	TL	*Quercus petraea*	P	
Germany	4_1501	1998	2011	TL	*Pinus sylvestris*	N/P	
Germany	4_1502	1998	2011	TL	*Pinus sylvestris*	N	
Germany	4_1605	2007	2011		*Picea abies*	Lack data	
Germany	4_1606	2007	2011		*Fagus sylvatica*	Lack data	
Germany	4_1607	2007	2011		*Pinus sylvestris*	Lack data	
Germany	4_1608				*Quercus petraea*	Lack data	
Germany	4_1609				*Abies alba*	Lack data	
Italy	5_1	1999	2011	ZTL	*Fagus sylvatica*	N	
Italy	5_9	1999	2011	ZTL	*Quercus cerris*	NS	
UK	6_512	2004	2011		*Quercus robur*	Lack data	
UK	6_517	2002	2010		*Quercus robur*	Lack data	
UK	6_715	2002	2011	TL	*Pinus sylvestris*	NS	
UK	6_716	2002	2009		*Pinus sylvestris*	Lack data	
UK	6_919	2004	2011		*Picea sichensis*	Lack data	
UK	6_920				*Picea sichensis*	Lack data	

UK	6_922	1997	2011	TL	*Picea sichensis*	P	
Ireland	7_1	1991	2000	ZTL/TL	*Picea sichensis*	P/NS	
Ireland	7_10	1991	2011	ZTL and others/ TL	*Picea sichensis*	NS/P	
Ireland	7_11	1991	2011	ZTL/TL	*Quercus petraea*	N/NS	
Denmark	8_11	1996	2011	TL	*Picea abies*	NS	
Denmark	8_34	1997	2011	TL	*Fagus sylvatica*	NS	
Denmark	8_74	2002	2012		*Fagus sylvatica*	Lack data/BP	
Denmark	8_85	2003	2011		*Quercus robur*	Lack data	
Greece	9_3					Lack data	
Greece	9_4					Lack data	
Sweden	13_1301	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_1403	1996	2006		*Picea abies*	Lack data	
Sweden	13_5201	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5202	1996	2006		*Picea abies*	Lack data	
Sweden	13_5401	1996	2006		*Picea abies*	Lack data	
Sweden	13_5501	1996	2006		*Picea abies*	Lack data	
Sweden	13_5502	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5601	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5602	1996	2006		*Picea abies*	Lack data	
Sweden	13_5603	1996	2006		*Picea abies*	Lack data	
Sweden	13_5701	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5702	1996	2006		*Picea abies*	Lack data	
Sweden	13_5703	1996	2006		*Picea abies*	Lack data	
Sweden	13_5801	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6001	1996	2006		*Fagus sylvatica*	Lack data	

Sweden	13_6002	1996	2006		*Quercus robur*	Lack data	
Sweden	13_6003	1996	2006		*Picea abies*	Lack data	
Sweden	13_6102	1996	2006		*Fagus sylvatica*	Lack data	
Sweden	13_6103	1996	2006		*Picea abies*	Lack data	
Sweden	13_6301	2000	2006		*Fagus sylvatica*	Lack data	
Sweden	13_6302	1996	2006		*Picea abies*	Lack data	
Sweden	13_6401	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6501	1996	2006		*Picea abies*	Lack data	
Sweden	13_6503	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6507	1996	2006		*Picea abies*	Lack data	
Sweden	13_6601	1996	2006		*Picea abies*	Lack data	
Sweden	13_6702	1996	2006		*Picea abies*	Lack data	
Sweden	13_6703	1996	2006		*Picea abies*	Lack data	
Sweden	13_6802	1996	2006		*Picea abies*	Lack data	
Sweden	13_6803	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6901	1996	2006		*Picea abies*	Lack data	
Sweden	13_7402	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_7404	1996	2006		*Picea abies*	Lack data	
Sweden	13_7501	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_7502	1996	2006		*Picea abies*	Lack data	
Austria	14_9	1997	2010	TL	*Fagus sylvatica*	N	
Austria	14_16	2001	2010	TL	*Picea abies*	NS	
Finland	15_1	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_3	1998	2011		*Picea abies*	Lack data	
Finland	15_5	1997	2011		*Picea abies*	Lack data	
Finland	15_6	1997	2011		*Pinus sylvestris*	Lack data	
Finland	15_11	1997	2011	ZTL	*Picea abies*	NS	

Finland	15_16	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_17	1998	2011		*Picea abies*	Lack data	
Finland	15_19	1999	2011		*Picea abies*	Lack data	
Finland	15_20	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_21	2000	2010		*Picea abies*	Lack data	
Finland	15_23	1998	2010		*Picea abies*	Lack data	
Switzerland	50_2	1999	2012	ZTL/TL	*Picea abies*	P	
Switzerland	50_3	1999	2012	Mix collector type one	*Fagus sylvatica*	N/NS	
Switzerland	50_4	1999	2011	ZTL/TL	*Pinus cembra*	NS/P	
Switzerland	50_8	1999	2012	ZTL/TL	*Fagus sylvatica*	NS/P	
Switzerland	50_12	1999	2012	ZTL/TL	*Quercus cerris*	NS	
Switzerland	50_15	1999	2011	ZTL/TL	*Abies alba*	N	
Switzerland	50_16	1999	2012	Mix collector type one	*Fagus sylvatica*	N/P	
Norway	55_1	1996	2011	ZTL/TL	*Picea abies*	NS/N	
Norway	55_9	1996	2011	TL	*Picea abies*	P/Weight_P	
Norway	55_14	1996	2011	TL	*Picea abies*	N	
Norway	55_18	1999	2010	TL	*Pinus sylvestris*	P	
Norway	55_19	1998	2011	TL	*Picea abies*	N	
Czech Republic	58_521	2006	2011		*Picea abies*	Lack data	
Czech Republic	58_2015	2006	2011		*Fagus sylvatica*	Lack data	
Czech Republic	58_2361	2006	2011		*Quercus fruticosa*	Lack data	
Estonia	59_2	1999	2011	ZTL	*Pinus sylvestris*	NS/N	
Estonia	59_3	1999	2011	ZTL	*Pinus sylvestris*	NS	
Estonia	59_7	2002	2011	ZTL	*Pinus sylvestris*	NS	

Description of the statistical methods

1) Overall trend analysis at European scale

Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution DOC concentrations at the European scale. For these models, the complete ICP Forests Level II dataset was used. Because the dependent variable (DOC concentration) was usually not normally distributed, it was log-transformed to improve normality. Different models were built per depth and per collector type (tension or zero-tension lysimeters). For each model, the variable describing the temporal effect was the year, centered on the year 2000 (year-2000), which was considered as fixed effect. Also, month (1-12) was considered as fixed effect to account for seasonality. Two random factors describing the country ($ctry_{int}$) and plot ($plot_{int}$) effects and one random coefficient accounting for the between plot variation of the temporal effect ($plot_{slp}$) were considered in each LMM (Equation 1). The LMMs were further adjusted by stratification of data according to forest type in order to investigate possible differences in DOC trends between broadleaved and coniferous forests. The models were built following Jonard et al. (2015).

$$logDOC = \left[a + month + ctry_{int}\,(0, \sigma_{ci}^2) + plot_{int}(0, \sigma_{pi}^2)\right] + \left[b + plot_{slp}(0, \sigma_{ps}^2)\ \right] \cdot (year - 2000) + \varepsilon(0, \sigma^2) \qquad (1)$$

where σ_{ci}^2, σ_{pi}^2, σ_{ps}^2 and σ^2 are the variances of the random factors 'country' and 'plot', of the random coefficient 'plot' and of the residual term (ε), respectively.

2) Trend analysis of individual time series

Temporal changes in terrestrial ecosystems can either be monotonic changes, or discontinuous with abrupt changes resulting in breakpoints (de Jong et al., 2013). Monotonicity of time series is generally assumed when analyzing DOC data for temporal trends (Filella and Rodriguez-Murillo, 2014). However, it is rarely statistically tested and, thus, potential abrupt changes in the time series may be overlooked. This issue becomes important in temporal trend analysis since a breakpoint may cause changes in the direction of the trend and could lead us, for example, to classify a time series as constant, when in reality we may have averaged out separate periods with significant changes (de Jong et al., 2013). On the other hand, breakpoints may erroneously induce the detection of a significant trend in long-term time series due to artifacts.

For these reasons, 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). When a breakpoint was detected in a time series, there were two possibilities: first, one of the segments (before or after the detected breakpoint) was longer than 9 years, and, in this case, only the longest segment was used for the subsequent analysis of monotonic trends; second, the breakpoint split the time series in two segments shorter than 9 years and then the time series was not used for the analysis of monotonic trends. We used a length threshold of 9 years, which is the minimum time series length recommended for long-term trend analysis (Libiseller and Grimvall, 2002; Waldner et al., 2014). In total, 258 time series from 97 plots were selected for analysis of monotonic trends (Table S2). No clear pattern could be observed in the distribution of time series of DOC with breakpoints, which appeared to occur randomly across the study plots (Figs. 3 and 4).

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) test was also used to test the influence of monthly precipitation as a co-variable, i.e., to test if the trend detection might be due to a DOC dilution/concentration effect (Libiseller and Grimvall, 2002). For the SMK and PMK tests, the trend slopes were estimated following Sen (1968), as the median of all the slopes determined by all pairs of sample points. The SMK and PMK account for seasonality of the time series by computing the test on each of the seasons (in our case months) separately. The resulting slopes were also tested against the slopes calculated by BFAST. Finally, the individual slopes calculated according to Sen (1968) for each time series using the SMK or PMK method were standardized by dividing them by the median DOC concentration over the sampling period to avoid the influence of the magnitude of DOC concentration in the between-site comparison. The resulting standardized slopes (relative slopes) were used for the subsequent statistical analysis.

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 then aggregated to a unique slope per depth interval in each plot (hereafter called “plot-soil depth combination”) and classified by the direction of the trend as significantly positive (P, $p < 0.05$), significantly negative (N, $p < 0.05$) and not significant

(NS, $p \geq 0.05$). When there was more than one collector per depth class, 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". The five plot-soil depth combinations for which the calculated slopes showed opposite trend directions were discarded. All aggregated trend slopes came from time series measured using the same collector type. After aggregation per plot-depth combinations, 191 trend slopes from 97 plots were available for analysis (Table S2).

Trends for soil solution parameters (NO_3^-, Ca, Mg, 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: individual time series were analyzed using the SMK test and the relative slopes were calculated and aggregated to plot-soil depth combinations.

Finally, we performed a multivariate statistical analysis to investigate the main factors explaining differences in DOC trends among the selected plots. We applied Structural Equation Models (SEM) to test whether deposition variables had an effect (direct, indirect or total) on the relative trends slopes of DOC through different pathways (Grace et al., 2010). For the SEMs, we assumed that there is no effect of soil depth on the DOC trends (see next section in Supplementary Material). We applied three SEM models: 1) for all the slopes in DOC, 2) only for the forests with low or medium total N deposition, and, 3) only for the forests with high total N deposition. For each case, we searched for the most parsimonious adequate model using the Akaike information criterion (AIC) and R^2. The significance level (*p* value) of the total, direct and indirect effects were calculated using the bootstrap (with 1200 repetitions) technique (Davison et al., 1986). Dependent variables were log-transformed to improve normality of the continuous variables and then standardized before performing the SEMs. 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 LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA).

Table S2. Summary of number of time series used in the study

	Entire dataset	Without breakpoints
All time series	1480 (173 plots)	--

Time series >60 observations and > 10 years	529	258
Aggregated plot-depth combinations	436	191
Plots	118	97

Depth effect on the individual trends in soil solution DOC

Trends in soil solution from different soil depth intervals were mixed for the Pearson's chi-squared test performed for Fig. 5 and the Structural Equation Models (SEM) (Fig. 6), as the number of cases available for each depth are insufficient to compute the statistics if we separate per soil depth interval. To check if the trends calculated at different depths were actually independent from the soil depth interval, we performed a Pearson's chi-squared test and found that the differences in trends among soil depth intervals were not statistically significant $\chi^2(8, N = 174) = 10.94$, $p = 0.21$) (Fig. S1). Therefore, we assumed that there is no difference in trends among soil depth layers and performed the subsequent statistical analysis mixing the trends from different soil depths.

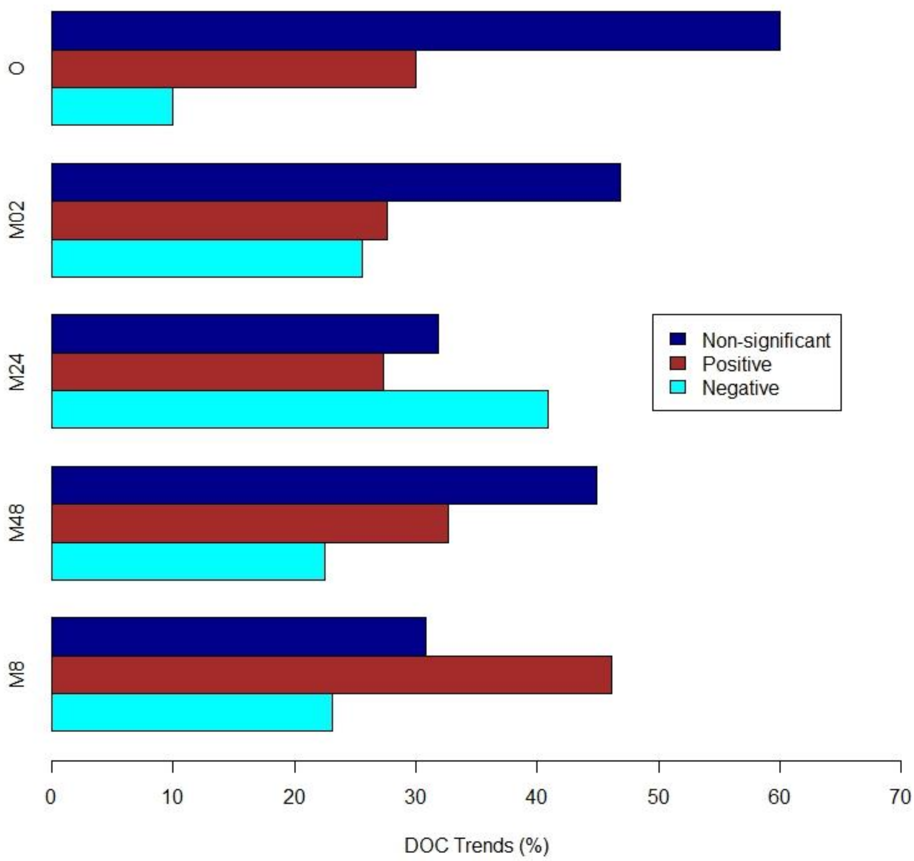

Figure S1. Percentage of non-significant, positive and negative trends per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm).

However, a real difference in DOC trends between soil depths may be obscured by the fact that datasets differ between different depths (not all the sites have DOC time series that could be analyzed for trends at all the soil depth intervals) and thus, we cannot rule out that there exists a difference in trends per soil depth. Although the number of sites with DOC trends analyzed at more than three soil depths (including the organic layer) is not enough to apply the same statistics for this subset, we visually compared the 11 sites with this information available and found that, at first sight, it was confirmed that there is no a real difference in trends between soil depth intervals (Fig. S2).

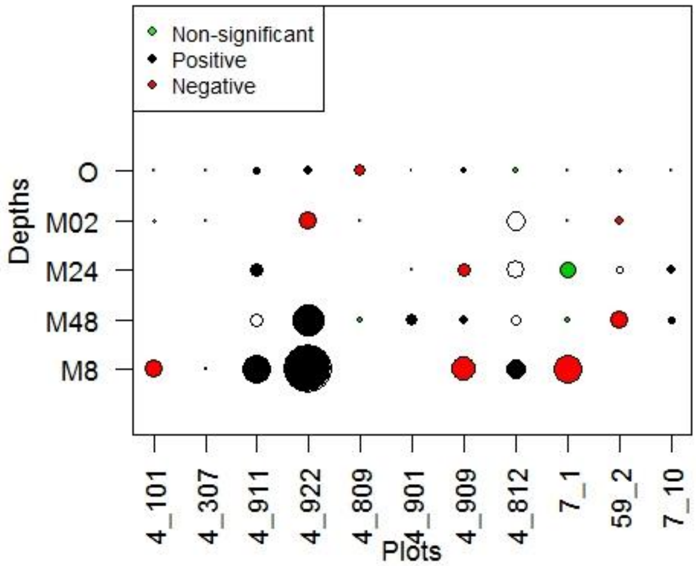

Figure S2. Direction of the trend (non-significant, positive and negative) per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm) for the 11 plots with DOC measured at least at 3 soil depth intervals including the organic layer. The size of the circle is proportional to the magnitude of the trend slope.

Structural equation model with trends in SO_4^{2-} and NO_3^- deposition

The same structural equation models (SEM) represented in Fig. 6 were performed using the trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) instead of the mean values of SO_4^{2-} and NO_3^- throughfall deposition (kg ha^{-1} yr^{-1}). The SEMs for all the cases and for cases with low and medium inorganic N deposition are shown in Fig. S3.

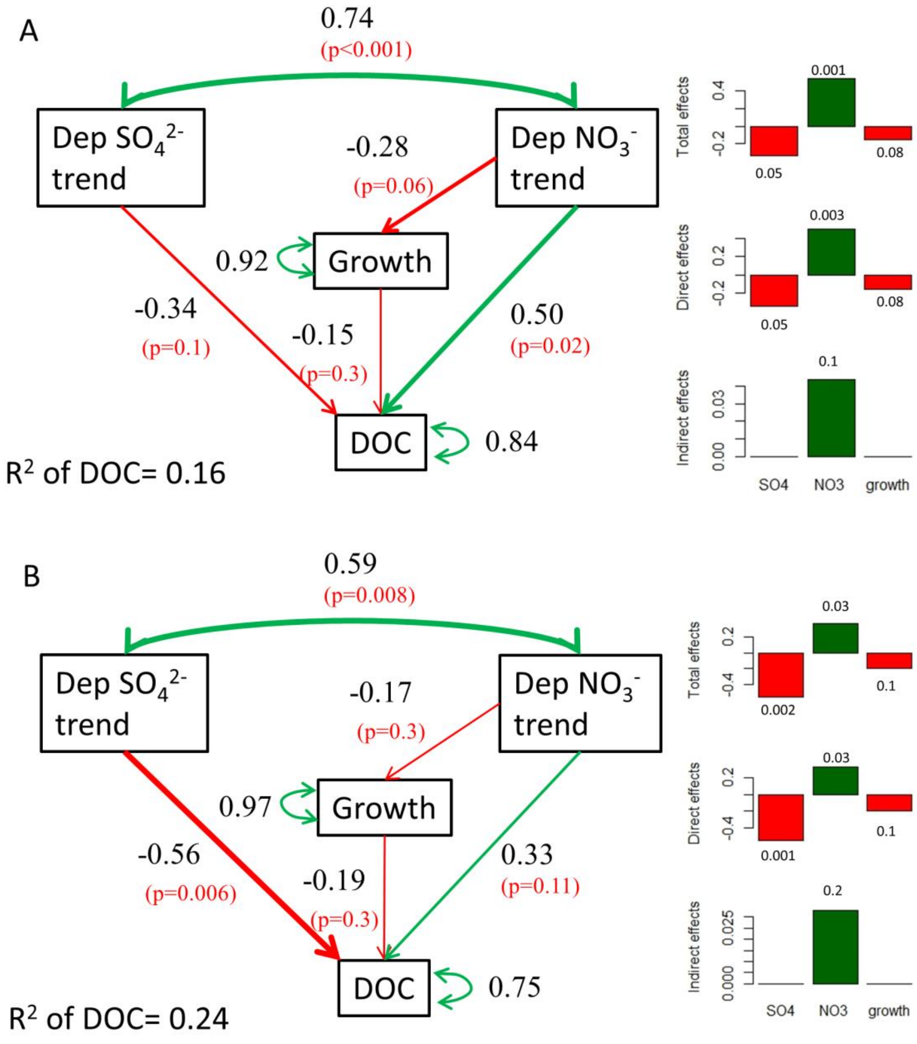

Figure S3. Diagram of the structural equation model (SEM) that best explains the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases and B) cases with low or medium inorganic N deposition, with trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) with direct effects and indirect effects through effects on mean annual stem volume increment (growth) in m^3 ha^{-1} yr^{-1}). P-values of the significance of the corresponding effect between brackets. Green arrows indicate positive effects and red arrows indicate negative effects.

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. S4). 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 in this paper correspond only to the trends of monotonic (breakpoint filtered) time series of soil solution DOC concentrations.

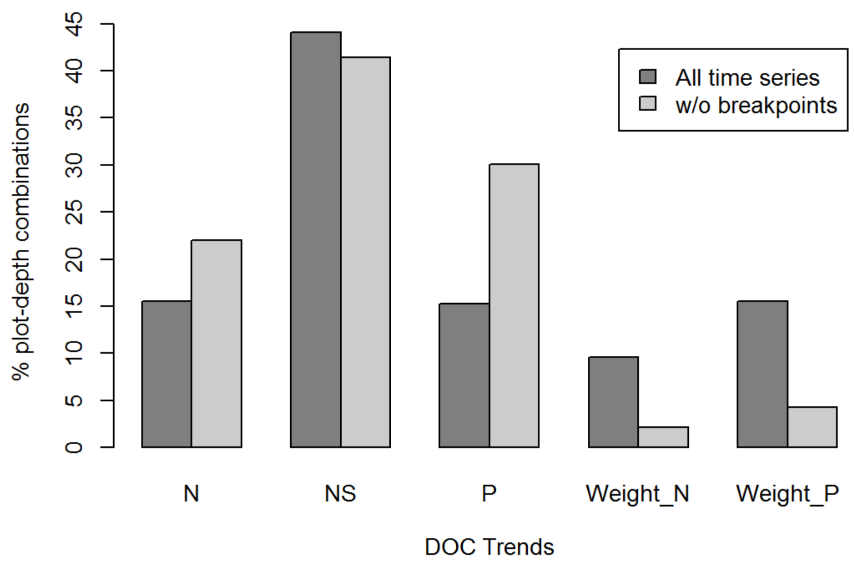

Figure S4. Percentage of plot-soil depth combinations for which negative (N), non-significant (NS), positive (P), negative and non-significant (Weight_N) and positive and non-significant (Weight_P) trends of DOC concentrations were found using SMK (seasonal Mann-Kendall) tests when 1) all the 436 time series were used, 2) only 191 time series without breakpoints (detected using the BFAST (*Breaks For Additive Seasonal and Trend*) analysis) were used.

There was a good agreement between results using the three methods: BFAST, SMK, and PMK. 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. The direction of the trend for SMK and PMK only differed for the intermediate soil layer (20-40 cm), as a result of the two extra sites for which SMK tests were performed, but not the PMK, that showed a marked positive trend (1.1 and 2 % yr^{-1}). However, when using exactly the same set of sites, the trend did not differ between the two methods.

Implications of using standardized DOC slopes versus absolute DOC slopes.

The standardized (relative) slopes of DOC concentrations were used for the study of the factors affecting the soil solution DOC trends (Fig. 5 and 6). The main reason for this decision was that using the median DOC concentration as a reference (as we did with the standardization) allowed us to determine whether the absolute trend in DOC was quantitatively large or not from an ecological perspective, because the absolute trend slope will be highly dependent on the initial DOC concentrations of the site.

The absolute trend slopes show the real magnitude and significance of the trend, but do not allow for comparison among sites or horizons. Since the aim of this study is to test whether there is a general DOC trend and to compare sites across Europe, we decided that using the relative slope was more consistent.

Moreover, due to limitations of the statistical analysis, we worked with time series per "plot-soil depth combinations", which means that different soil layers were mixed in the statistical analysis. Again, the standardization of the slopes of DOC concentrations allowed us to compare trends among different soil horizons by removing the effect of the decreasing soil solution DOC concentrations with soil depth. Otherwise, using the absolute trends would introduce a bias when we try to explain the DOC trends in relation with other parameters, because the trend slope would be highly dependent on the actual DOC concentrations, which, in turn, are very variable, not only among sites, but also among soil depths.

The influence of the DOC concentration levels was checked before deciding to use the standardized slopes (Fig. S5). It seemed that there was no relationship between the DOC trend slopes (relative and absolute) and the median DOC concentrations, with positive and negative trends occurring at both low and high DOC concentrations and, thus, we decided that using the standardized slopes will not hide any effect of the median DOC concentrations on the direction of the DOC trends.

This decision, however, has a drawback: the strength of the trend is clearly influenced by the DOC concentration levels. The fact that we used the standardized slope of DOC implied that it may be identical for two sites with very different mean DOC concentrations. DOC concentration decreases with depth and is lower in the deep mineral soil than in the upper mineral soil (Table S3) and by standardizing the slope, the magnitude of the trend was exaggerated in lower soil layers where both the absolute slope of DOC and the median DOC concentration are low (Table S3). This issue is well illustrated in Fig. S5, that shows how the highest standardized slopes are usually at low DOC concentrations (mostly in mineral soil layers), while the highest absolute slopes are at higher DOC concentrations (mostly in organic and upper soil layers).

In other words, in quantitative terms DOC trends are much higher in the organic layer than in the mineral soils but, in relative terms, DOC is increasing in the same proportion (Table S3). Because the aim of this study is to explain the high heterogeneity of DOC trends found across Europe, instead of the quantification of the trends at local scale, the relative trends were discussed throughout the manuscript. Consequently, our results should be interpreted with caution, keeping in mind that the relations between DOC trends and explaining factors are discussed only from a relative point of view.

Nevertheless, the statistical analyses (LMM, SMK, PMK and BFAST) were done on the absolute value and the resulting Sen's slopes were then standardized. Thus, the fact that trends are expressed in relative terms has consequences on the interpretation of the results, but has no influence on the statistical test itself (carried out on the absolute values of DOC), that is, on the significance and direction of the trends.

Table S3. Comparison of median relative trend slope (rslope in % yr-1) and absolute trend slope (abs slope in mg L^{-1} yr^{-1}) of DOC concentrations in soil solution and their interquartile range using the Seasonal Mann-Kendall test (SMK). (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	rslope (% yr^{-1})	abs slope (mg L^{-1} yr^{-1})
O	1.18 (±3.37)	0.32 (±1.2)
M02	0.04 (±3.41)	0.008 (±0.52)
M24	0.61 (±8.62)	0.025 (±0.48)
M48	1.01 (±4.79)	0.013 (±0.22)
M8	1.18 (±9.39)	0.032 (±0.31)

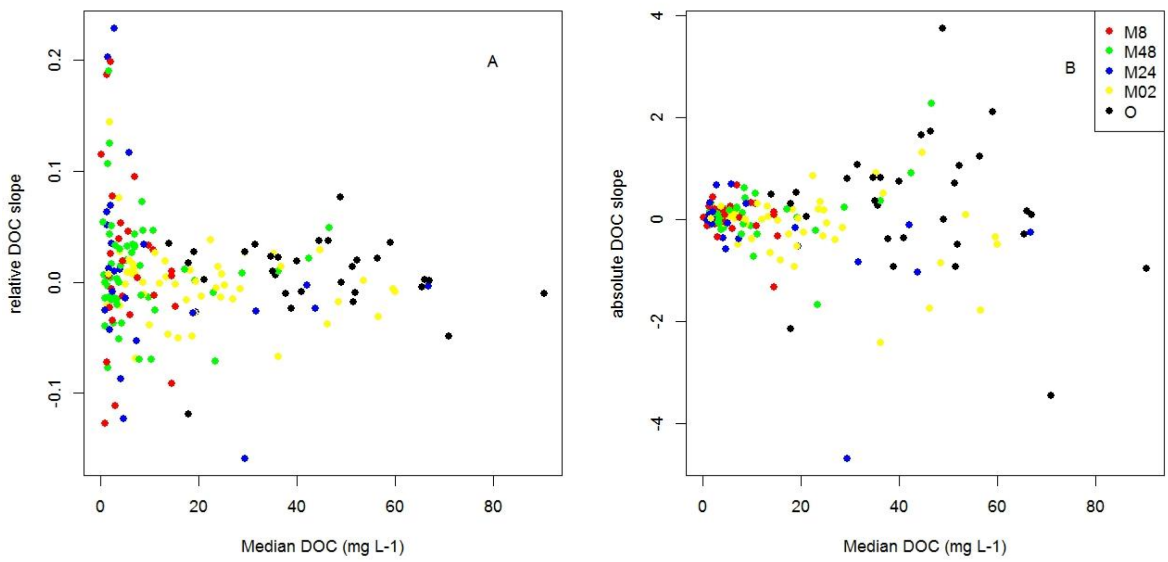

Figure S5. A) Standardized trends (relative DOC slope) versus median DOC concentrations. B) Absolute trends (absolute slope DOC) versus median DOC concentrations. The different colors represent the different soil layers.

Information on the soil solution chemistry at the studied ICP Forests Level II plots

Table S4. Median soil solution DOC concentrations (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [DOC]	25% percentile	75% percentile	n	median [DOC]	25% percentile	75% percentile	n
Broadleaved									
TL	O	41.35	28.99	56.05	637	44.56	32.00	59.10	475
	M02	8.80	4.30	21.20	8397	8.68	4.50	23.50	3104
	M24	3.78	1.67	8.90	2584	3.19	1.85	4.76	928
	M48	2.60	1.10	6.40	10635	2.70	1.08	5.80	4634
	M8	2.60	1.17	6.53	4354	2.65	1.53	7.00	1797
ZTL	O	33.33	21.00	51.12	4057	30.88	18.01	51.10	1956
	M02	4.26	3.51	6.28	608	4.30	2.80	9.30	192
	M24	20.44	13.40	34.37	94				0
	M48	3.42	2.61	4.51	427	0.91	0.50	1.64	85
	M8	2.42	2.11	3.62	34				0
Coniferous									
TL	O	49.00	35.10	67.36	2496	50.90	38.20	65.40	693
	M02	15.70	7.09	31.15	10914	12.80	5.90	25.50	5813
	M24	5.72	2.40	16.50	5116	5.00	2.10	21.89	2476
	M48	4.44	2.30	11.40	13979	4.30	2.29	10.90	6431
	M8	3.70	1.60	7.91	5024	4.29	2.55	10.12	1597
ZTL	O	42.92	29.03	60.80	4079	44.60	30.18	60.80	2703
	M02	36.90	22.20	56.40	2781	36.00	24.00	53.00	253
	M24	16.34	8.76	31.59	645				0
	M48	44.00	17.40	62.35	227	13.70	10.30	36.25	251
	M8	4.14	3.28	4.81	84				0

Table S5. Median soil solution pH, 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS	WITHOUT BREAKPOINTS

		median pH	25% percentile	75% percentile	n	median pH	25% percentile	75% percentile	n
Broadleaved									
TL	O	3.9	3.8	4.1	636	3.90	3.80	4.10	518
	M02	4.5	4.2	5.2	8346	4.60	4.20	6.2	3322
	M24	6.3	4.9	7.1	2482	6.10	4.90	6.7	993
	M48	5.1	4.5	6.7	10496	5.10	4.40	6.5	5162
	M8	6.4	4.6	7.8	4228	4.50	4.30	6.46	2115
ZTL	O	5.30	4.40	6.30	4026	5.30	4.30	6.60	2025
	M02	6.15	5.00	7.6	608	5.00	4.80	5.75	227
	M24	4.70	4.50	5	93	0.00	0.00	0	0
	M48	8.30	8.20	8.4	426	5.20	5.10	5.3	108
	M8	8.20	8.00	8.3	34	0.00	0.00	0	0
Coniferous									
TL	O	4.00	3.80	4.40	2496	3.80	3.60	4.00	726
	M02	4.30	4.00	4.7	10634	4.30	4.00	4.7	6930
	M24	4.60	4.30	5	4739	4.60	4.30	4.8	2849
	M48	4.50	4.30	4.9	13596	4.50	4.20	4.9	7462
	M8	4.57	4.30	6.4	4837	4.48	4.29	4.7	1660
ZTL	O	4.02	3.80	4.60	4038	4.00	3.80	4.80	2839
	M02	4.40	4.10	4.9	2412	4.80	4.53	5.3	254
	M24	4.90	4.50	5.4	551	0.00	0.00	0	0
	M48	4.80	4.10	5.1	225	4.40	4.27	4.9	319
	M8	4.70	4.60	4.8	84	0.00	0.00	0	0

Table S6. Median soil solution conductivity (μS cm^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median COND	25% percentile	75% percentile	n	median COND	25% percentile	75% percentile	n
Broadleaved									
TL	O	128.00	93.50	189.50	631	140.00	103.00	212.50	507
	M02	60.00	42.25	99	7651	69.55	45.00	104	3066
	M24	86.00	47.00	180	1503	70.45	45.90	120	548
	M48	68.00	45.00	137	8538	70.00	48.58	145	4320
	M8	148.50	61.63	305.75	3006	133.00	59.00	210	1736

ZTL	O	71.00	48.00	110.00	2750	70.00	46.60	111.00	1489
	M02	63.35	34.00	86.775	608	28.20	19.10	51.05	227
	M24	44.00	28.00	56	93	0.00	0.00	0	0
	M48	282.00	254.00	318	425	19.30	16.38	25.325	108
	M8	485.50	446.50	539.75	34	0.00	0.00	0	0
Coniferous									
TL	O	77.00	56.00	124.00	2425	85.00	65.00	155.00	725
	M02	58.00	31.00	92	9222	61.00	33.00	105.5	5699
	M24	50.00	30.00	97	2954	56.00	31.00	111	1715
	M48	56.00	37.00	94	10270	56.00	37.20	99	6658
	M8	104.00	55.00	207.75	2850	120.50	66.00	259	1118
ZTL	O	65.30	45.00	104.00	2296	64.00	42.30	106.00	1537
	M02	39.20	25.00	59	2627	27.00	20.08	41.1	228
	M24	32.00	21.00	57.95	615	0.00	0.00	0	0
	M48	39.05	28.00	150.5	214	95.85	46.48	155.5	290
	M8	50.00	31.75	69.25	84	0.00	0.00	0	0

Table S7. Median soil solution Ca (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [Ca]	25% percentile	75% percentile	n	median [Ca]	25% percentile	75% percentile	n
Broadleaved									
TL	O	4.18	1.83	7.85	633	5.369	3.193	9.204	515
	M02	2.12	0.80	5.3	8381	2.80	1.04	9.56525	3396
	M24	4.09	1.50	14.18	2555	3.69	0.92	9.005	999
	M48	2.31	0.70	9.385	10600	2.80	0.92	7.7	5204
	M8	5.68	1.50	41.7825	4322	2.80	0.51	13.75	2151
ZTL	O	4.10	2.05	7.06	4049	3.90	1.40	6.36	2030
	M02	8.33	1.67	13.59	608	1.23	0.75	2.425	227
	M24	2.35	1.25	3.296	94	0.00	0.00	0	0
	M48	58.86	51.26	67.485	419	0.72	0.58	1.06	108
	M8	73.75	60.78	92.8	34	0.00	0.00	0	0
Coniferous									

TL	O	3.36	1.47	6.39	2490	1.55	0.98	3.66	722
	M02	0.66	0.25	1.72	10890	1.00	0.36	2.45	6985
	M24	0.82	0.30	1.8665	5079	0.90	0.30	1.61	2901
	M48	0.82	0.32	2.07	13901	0.92	0.32	2.285	7511
	M8	2.10	0.49	10.6575	4986	1.97	0.53	8.285	1700
ZTL	O	1.50	0.72	2.80	4052	1.50	0.72	2.80	4052
	M02	1.13	0.53	2.14	2777	1.13	0.53	2.14	2777
	M24	1.20	0.62	2.31	644	1.20	0.62	2.31	644
	M48	3.00	1.81	3.895	227	3.00	1.81	3.895	227
	M8	0.76	0.47	1.1975	84	0.76	0.47	1.1975	84

Table S8. Median soil solution Mg (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [Mg]	25% percentile	75% percentile	n	median [Mg]	25% percentile	75% percentile	n
Broadleaved									
TL	O	1.05	0.48	1.90	633	1.18	0.62	2.08	515
	M02	0.80	0.42	1.5	8382	0.86	0.51	1.46	3395
	M24	1.01	0.50	2.13	2563	1.18	0.62	2.295	999
	M48	0.95	0.37	2.0745	10611	1.02	0.46	2.19	5205
	M8	1.72	0.73	3.94	4323	1.29	0.51	2.88	2152
ZTL	O	1.06	0.61	1.80	4049	0.98	0.57	1.60	2029
	M02	0.70	0.28	1.05	608	0.32	0.21	0.545	227
	M24	0.63	0.30	0.808	94	0.00	0.00	0	0
	M48	0.63	0.50	0.785	419	0.29	0.24	0.33	108
	M8	3.76	3.18	4.01	34	0.00	0.00	0	0
Coniferous									
TL	O	0.72	0.33	1.24	2490	0.24	0.17	0.63	722
	M02	0.36	0.20	0.68	10899	0.47	0.28	0.84	6990
	M24	0.40	0.22	0.898	5081	0.40	0.22	0.83	2902
	M48	0.44	0.21	0.9	13910	0.55	0.31	1.1	7518
	M8	0.98	0.39	1.875	4990	0.93	0.50	2	1699
ZTL	O	0.40	0.20	0.76	4061	0.40	0.20	0.83	2789
	M02	0.37	0.20	0.616	2773	0.49	0.38	0.6375	262

	M24	0.44	0.25	0.927	644	0.00	0.00	0	0
	M48	0.76	0.49	3.725	227	0.55	0.35	0.91	321
	M8	0.85	0.37	1.3425	84	0.00	0.00	0	0

Table S9. Median soil solution S-SO_4^{2-} (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [SO_4^{2-}]	25% percentile	75% percentile	n	median [SO_4^{2-}]	25% percentile	75% percentile	n
Broadleaved									
TL	O	2.50	1.30	4.17	592	3.20	1.63	4.58	476
	M02	2.00	1.33	3.3875	8383	1.93	1.19	3.3	3370
	M24	2.63	1.60	3.8	2556	2.70	1.98	3.565	1007
	M48	2.80	1.50	4.7	10571	3.10	1.90	5.5	5188
	M8	4.04	2.83	6.371	4323	5.05	3.10	9.2	2116
ZTL	O	1.01	0.60	1.70	4041	0.86	0.53	1.40	2029
	M02	0.75	0.52	1.21275	608	0.76	0.63	0.8785	227
	M24	2.05	1.02	3.15975	94	0.00	0.00	0	0
	M48	1.06	0.80	1.52	426	0.79	0.67	0.8625	108
	M8	10.38	9.15	11.855	34	0.00	0.00	0	0
Coniferous									
TL	O	1.27	0.67	2.30	2483	0.80	0.46	1.37	722
	M02	1.51	0.90	3	10885	1.94	1.08	3.608	7021
	M24	2.39	1.40	3.862	5086	2.25	1.40	3.558	2933
	M48	2.96	1.60	4.6	13941	2.90	1.70	4.63	7537
	M8	4.34	2.42	7.2	4977	5.46	3.13	9.30125	1672
ZTL	O	0.71	0.34	1.48	4064	0.67	0.31	1.38	2800
	M02	0.66	0.38	1.337	2776	0.57	0.42	0.77	261
	M24	1.74	0.77	4.5975	644	0.00	0.00	0	0
	M48	1.20	0.89	11.315	226	4.45	1.30	8.291	318
	M8	1.33	1.09	1.60325	84	0.00	0.00	0	0

Table S10. Median soil solution N-NO_3^- (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [NO_3^-]	25% percentile	75% percentile	n	median [NO_3^-]	25% percentile	75% percentile	n
Broadleaved									
TL	O	3.74	1.46	9.29	617	4.88	1.94	11.04	518
	M02	0.56	0.04	2.5285	8123	0.91	0.24	2.6825	3372
	M24	0.50	0.02	3.23	2535	0.62	0.02	2.8615	991
	M48	0.26	0.02	1.659	10358	0.33	0.03	2.3	5165
	M8	0.40	0.05	5.0275	4218	0.73	0.13	6.1595	2002
ZTL	O	1.60	0.56	3.79	3975	1.03	0.21	2.60	1994
	M02	0.86	0.40	1.8725	608	0.70	0.30	1.6	227
	M24	0.47	0.14	0.87975	94	0.00	0.00	0	0
	M48	0.35	0.06	0.8	423	0.52	0.23	0.8525	108
	M8	0.02	0.02	0.022	34	0.00	0.00	0	0
Coniferous									
TL	O	1.14	0.16	4.19	2388	1.06	0.08	4.87	677
	M02	0.14	0.02	1.3	10431	0.27	0.02	1.87775	6940
	M24	0.17	0.02	1.267	4745	0.10	0.02	1.334	2844
	M48	0.10	0.02	1.2	13195	0.11	0.02	1.3	7194
	M8	0.27	0.02	1.0895	4971	0.37	0.06	1.2	1691
ZTL	O	0.56	0.13	1.74	4055	0.34	0.05	1.18	2777
	M02	0.02	0.02	0.06	2275	0.05	0.02	0.17	260
	M24	0.02	0.02	0.03	489	0.00	0.00	0	0
	M48	0.02	0.02	0.09875	226	0.65	0.03	7.988	321
	M8	2.54	0.50	4.6805	84	0.00	0.00	0	0

Table S11. Median soil solution Al (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the 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).

		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median [Al]	25% percentile	75% percentile	n	median [Al]	25% percentile	75% percentile	n
Broadleaved									

TL	O	0.38	0.17	0.76	574	0.30	0.15	0.76	490
	M02	0.81	0.39	1.62	7767	0.78	0.30	1.7	3107
	M24	0.05	0.02	0.387	2406	0.05	0.02	0.333	979
	M48	0.30	0.02	1.02	9871	0.30	0.02	1	4918
	M8	0.05	0.02	0.87	4180	0.91	0.17	2.79	2101
ZTL	O	0.17	0.06	0.32	3278	0.12	0.03	0.22	1536
	M02	0.14	0.02	0.45	577	0.22	0.14	0.35	222
	M24	0.37	0.22	0.48	94	0.00	0.00	0	0
	M48	0.02	0.02	0.04	378	0.14	0.09	0.21	107
	M8	0.02	0.02	0.02	30	0.00	0.00	0	0
Coniferous									
TL	O	1.14	0.74	1.79	2162	0.93	0.59	1.27	622
	M02	1.35	0.69	2.19	10398	1.44	0.72	2.44875	6514
	M24	0.92	0.36	2.2145	4871	0.90	0.38	2.391	2762
	M48	1.11	0.38	2.341	13454	0.96	0.32	2.2	7157
	M8	1.58	0.02	3.399	4857	2.63	1.01	5.475	1674
ZTL	O	0.24	0.12	0.49	3944	0.21	0.11	0.39	2704
	M02	0.87	0.44	1.48	2709	1.10	0.81	1.7	262
	M24	0.73	0.22	1.7235	611	0.00	0.00	0	0
	M48	2.01	1.20	7.015	210	2.95	1.90	5.568	303
	M8	1.62	1.01	2.3275	66	0.00	0.00	0	0

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