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

M. Camino-Serrano[1], E. Graf Pannatier[2], S. Vicca[1], S. Luyssaert[3,22], M. Jonard[4], P. Ciais[3], B. Guenet[3], B. Gielen[1], J. Peñuelas[5,6], J. Sardans[5,6], P. Waldner[2], S. Etzold[2], G. Cecchini[7], N. Clarke[8], Z. Galić[9], L. Gandois[10,11], K. Hansen[12], J. Johnson[13], U. Klinck[14], Z. Lachmanová[15], A.J. Lindroos[16], H. Meesenburg[14], T.M. Nieminen[16], T.G.M. Sanders[17], K. Sawicka[18], W. Seidling[17], A. Thimonier[2], E. Vanguelova[19], A. Verstraeten[20], L. Vesterdal[21], I.A. Janssens[1]

[1]{Department of Biology, PLECO, University of Antwerp, Belgium}

[2] {WSL, Swiss Federal Institute for Forest, Snow and Landscape Research, Zürcherstrasse 111, 8903, Birmensdorf, Switzerland}

[3] {Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France}

[4] {UCL-ELI, Université catholique de Louvain, Earth and Life Institute, Croix du Sud 2, BE-1348 Louvain-la-Neuve , Belgium}

[5] {CREAF, Cerdanyola del Vallès, Catalonia, Spain}

[6] {CSIC, Global Ecology Unit CREAF-CSIC-UAB, Cerdanyola del Vallès, Catalonia, Spain}

[7] {Earth Sciences Department, University of Florence, Italy}

[8] {Norwegian Institute of Bioeconomy Research, N-1431, Ås, Norway}

[9] {University of Novi Sad-Institute of Lowland Forestry and Environment, Serbia}

[10] {Université de Toulouse: UPS, INP, EcoLab (Laboratoire Ecologie fonctionnelle et Environnement), ENSAT, Castanet-Tolosan, France}

[11] {CNRS, EcoLab, Castanet-Tolosan, France}

[12] {IVL Swedish Environmental Research Institute, Natural Resources & Environmental Effects, SE-100 31, Stockholm, Sweden}

[13] {UCD School of Agriculture and Food Science, University College Dublin, Belfield, Ireland}

[14] {Northwest German Forest Research Institute, Grätzelstr. 2, D-37079, Göttingen, Germany}

[15] {FGMRI, Forestry and Game Management Research Institute, Strnady 136, 252 02 Jíloviště,Czech Republic}

[16] {Natural Resources Institute Finland (Luke), P.O. Box 18, 01301 Vantaa, Finland }

[17] {Thünen Institute of Forest Ecosystems, Alfred-Möller-Strasse 1, D-16225, Eberswalde, Germany}

[18] {University of Reading, Environmental Science, UK}

[19] {Centre for Ecosystem, Society and Biosecurity, Forest Research, Alice Holt Lodge, Wrecclesham, Farnham, Surrey GU10 4LH, UK}

[20] {Research Institute for Nature and Forest (INBO), Kliniekstraat 25, BE-1070 Brussels, Belgium}

[21] {University of Copenhagen, Department of Geosciences and Natural Resource Management, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark}

[22] now at {Free University of Amsterdam, Department of Ecological Science, Boelelaan 1085, NL-1081HV, the Netherlands}

Correspondence to: M. Camino-Serrano (marta.caminoserrano@uantwerpen.be)

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. 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. 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. 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. 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. 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. 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. 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. 2 and 3), 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. 4). 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. 5A). 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. 5B). 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. 6A). According to this model, lower mean throughfall SO_4^{2-} deposition resulted in increasing trend slopes of DOC in soil solution. On the other hand, higher mean throughfall NO_3^- deposition resulted in increasing trend slopes of DOC (Fig. 6A). When 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. 6B). 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. 6C). 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. 6C). 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. 2). 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. 4). 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. 2 and 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. 5 and 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. 2 and 3). 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. 6). 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. 6A, 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).

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. 6). Finally, modifications of soil properties induced by changes in atmospheric deposition are probably an order of magnitude lower than the spatial variation of these soil properties across sites, making it difficult to isolate controlling factors on the final observed response of soil solution DOC at continental scale (Clark et al., 2010).

In conclusion, 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 (Löfgren and Zetterberg, 2011). Further monitoring studies in forest soils with high hydraulic connectivity to streams are needed to be able to link dynamics of DOC in forest soil with dynamics of DOC in stream waters.

5 Conclusions

Different monotonic long-term trends of soil solution DOC have been found across European forests at plot scale, with the majority of the trends for specific plots and depths not being statistically significant (40%), followed by significantly positive (35%) and significantly negative trends (25%). The distribution of the trends did not follow a specific regional pattern. 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.

Acknowledgements

We want to thank the numerous scientists and technicians who were involved in the data collection, analysis, transmission, and validation of the ICP Forests Monitoring Programme across the UNECE region from which data have been used in this work. The evaluation was mainly based on data that are part of the UNECE ICP Forests PCC Collaborative Database (see www.icp-forests.net) or national Databases (e.g., Eberswalde Forestry State Center of Excellence *(Landeskompetenzzentrum Forst Eberswalde, LFE)* for parts of the data for Germany). For soil, we used and acknowledge the aggregated forest soil condition database (AFSCDB.LII.2.1) compiled by the ICP Forests Forest Soil Coordinating Centre. The long-term collection of forest monitoring data was to a large extent funded by national research institutions and ministries, with support from further bodies, services and land owners. It was partially funded by the European Union under the Regulation (EC) No. 2152/2003 concerning monitoring of forests and environmental interactions in the Community (Forest

Focus) and the project LIFE 07 ENV/D/000218. SV is a postdoctoral research associate of the Fund for Scientific Research – Flanders. IAJ, JP and PC acknowledge support from the European Research Council Synergy grant ERC-2013-SyG-610028 IMBALANCE-P. Finally, we acknowledge the E-OBS dataset from the EU-FP6 project ENSEMBLES (http://ensembles-eu.metoffice.com) and the data providers in the ECA&D project (http://www.ecad.eu).

References

Akselsson, C., Hultberg, H., Karlsson, P. E., Karlsson, G. P., and Hellsten, S.: Acidification trends in south Swedish forest soils 1986-2008-Slow recovery and high sensitivity to sea-salt episodes, Sci Total Environ, 444, 271-287, 2013.

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J.: The boundless carbon cycle. Nature Geoscience, 9, 2009.

Bianchi, T. S.: The role of terrestrially derived organic carbon in the coastal ocean: A changing paradigm and the priming effect, P Natl Acad Sci USA, 108, 19473-19481, 2011.

Billett, M. F., Charman, D. J., Clark, J. M., Evans, C. D., Evans, M. G., Ostle, N. J., Worrall, F., Burden, A., Dinsmore, K. J., Jones, T., McNamara, N. P., Parry, L., Rowson, J. G., and Rose, R.: Carbon balance of UK peatlands: current state of knowledge and future research challenges, Clim Res, 45, 13-29, 2010.

Bolan, N. S., Adriano, D. C., Kunhikrishnan, A., James, T., McDowell, R., and Senesi, N.: Dissolved Organic Matter: Biogeochemistry, Dynamics, and Environmental Significance in Soils. Adv Agron, 2011.

Borken, W., Ahrens, B., Schulz, C., and Zimmermann, L.: Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils, Global Change Biol, 17, 2428-2443, 2011.

Bragazza, L., Freeman, C., Jones, T., Rydin, H., Limpens, J., Fenner, N., Ellis, T., Gerdol, R., Hajek, M., Hajek, T., Lacumin, P., Kutnar, L., Tahvanainen, T., and Toberman, H.: Atmospheric nitrogen deposition promotes carbon loss from peat bogs. P Natl Acad Sci USA, 51, 2006.

Buckingham, S., Tipping, E., and Hamilton-Taylor, J.: Concentrations and fluxes of dissolved organic carbon in UK topsoils. In: Sci Total Environ, 1, 2008.

Camino-Serrano, M., Gielen, B., Luyssaert, S., Ciais, P., Vicca, S., Guenet, B., De Vos, B., Cools, N., Ahrens, B., Arain, M. A., Borken, W., Clarke, N., Clarkson, B., Cummins, T., Don, A., Pannatier, E. G., Laudon, H., Moore, T., Nieminen, T. M., Nilsson, M. B., Peichl, M., Schwendenmann, L., Siemens, J., and Janssens, I.: Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type, Global Biogeochem Cy, 28, 497-509, 2014.

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., Newton, R. J., and Chapman, P. J.: The importance of the relationship between scale and process in understanding long-term DOC dynamics, Sci Total Environ, 408, 2768-2775, 2010.

Cools, N. and De Vos, B.: A harmonised Level II soil database to understand processes and changes in forest condition at the European Level. In: Michel, A., Seidling, W., editors. 2014. Forest Condition in Europe: 2014 Technical Report of ICP Forests. , Vienna, 72-90 pp., 2014.

Davidson, E. A. and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165-173, 2006.

Dawson, J. J. C., Malcolm, I. A., Middlemas, S. J., Tetzlaff, D., and Soulsby, C.: Is the Composition of Dissolved Organic Carbon Changing in Upland Acidic Streams?, Environ Sci Technol, 43, 7748-7753, 2009.

de Jong, R., Verbesselt, J., Zeileis, A., and Schaepman, M. E.: Shifts in Global Vegetation Activity Trends, Remote Sens-Basel, 5, 1117-1133, 2013.

de Vries, W., Du, E., and Butterbach-Bahl, K.: Short and long-term impacts of nitrogen deposition on carbon sequestration by forest ecosystems, Current Opinion in Environmental Sustainability, 9–10, 90-104, 2014.

De Vries, W., Reinds, G. J., Posch, M., Sanz, M. J., Krause, G. H. M., Calatayud, V., Renaud, J. P., Dupouey, J. L., Sterba, H., Gundersen, P., Voogd, J. C. H., and Vel, E. M.: Intensive Monitoring of Forest Ecosystems in Europe. , Brussels, Geneva, 161 pp., 2003.

de Vries, W., Solberg, S., Dobbertin, M., Sterba, H., Laubhann, D., van Oijen, M., Evans, C., Gundersen, P., Kros, J., Wamelink, G. W. W., Reinds, G. J., and Sutton, M. A.: The impact of nitrogen deposition on carbon sequestration by European forests and heathlands, Forest Ecol Manag, 258, 1814-1823, 2009.

de Wit, H. A., Groseth, T., and Mulder, J.: Predicting Aluminum and Soil Organic Matter Solubility Using the Mechanistic Equilibrium Model WHAM, Soil Sci. Soc. Am. J., 65, 1089-1100, 2001.

De Wit, H. A., Mulder, J., Hindar, A., and Hole, L.: Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition, Environ Sci Technol, 41, 7706-7713, 2007.

Dinsmore, K. J., Billett, M. F., and Dyson, K. E.: Temperature and precipitation drive temporal variability in aquatic carbon and GHG concentrations and fluxes in a peatland catchment, Global Change Biol, 19, 2133-2148, 2013.

Evans, C. D., Chapman, P. J., Clark, J. M., Monteith, D. T., and Cresser, M. S.: Alternative explanations for rising dissolved organic carbon export from organic soils, Global Change Biol, 12, 2044-2053, 2006.

Evans, C. D., Jones, T. G., Burden, A., Ostle, N., Zielinski, P., Cooper, M. D. A., Peacock, M., Clark, J. M., Oulehle, F., Cooper, D., and Freeman, C.: Acidity controls on dissolved organic carbon mobility in organic soils, Global Change Biol, 18, 3317-3331, 2012.

Evans, C. D., Monteith, D. T., and Cooper, D. M.: Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts, Environ Pollut, 137, 55-71, 2005.

Ferretti, M. and Fischer, R.: Forest monitoring, methods for terrestrial investigation in Europe with an overview of North Ameria and Asia, Elsevier, UK, 2013.

Ferretti, M. and König, N.: Chapter 20 - Quality Assurance in International Forest Monitoring in Europe. In: Developments in Environmental Science, Ferretti, M. and Fischer, R. (Eds.), Elsevier, 2013.

Ferretti, M., Marchetto, A., Arisci, S., Bussotti, F., Calderisi, M., Carnicelli, S., Cecchini, G., Fabbio, G., Bertini, G., Matteucci, G., de Cinti, B., Salvati, L., and Pompei, E.: On the tracks of Nitrogen deposition effects on temperate forests at their southern European range – an observational study from Italy, Global Change Biol, 20, 3423-3438, 2014.

Fox, J., Nie, Z., and Byrnes, J.: sem: Structural Equation Models., 2013.

Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A., Sleep, D., Hughes, S., and Hudson, J.: Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels, Nature, 430, 195-198, 2004.

Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., and Mulder, J.: Concentration and fluxes of dissolved organic carbon (DOC) in three Norway spruce stands along a climatic gradient in Sweden, Biogeochemistry, 77, 1-23, 2006.

Graf Pannatier, E. G., Thimonier, A., Schmitt, M., Walthert, L., and Waldner, P.: A decade of monitoring at Swiss Long-Term Forest Ecosystem Research (LWF) sites: can we observe trends in atmospheric acid deposition and in soil solution acidity?, Environmental monitoring and assessment, 174, 3-30, 2011.

Granke, O.: Chapter 23 - Methods for Database Quality Assessment. Developments in Environmental Science, Ferretti, M. and Fischer, R. (Eds.), Elsevier, 2013.

Haaland, S., Hongve, D., Laudon, H., Riise, G., and Vogt, R. D.: Quantifying the Drivers of the Increasing Colored Organic Matter in Boreal Surface Waters, Environ Sci Technol, 44, 2975-2980, 2010.

Hansen, K., Vesterdal, L., Bastrup-Birk, A., and Bille-Hansen, J.: Are indicators for critical load exceedance related to forest condition?, Water Air Soil Poll, 183, 293-308, 2007.

Harrison, A. F., Taylor, K., Scott, A., Poskitt, J., Benham, D., Grace, J., Chaplow, J., and Rowland, P.: Potential effects of climate change on DOC release from three different soil types on the Northern Pennines UK: examination using field manipulation experiments, Global Change Biol, 14, 687-702, 2008.

Hartley, I. P. and Ineson, P.: Substrate quality and the temperature sensitivity of soil organic matter decomposition, Soil Biol Biochem, 40, 1567-1574, 2008.

Haylock, M. R., Hofstra, N., Tank, A. M. G. K., Klok, E. J., Jones, P. D., and New, M.: A European daily high-resolution gridded data set of surface temperature and precipitation for 1950-2006, J Geophys Res-Atmos, 113, 2008.

Hirsch, R. M., Slack, J. R., and Smith, R. A.: Techniques of Trend Analysis for Monthly Water-Quality Data, Water Resour Res, 18, 107-121, 1982.

Hruška, J., Kram, P., Mcdowell, W. H., and Oulehle, F.: Increased Dissolved Organic Carbon (DOC) in Central European Streams is Driven by Reductions in Ionic Strength Rather than Climate Change or Decreasing Acidity, Environ Sci Technol, 43, 4320-4326, 2009.

ICP Forests: Manual on methods and for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. , UNECE ICP Forests Programme Co-ordinating Centre, Hamburg, Germany, 2010.

Janssens, I. A., Dieleman, W., Luyssaert, S., Subke, J. A., Reichstein, M., Ceulemans, R., Ciais, P., Dolman, A. J., Grace, J., Matteucci, G., Papale, D., Piao, S. L., Schulze, E. D., Tang, J., and Law, B. E.: Reduction of forest soil respiration in response to nitrogen deposition, Nature Geoscience, 3, 315-322, 2010.

Kalbitz, K., Solinger, S., Park, J. H., Michalzik, B., and Matzner, E.: Controls on the dynamics of dissolved organic matter in soils: A review, Soil Sci, 165, 277-304, 2000.

König, N., Cools, N., Derome, K., Kowalska, A., De Vos, B., Fürst, A., Marchetto, A., O'Dea, P., and Tartari, G. A.: Chapter 22 - Data Quality in Laboratories: Methods and Results for Soil, Foliar, and Water Chemical Analyses. Developments in Environmental Science, Ferretti, M. and Fischer, R. (Eds.), Elsevier, 2013.

Kvaalen, H., Solberg, S., Clarke, N., Torp, T., and Aamlid, D.: Time series study of concentrations of SO42- and H+ in precipitation and soil waters in Norway, Environ Pollut, 117, 215-224, 2002.

Lange, H., Solberg, S., and Clarke, N.: Aluminum dynamics in forest soil waters in Norway, Sci Total Environ, 367, 942-957, 2006.

Lepistö, A., Futter, M. N., and Kortelainen, P.: Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed, Global Change Biol, 20, 1225-1237, 2014.

Libiseller, C. and Grimvall, A.: Performance of partial Mann-Kendall tests for trend detection in the presence of covariates, Environmetrics, 13, 71-84, 2002.

Lindroos, A.-J., Derome, J., Starr, M., and Ukonmaanaho, L.: Effects of Acidic Deposition on Soil Solution Quality and Nutrient Leaching in Forest Soils. In: Forest Condition in a Changing Environment, Mälkönen, E. (Ed.), Forestry Sciences, Springer Netherlands, 2000.

Liu, L. and Greaver, T. L.: A global perspective on belowground carbon dynamics under nitrogen enrichment, Ecol Lett, 13, 819-828, 2010.

Löfgren, S., Gustafsson, J. P., and Bringmark, L.: Decreasing DOC trends in soil solution along the hillslopes at two IM sites in southern Sweden - Geochemical modeling of organic matter solubility during acidification recovery, Sci Total Environ, 409, 201-210, 2010.

Löfgren, S. and Zetterberg, T.: Decreased DOC concentrations in soil water in forested areas in southern Sweden during 1987-2008, Sci Total Environ, 409, 1916-1926, 2011.

Marchetto, A., Mosello, R., Tartari, G., Derome, J., Derome, K., König, N., Clarke, N., and Kowalska, A.: Atmospheric Deposition and Soil Solution Working Ring Test 2009, Project FutMon, Verbania Pallanza, 41 pp., 2011.

Marchetto, A., Rogora, M., and Arisci, S.: Trend analysis of atmospheric deposition data: A comparison of statistical approaches, Atmos Environ, 64, 95-102, 2013.

McDowell, W. H. and Likens, G. E.: Origin, Composition, and Flux of Dissolved Organic-Carbon in the Hubbard Brook Valley, Ecol Monogr, 58, 177-195, 1988.

Moffat, A. J., Kvaalen, H., Solberg, S., and Clarke, N.: Temporal trends in throughfall and soil water chemistry at three Norwegian forests, 1986-1997, Forest Ecol Manag, 168, 15-28, 2002.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Hogasen, T., Wilander, A., Skjelkvale, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopacek, J., and Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, Nature, 450, 537-U539, 2007.

Mulder, J., De Wit, H. A., Boonen, H. W. J., and Bakken, L. R.: Increased levels of aluminium in forest soils: Effects on the stores of soil organic carbon, Water Air Soil Poll, 130, 989-994, 2001.

Nieminen, T. M.: Soil Solution Collection and Analysis. Manual Part XI, UNECE ICP Forests Programme Co-ordinating Centre, Hamburg978-3-926301-03-1, 30 pp., 2011.

Oulehle, F., Evans, C. D., Hofmeister, J., Krejci, R., Tahovska, K., Persson, T., Cudlin, P., and Hruska, J.: Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition, Global Change Biol, 17, 3115-3129, 2011.

Oulehle, F. and Hruska, J.: Rising trends of dissolved organic matter in drinking-water reservoirs as a result of recovery from acidification in the Ore Mts., Czech Republic, Environ Pollut, 157, 3433-3439, 2009.

Pitman, R. M., Vanguelova, E. I., and Benham, S. E.: The effects of phytophagous insects on water and soil nutrient concentrations and fluxes through forest stands of the Level II monitoring network in the UK, Sci Total Environ, 409, 169-181, 2010.

Poorter, H., Niklas, K. J., Reich, P. B., Oleksyn, J., Poot, P., and Mommer, L.: Biomass allocation to leaves, stems and roots: meta-analyses of interspecific variation and environmental control, New Phytologist, 193, 30-50, 2012.

Pregitzer, K. S., Zak, D. R., Burton, A. J., Ashby, J. A., and MacDonald, N. W.: Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems, Biogeochemistry, 68, 179-197, 2004.

R Core Team: R: A language and environment for statistical computing., R Foundation for Statistical Computing, Vienna, Austria, 2014.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G., Raymond, P. A., Spahni, R., Suntharalingam, P., and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nature Geoscience, 6, 2013.

Rosemond, A. D., Benstead, J. P., Bumpers, P. M., Gulis, V., Kominoski, J. S., Manning, D. W. P., Suberkropp, K., and Wallace, J. B.: Experimental nutrient additions accelerate terrestrial carbon loss from stream ecosystems, Science, 347, 1142-1145, 2015.

Sarkkola, S., Koivusalo, H., Lauren, A., Kortelainen, P., Mattsson, T., Palviainen, M., Piirainen, S., Starr, M., and Finer, L.: Trends in hydrometeorological conditions and stream water organic carbon in boreal forested catchments, Sci Total Environ, 408, 92-101, 2009.

Sawicka, K., Monteith, D. T., Vanguelova, E. I., Wade, A. J., and Clark, J. M.: Fine-scale temporal characterization of trends in soil water dissolved organic carbon and potential drivers, Ecological Indicators, 68, 36-51, 2016.

Schwertman, N. C., Owens, M. A., and Adnan, R.: A simple more general boxplot method for identifying outliers, Comput Stat Data An, 47, 165-174, 2004.

Schwesig, D., Kalbitz, K., and Matzner, E.: Effects of aluminium on the mineralization of dissolved organic carbon derived from forest floors, Eur J Soil Sci, 54, 311-322, 2003.

Sen, P. K.: Estimates of the Regression Coefficient Based on Kendall's Tau, Journal of the American Statistical Association, 63, 1379-1389, 1968.

Skjelkvåle, B. L., Evans, C., Larssen, T., Hindar, A., and Raddum, G. G.: Recovery from acidification in European surface waters: A view to the future, Ambio, 32, 170-175, 2003.

Stutter, M. I., Lumsdon, D. G., and Rowland, A. P.: Three representative UK moorland soils show differences in decadal release of dissolved organic carbon in response to environmental change, Biogeosciences, 8, 3661-3675, 2011.

Sucker, C. and Krause, K.: Increasing dissolved organic carbon concentrations in freshwaters: what is the actual driver?, Iforest, 3, 106-108, 2010.

Sulkava, M., Rautio, P., and Hollmen, J.: Combining measurement quality into monitoring trends in foliar nutrient concentrations, Lect Notes Comput Sc, 3697, 761-767, 2005.

Tetzlaff, D., Malcolm, I. A., and Soulsby, C.: Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments, J Hydrol, 346, 93-111, 2007.

Tian, D. and Niu, S.: A global analysis of soil acidification caused by nitrogen addition, Environmental Research Letters, 10, 024019, 2015.

Tipping, E. and Woof, C.: The distribution of humic substances between the solid and aqueous phases of acid organic soils; a description based on humic heterogeneity and charge-dependent sorption equilibria, Journal of Soil Science, 42, 437-448, 1991.

Ukonmaanaho, L., Starr, M., Lindroos, A. J., and Nieminen, T. M.: Long-term changes in acidity and DOC in throughfall and soil water in Finnish forests, Environ Monit Assess, 186, 7733-7752, 2014.

Vanguelova, E. I., Benham, S., Pitman, R., Moffat, A. J., Broadmeadow, M., Nisbet, T., Durrant, D., Barsoum, N., Wilkinson, M., Bochereau, F., Hutchings, T., Broadmeadow, S., Crow, P., Taylor, P., and Houston, T. D.: Chemical fluxes in time through forest ecosystems in the UK - Soil response to pollution recovery, Environ Pollut, 158, 1857-1869, 2010.

Vanguelova, E. I., Hirano, Y., Eldhuset, T. D., Sas-Paszt, L., Bakker, M. R., Puttsepp, U., Brunner, I., Lohmus, K., and Godbold, D.: Tree fine root Ca/Al molar ratio - Indicator of Al and acidity stress, Plant Biosyst, 141, 460-480, 2007.

Verbesselt, J., Hyndman, R., Newnham, G., and Culvenor, D.: Detecting trend and seasonal changes in satellite image time series, Remote Sens Environ, 114, 106-115, 2010.

Verstraeten, A., De Vos, B., Neirynck, J., Roskams, P., and Hens, M.: Impact of air-borne or canopy-derived dissolved organic carbon (DOC) on forest soil solution DOC in Flanders, Belgium, Atmos Environ, 83, 155-165, 2014.

Verstraeten, A., Neirynck, J., Genouw, G., Cools, N., Roskams, P., and Hens, M.: Impact of declining atmospheric deposition on forest soil solution chemistry in Flanders, Belgium, Atmos Environ, 62, 50-63, 2012.

Vicca, S., Balzarolo, M., Filella, I., Granier, A., Herbst, M., Knohl, A., Longdoz, B., Mund, M., Nagy, Z., Pintér, K., Rambal, S., Verbesselt, J., Verger, A., Zeileis, A., Zhang, C., and Peñuelas, J.: Remotely-sensed detection of effects of extreme droughts on gross primary production, Scientific Reports, 6, 28269, 2016.

Vicca, S., Luyssaert, S., Penuelas, J., Campioli, M., Chapin, F. S., Ciais, P., Heinemeyer, A., Hogberg, P., Kutsch, W. L., Law, B. E., Malhi, Y., Papale, D., Piao, S. L., Reichstein, M., Schulze, E. D., and Janssens, I. A.: Fertile forests produce biomass more efficiently, Ecol Lett, 15, 520-526, 2012.

Waldner, P., Marchetto, A., Thimonier, A., Schmitt, M., Rogora, M., Granke, O., Mues, V., Hansen, K., Karlsson, G. P., Zlindra, D., Clarke, N., Verstraeten, A., Lazdins, A., Schimming, C., Iacoban, C., Lindroos, A. J., Vanguelova, E., Benham, S., Meesenburg, H., Nicolas, M., Kowalska, A., Apuhtin, V., Napa, U., Lachmanova, Z., Kristoefel, F., Bleeker, A., Ingerslev, M., Vesterdal, L., Molina, J., Fischer, U., Seidling, W., Jonard, M., O'Dea, P., Johnson, J., Fischer, R., and Lorenz, M.: Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe, Atmos Environ, 95, 363-374, 2014.

Worrall, F. and Burt, T.: Time series analysis of long-term river dissolved organic carbon records, Hydrological Processes, 18, 893-911, 2004.

Wu, Y. J., Clarke, N., and Mulder, J.: Dissolved Organic Carbon Concentrations in Throughfall and Soil Waters at Level II Monitoring Plots in Norway: Short- and Long-Term Variations, Water Air Soil Poll, 205, 273-288, 2010.

Zech, W., Guggenberger, G., and Schulten, H. R.: Budgets and Chemistry of Dissolved Organic-Carbon in Forest Soils - Effects of Anthropogenic Soil Acidification, Sci Total Environ, 152, 49-62, 1994.

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

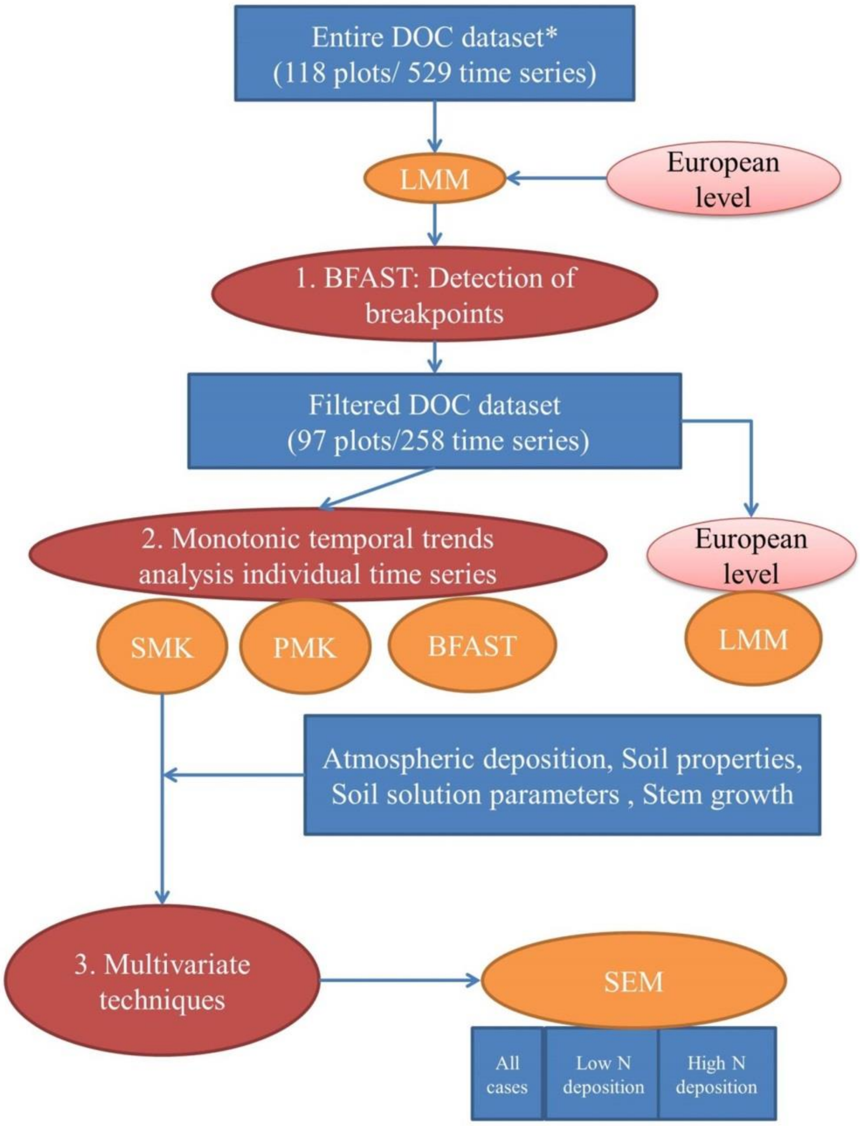
								(±3.98)			
	M24	5.72	5116	2.71	n.s.	2476	3.66	n.s.	-0.3 (±7.82)	7	7	8
	M48	4.44	13979	1.24	n.s.	6431	0.05	n.s.	0.3 (±4.32)	16	22	11
	M8	3.70	5024	**9.93**	**<0.001**	1597	7.58	n.s.	2.89 (±10.28)	4	4	10
ZTL	O	42.9	4079	**3.59**	**0.0018**	2703	**3.09**	**0.0045**	**1.85 (±2.88)**	1	9	5
	M02	36.9	2781	-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 Cambisol	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+} ($\% yr^{-1}$)
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



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

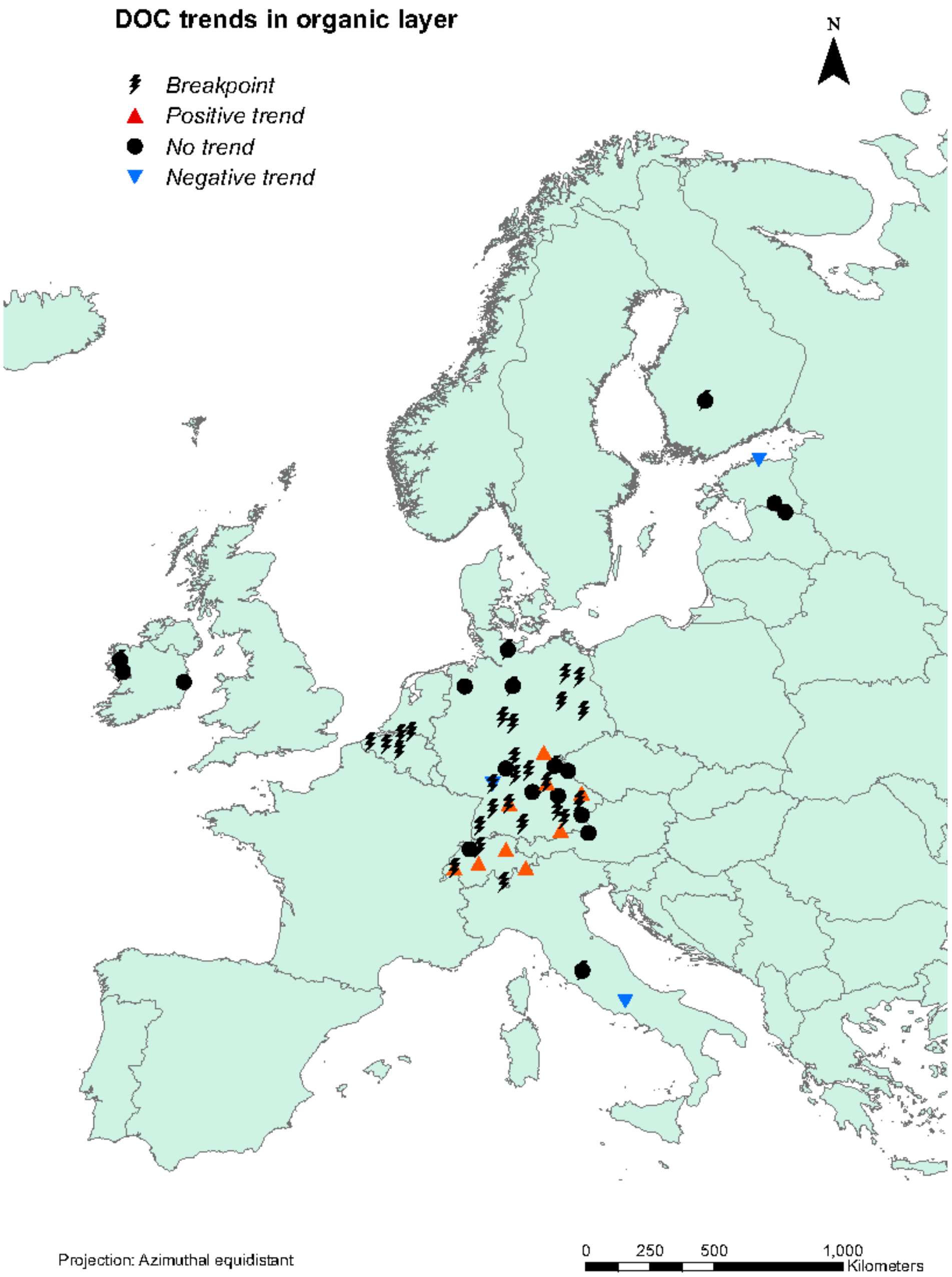


Figure 2. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

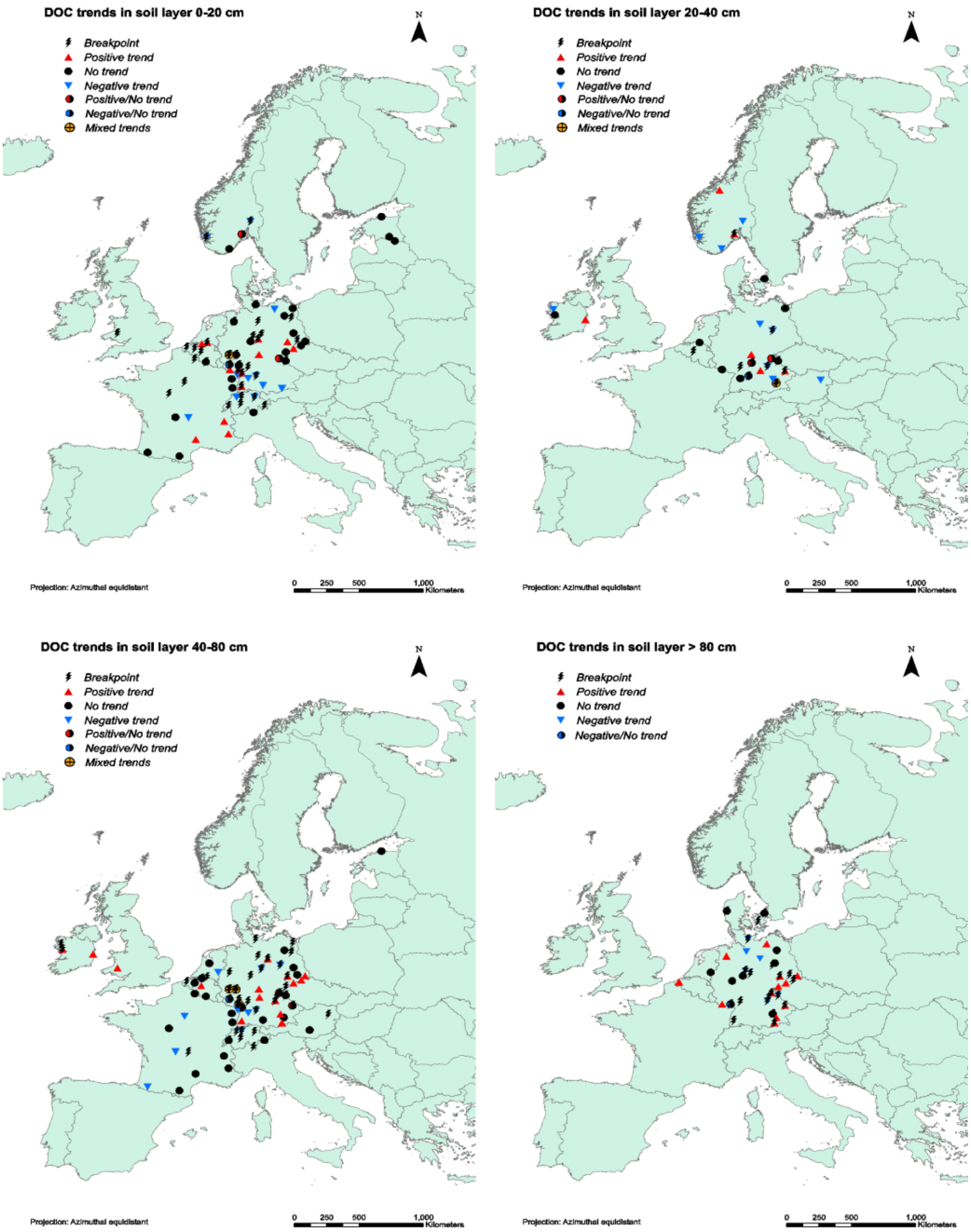


Figure 3. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0–20 cm), b) intermediate (20–40 cm), c) subsoil (40–80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

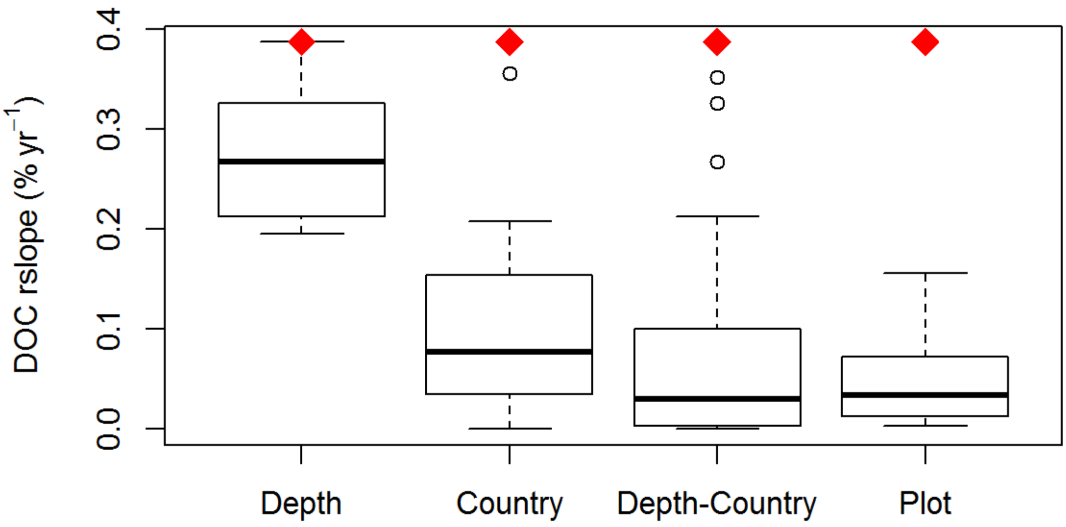


Figure 4. Range of relative trend slopes (max-min) for trends of DOC concentration in soil solution within each 1) depth interval, 2) country, 3) depth interval per country, and 4) plot. The boxplots show the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers)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

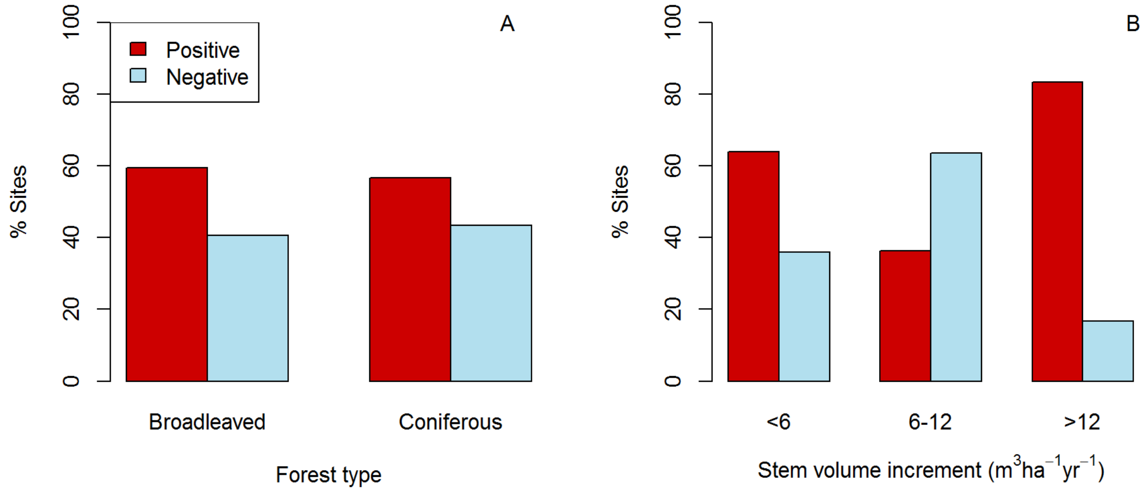


Figure 5. Percentage of occurrence of positive and negative trends of DOC concentration in soil solution separated by A) forest type and B) stem volume increment (m^3 ha^{-1} yr^{-1}).

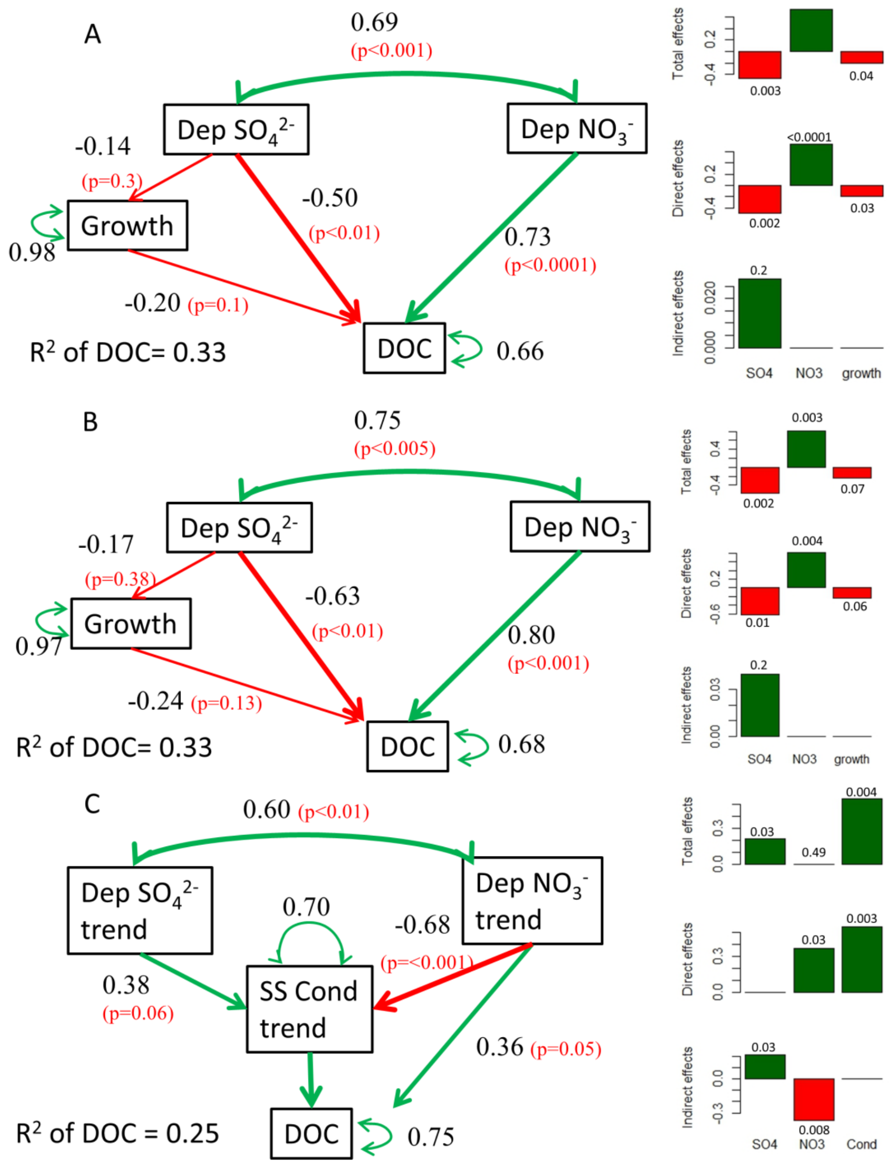


Figure 6. Diagrams of the structural equation models (SEM) that best explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium throughfall inorganic N deposition (< 15 kg N ha^{-1} yr^{-1}), and C) cases with high throughfall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