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

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47

48   **Abstract**

49   Dissolved organic carbon (DOC) in surface waters is connected to DOC in soil solution
50   through hydrological pathways. Therefore, it is expected that long-term dynamics of DOC in
51   surface waters reflect DOC trends in soil solution. However, a multitude of site-studies has
52   failed so far to establish consistent trends in soil solution DOC, whereas increasing
53   concentrations in European surface waters over the past decades appear to be the norm,
54   possibly as a result of recovery from acidification. The objectives of this study were therefore
55   to understand the long-term trends of soil solution DOC from a large number of European
56   forests (ICP Forests Level II plots) and determine their main physico-chemical and biological
57   controls. We applied trend analysis at two levels: 1) to the entire European dataset and 2) to

58   the individual time series and related trends with plot characteristics, i.e., soil and vegetation

59   properties, soil solution chemistry and atmospheric deposition loads. Analyses of the entire

60   dataset showed an overall increasing trend in DOC concentrations in the organic layers, but,

61   at individual plots and depths, there was no clear overall trend in soil solution DOC. The rate

62   change of soil solution DOC ranged between -16.8% yr^{-1} and +23% yr^{-1} (median= +0.4% yr^{-1}

63   ) across Europe. The non-significant trends (40%) outnumbered the increasing (35%) and

64   decreasing trends (25%) across the 97 ICP Forests Level II sites. By means of multivariate

65   statistics, we found increasing trends in DOC concentrations with increasing mean nitrate

66   (NO_3^-) deposition and increasing trends in DOC concentrations with decreasing mean

67   sulphate (SO_4^{2-}) deposition, with the magnitude of these relationships depending on plot

68   deposition history. While the attribution of increasing trends in DOC to the reduction of SO_4^{2-}

69   deposition could be confirmed in low to medium N deposition areas, in agreement with

70   observations in surface waters, this was not the case in high N deposition areas. In

71   conclusion, long-term trends of soil solution DOC reflected the interactions between controls

72   acting at local (soil and vegetation properties) and regional (atmospheric deposition of SO_4^{2-}

73   and inorganic N) scales.

1   Introduction

74

75   Dissolved organic carbon (DOC) in soil solution is the source of much of the terrestrially

76   derived DOC in surface waters (Battin et al., 2009; Bianchi, 2011; Regnier et al., 2013). Soil

77   solution DOC in forests is connected to streams through different hydrological pathways:

78   DOC mobilized in the forest floor may be transported laterally at the interface of forest floor

79   and mineral soil to surface waters or percolates into the mineral soil, where additional DOC

80   can be mobilized and/or DOC is partly adsorbed on particle surfaces and mineralized

81   thereafter (Fig. 1). From the mineral soil DOC may be either leached laterally or vertically

82   via groundwater into surface waters (McDowell and Likens, 1988). Therefore, it could be

83   expected that long-term dynamics of DOC in surface waters mirror those observed in

84   ecosystem soil solutions.

85   Drivers related to climate change (temperature increase, precipitation change, atmospheric

86   CO_2 increase), the decrease in acidifying deposition or land use change and management may

87   individually or jointly explain trends in surface water DOC concentrations (Evans et al.,

88   2012; Freeman et al., 2004; Oulehle et al., 2011; Sarkkola et al., 2009; Worrall and Burt,

89   2004). Increasing air temperatures warm the soil, thus stimulating soil organic matter (SOM)

90   decomposition through greater microbial activity (Davidson and Janssens, 2006; Hartley and

91   Ineson, 2008; Kalbitz et al., 2000). Other drivers, such as increased atmospheric CO_2 and the
92   accumulation of atmospherically deposited inorganic nitrogen are thought to increase the
93   sources of DOC by enhancing primary plant productivity (i.e., through stimulating root
94   exudates or, increased litterfall) (de Vries et al., 2014; Ferretti et al., 2014; Sucker and
95   Krause, 2010). Changes in precipitation, land use and management (e.g. drainage of
96   peatlands, changes in forest management or grazing systems) may alter the flux of DOC
97   leaving the ecosystem but no consistent trends in the hydrologic regime or land use changes
98   were detected in areas where increasing DOC trends have been observed (Monteith et al.,
99   2007).

100   Recent focus was mainly on decreasing acidifying deposition as an explanatory factor for
101   DOC increases in surface waters in Europe and North America by means of decreasing ionic
102   strength (De Wit et al., 2007; Hruška et al., 2009) and increasing the pH of soil solution,
103   consequently increasing DOC solubility (Evans et al., 2005; Haaland et al., 2010; Monteith et
104   al., 2007). Although the hypothesis of an increase in surface water DOC concentration due to
105   a recovery from past acidification was confirmed in studies of soil solution DOC in the UK
106   and northern Belgium (Sawicka et al., 2016; Vanguelova et al., 2010; Verstraeten et al.,
107   2014), it is not consistent with trends in soil solution DOC concentrations reported from
108   Finnish, Norwegian, and Swedish forests (Löfgren and Zetterberg, 2011; Ukonmaanaho et
109   al., 2014; Wu et al., 2010). This inconsistency between soil solution DOC and stream DOC
110   trends could suggest that DOC in surface water and soil solution responds differently to
111   (changes in) environmental conditions in different regions (Akselsson et al., 2013; Clark et
112   al., 2010; Löfgren et al., 2010). Alternatively, other factors such as tree species and soil type,
113   may be co-drivers of organic matter dynamics and input, generation and retention of DOC in
114   soils.

115   Trends of soil solution DOC not only vary among forests but often also within the same site
116   (Borken et al., 2011; Löfgren et al., 2010). Forest characteristics such as tree species
117   composition, soil fertility, texture or sorption capacity may affect the response of soil solution
118   DOC to environmental controls, for instance, by controlling the rate of soil acidification
119   through soil buffering and nutrient plant uptake processes (Vanguelova et al., 2010). Within a
120   site, DOC variability with soil depth is typically caused by different intensity of DOC
121   production, transformation, and sorption along the soil profile (Fig. 1). Positive temporal
122   trends in soil solution DOC (increasing concentrations over time) were frequently reported
123   for the organic layers and shallow soils where production and decomposition processes

124 control the DOC concentration (Löfgren and Zetterberg, 2011). However, no dominant trends
125 are found for the mineral soil horizons, where physico-chemical processes, such as sorption,
126 become more influential (Borken et al., 2011; Buckingham et al., 2008). Furthermore,
127 previous studies have used different temporal and spatial scales which may have further
128 added to the inconsistency in the DOC trends reported in the literature (Clark et al., 2010).

129 In this context, the International Co-operative Programme on Assessment and Monitoring of
130 Air Pollution Effects on Forests (ICP Forests, 2010) compiled a unique dataset containing
131 data from more than 100 intensively monitored forest plots (Level II) which allow to unravel
132 regional trends in soil solution DOC of forests at a European scale, and perform statistical
133 analysis of the main controls behind these regional trends. Long-term measurements of soil
134 solution DOC are available for these plots, along with information on aboveground biomass,
135 soil properties, and atmospheric deposition of inorganic N and SO_4^{2-}, collected using a
136 harmonized sampling protocol across Europe (Ferretti and Fischer, 2013). This dataset has
137 previously been used to investigate the spatial variability of DOC in forests at European scale
138 (Camino-Serrano et al., 2014), but an assessment of the temporal trends in soil solution DOC
139 using this large dataset has not been attempted so far.

140 The main objective of this study is to understand the long-term temporal trends of DOC
141 concentrations in soil solution measured at the ICP Forests Level II plots across Europe.
142 Based on the increasing DOC trends in surface waters, we hypothesize that temporal trends in
143 soil solution DOC will also be positive, but with trends varying locally depending on plot
144 characteristics. We further investigated whether plot characteristics, specifically climate,
145 inorganic N and SO_4^{2-} deposition loads, forest type, soil properties, and changes in soil
146 solution chemistry can explain differences across sites in DOC trends.

2 Materials and Methods

2.1 Data description

149 Soil solution chemistry has been monitored within the ICP Forests Programme since the
150 1990s on most Level II plots. The ICP Forests data were extracted from the pan-European
151 Forest Monitoring Database (Granke, 2013). A list of the Level II plots used for this study
152 can be found in Supplementary material, Table S1. The methods for collection and analysis
153 of soil solution used in the various countries (Switzerland: Graf Pannatier et al. (2011);
154 Flanders: Verstraeten et al. (2012); Finland: Lindroos et al. (2000); UK: Vanguelova et al.

155 (2010), Denmark: Hansen et al. (2007)) follow the ICP Forests manual (Nieminen, 2011).

156 Generally, lysimeters were installed at several fixed depths starting at 0 cm, defined as the

157 interface between the surface organic layer and underlying mineral soil. These depths are

158 typically aligned with soil "organic layer", "mineral topsoil", "mineral subsoil", and "deeper

159 mineral soil" but sampling depths vary among countries and even among plots within a

160 country. Normally, zero-tension lysimeters were installed under the surface organic layer and

161 tension lysimeters within the mineral soil. However, in some countries zero-tension

162 lysimeters were also used within the mineral layers and in some tension lysimeters below the

163 organic layer. Multiple collectors (replicates) were installed per plot and per depth to assess

164 plots spatial variability. However, in some countries, samples from these replicates were

165 pooled before analyses or averaged prior to data transmission. The quality assurance and

166 control procedures included the use of control charts for internal reference material to check

167 long-term comparability within national laboratories as well as participation in periodic

168 laboratory ring tests (e.g., Marchetto et al., 2011) to check the international comparability.

169 Data were reported annually to the pan-European data center, checked for consistency and

170 stored in the pan-European Forest Monitoring Database (Granke, 2013).

171 Soil water was usually collected fortnightly or monthly, although for some plots sampling

172 periods with sufficient soil water for collection were scarce, especially in prolonged dry

173 periods or in winter due to snow and ice. After collection, the samples were filtered through a

174 0.45 μm membrane filter, stored below 4 °C and then analyzed for DOC, together with other

175 soil solution chemical properties (NO_3^-, Ca, Mg, NH_4^+, SO_4^{-2}, total dissolved Al, total

176 dissolved Fe, pH, electrical conductivity). Information on the soil solution chemistry at the

177 studied plots can be found in Supplementary material (Table S4-S11). The precision of DOC

178 analysis differed among the laboratories. The coefficient of variation of repeatedly measured

179 reference material was 3.7% on average. The time span of soil solution time series used for

180 this study ranged from 1991 to 2011, although coverage of this period varied from plot to plot

181 (Supplementary material, Table S1).

182 Soil properties, open field bulk deposition and throughfall deposition of NO_3^-, NH_4^+, and

183 SO_4^{2-}, are measured at the same plots as well as stem volume increment. The atmospheric

184 deposition of NO_3^-, NH_4^+ and SO_4^{2-} data covers the period 1999-2010 (Waldner et al., 2014).

185 Stem volume growth was calculated by the ICP Forests network from diameter at breast

186 height (DBH), live tree status, and tree height which were assessed for every tree (DBH > 5

187 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 $\pm$ 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

220   of inorganic N (NH_4^+ and NO_3^-) and SO_4^{2-} throughfall and open field bulk deposition

221   measured at the plots were interpolated to monthly data (Waldner et al., 2014).

222   The plots were classified according to their forest type (broadleaved/coniferous dominated),

223   soil type (World Reference Base, (WRB 2006)), their stem growth (slow, < 6 m^3 ha^{-1} yr^{-1},

224   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,

225   intermediate, 4.2–5, high, >5). Plots were also classified based on mean throughfall inorganic

226   N (NO_3^- +NH_4^+) deposition level, defined as: high deposition (HD, >15 kg N ha^{-1} yr^{-1}),

227   medium deposition (MD, 5–15 kg N ha^{-1} yr^{-1}), and low deposition (LD, <5 kg N ha^{-1} yr^{-1}) and

228   mean throughfall SO_4^{2-} deposition level, defined as: high deposition (HD, >6 kg S ha^{-1} yr^{-1}),

229   and low deposition (LD, < 6 kg S ha^{-1} yr^{-1}).

2.3   Statistical methods

231   Time series can typically decomposed into random noise, seasonal, and trend components

232   (Verbesselt et al., 2010). In this paper, we used methods to detect the actual trend (change in

233   time) after removing the seasonal and random noise components. The sequence of methods

234   applied is summarized in Fig. 2. The analysis of temporal trends in soil solution DOC

235   concentrations was carried out at two levels: 1) the European level and 2) the plot level.

236   While the first analysis allows an evaluation of the overall trend in soil solution DOC at a

237   continental scale, the second analysis indicates whether the observed large scale trends are

238   occurring at local scales as well, and tests whether local trends in DOC can be attributed to

239   certain driver variables.

240   Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution

241   DOC concentration at the European scale (Fig. 2). For these models, the selected 529 time

242   series were used. For the trend analysis of individual time series, however, we focused on the

243   long-term trends in soil solution DOC at European forests that show monotonicity. Therefore,

244   DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend

245   (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010; Vicca et al.,

246   2016) with the time series showing breakpoints, i.e., not monotonic, being discarded (see

247   Description of the statistical methods in Supplementary material). In total, 258 monotonic

248   time series from 97 plots were used for our analysis after filtering (Fig. 2). Then, monotonic

249   trend analyses were carried out from the filtered dataset using the Seasonal Mann Kendall

250   (SMK) test for monthly DOC concentrations (Hirsch et al., 1982; Marchetto et al., 2013).

251   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).

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). 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. 3 and 4), which made it difficult to draw firm conclusions about the spatial pattern of the trends in soil solution DOC concentrations in European forests.

311 The variability in trends was high, not only at continental scale, but also at plot level (Fig. 5).
312 We found consistent within-plot trends only for 50 out of the 97 sites. Moreover, some plots
313 even showed different trends (P, N or NS) in DOC within the same depth interval, which was
314 the case for 17 plot-depth combinations (16 in Germany and one in Norway), evidencing a
315 high small-scale plot heterogeneity.

316 Trend directions (P, N or NS) often differed among depths. For instance, in the organic layer,
317 we found mainly non-significant trends and, if a trend was detected, it was more often
318 positive than negative, while positive trends were the most frequent in the subsoil (below 40
319 cm) (Table 1). Nevertheless, it is important to note that a statistical test of whether there was
320 a real difference in DOC trends between depths was not possible as the set of plots differed
321 between the different soil depth intervals. However, a visual comparison of trends for the few
322 plots in which trends were evaluated for more than three soil depths showed that there was no
323 apparent difference in DOC trends between soil depths (Supplementary material, Fig. S1 and
324 S2).

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

329 ### 3.3 Factors explaining the soil solution DOC trends

330 ### 3.3.1 Effects of vegetation, soil and climate

331 There was no direct effect of forest type (broadleaved vs. coniferous) on the direction of the
332 statistically significant trends in soil solution DOC (Fig. 6A). Both positive and negative
333 trends were equally found under broadleaved and coniferous forests (χ^2(1, n = 97) = 0.073, p
334 = 0.8). Increasing DOC trends, however, occurred more often under forests with a mean stem
335 growth increment below 6 m^3 ha^{-1} yr^{-1} over the study period, whereas decreasing DOC trends
336 were more common in forests with a mean stem growth increment between 6 and 12 m^3 ha^{-1}
337 yr^{-1} (χ^2(2, n = 53) = 5.8, p = 0.05) (Fig. 6B). Only six forests with a mean stem growth above
338 12 m^3 ha^{-1} yr^{-1} were available for this study (five showing increasing DOC trends and one
339 showing a decreasing DOC trend) and, thus, there is not enough information to draw
340 conclusions about the relationship between stem growth and soil solution DOC trends for
341 forests with very high stem growth (> 12 m^3 ha^{-1} yr^{-1}).

342 The DOC trends also varied among soil types, more than half of the plots showing a
343 consistent increasing DOC trend at all evaluated soil depth intervals were located in
344 Cambisols, (6 out of 11 plots), which are rather fertile soils, whereas plots showing consistent
345 negative trends covered six different soil types. Other soil properties, like clay content, cation
346 exchange capacity or pH, did not clearly differ between sites with positive and negative DOC
347 trends (Table 2). It is remarkable that trends in soil solution pH, Mg and Ca concentrations
348 were similar across plots with both positive and negative DOC trends. Soil solution pH
349 increased distinctly in almost all the sites, while Ca and Mg decreased markedly (Table 2).

350 Finally, no significant correlations were found between trends in temperature or precipitation
351 and trends in soil solution DOC, with the exception of a positive correlation between trends
352 in soil solution DOC in the soil depth interval 20-40 cm and the trend in temperature (r =
353 0.47, $p = 0.03$).

3.3.2 Effects of mean and trends in atmospheric deposition and soil solution parameters

356 Analyzing different models that could explain the DOC trends using the overall dataset
357 indicated both direct and indirect effects of the annual mean SO_4^{2-} and NO_3^- throughfall
358 atmospheric deposition on the trend slopes of DOC. The Structural Equation Model
359 accounted for 32.7% of the variance in DOC trend slopes (Fig. 7A). According to this model,
360 lower mean throughfall SO_4^{2-} deposition resulted in increasing trend slopes of DOC in soil
361 solution and higher mean throughfall NO_3^- deposition resulted in increasing trend slopes of
362 DOC (Fig. 7A). When considering trends in SO_4^{2-} and NO_3^- deposition, there was no
363 apparent spatial correlation with soil solution DOC trends, with deposition mainly decreasing
364 or not changing over time (Fig. 8) and the DOC trends varying greatly across Europe (Fig. 3
365 and 4). However, when SEM was run using the trend slopes in SO_4^{2-} and NO_3^- deposition
366 instead of the mean values, we found that trend slopes of DOC significantly increased with
367 increasing trend in NO_3^- and decreased with increasing trend in SO_4^{2-} deposition, but the
368 latter was a non-significant relationship (Supplementary Material, Fig. S3). However, the
369 percentage of variance in DOC trend slopes explained by the model was much twice lower
370 (16%).

Sites with low and medium N deposition

372 The variables in the model that best explained the temporal changes in DOC were the same
373 for the forests with low and medium N deposition; for both groups, NO_3^- deposition and

374   SO_4^{2-} deposition (directly, or indirectly through its influence on plant growth) influenced the

375   trend in DOC (Fig. 7B). Lower mean SO_4^{2-} deposition again resulted in a significant increase

376   in trend slopes, while increasing NO_3^- deposition resulted in increasing DOC trend slopes.

377   The percentage of variance in DOC trend slopes explained by the model was 33%. The SEM

378   run with the trends in SO_4^{2-} and NO_3^- throughfall deposition for forests with low and medium

379   N deposition explained 24.4% of the variance in DOC trends, and showed a significant

380   increase of trend slopes of DOC with decreasing trend in SO_4^{2-} deposition (Supplementary

381   Material, Fig. S3).

382   **Sites with high N deposition**

383   For the plots with high N deposition, however, we found no model for explaining the trends

384   in DOC using the mean annual SO_4^{2-} and NO_3^- throughfall deposition. In contrast, the best

385   model included the relative trend slopes in SO_4^{2-} and NO_3^- deposition as well as in median

386   soil solution conductivity (% yr^{-1}) as explaining variables (Fig. 7C). Increasing the relative

387   trend slopes of NO_3^- deposition resulted in increasing the DOC trend slopes. Also both the

388   trend slopes of SO_4^{2-} and NO_3^- deposition affected the trend slopes of DOC indirectly through

389   an effect on the trends in soil solution conductivity, although acting in opposite directions:

390   while increasing NO_3^- deposition led to decreasing soil solution conductivity, increasing

391   SO_4^{2-} deposition resulted in increasing trends in soil solution conductivity, but the latter

392   relationship was only marginally significant (p=0.06). Increasing trends in conductivity, in

393   turn, resulted in increasing trend slopes of DOC. The percentage of the variance in DOC

394   trend slopes explained by the model was 25% (Fig. 7C). Nevertheless, trends in soil solution

395   DOC were not directly affected by trends in SO_4^{2-} deposition in forests with high N

396   deposition.

397   **4   Discussion**

398   **4.1   Trend analysis of soil solution DOC in Europe**

399   **4.1.1   Evaluation of the trend analysis techniques**

400   A substantial proportion (40%) of times series did not indicate any significant trend in site-

401   level DOC concentrations across the ICP Forests network. Measurement precision, strength

402   of the trend, and the choice of the method may all affect trend detection (Sulkava et al., 2005;

403   Waldner et al., 2014). Evidently, strong trends are easier to detect than weak trends. To detect

404   a weak trend, either very long time series or very accurate and precise datasets are needed.

405 The quality of the data is assured within the ICP Forests by means of repeated ring tests that
406 are required for all participating laboratories and the accuracy of the data has been improved
407 considerably over an eight years period (Ferretti and König, 2013; König et al., 2013).
408 However, the precision and accuracy of the dataset still varies across countries and plots. We
409 enhanced the probability of trend detection by the SMK, PMK, and BFAST tests by
410 removing time series with breakpoints caused by artifacts (such as installation effects).

411 Nevertheless, we found a majority of non-significant trends. For these cases, we cannot state
412 with certainty that DOC did not change over time: it might be that the trend was not strong
413 enough to be detected, or that the data quality was insufficient for the period length available
414 for the trend analysis (more than 9 years in all the cases). For example, the mixed-effects
415 models detected a positive trend in the organic layer, and while many of the individual time
416 series measured in the organic layer also showed a positive trend, most were classified as
417 non-significant trends (Table 1; Fig. 3). This probably led to an underestimation of trends that
418 separately might not be strong enough to be detected by the individual trend analysis but
419 combined with the other European data these sites may contribute to an overall trend of
420 increasing DOC concentrations in soils of European forests. Nevertheless, the selected trend
421 analysis techniques (SMK and PMK) are the most suitable to detect weak trends (Marchetto
422 et al., 2013; Waldner et al., 2014), thus reducing the chances of hidden trends within the non-
423 significant trends category.

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

4.1.2 Analysis of breakpoints in the time series

433 Soil solution DOC time series measured with lysimeters are subject to possible interruptions
434 of monotonicity, which is manifested by breakpoints. For instance, installation effect,
435 collector replacement, local forest management, disturbance by small animals, or by single or
436 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. 5). 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,

469 and an increasing trend in soil solution DOC concentration under 80 cm depth only when the
470 entire dataset (with breakpoints) was analyzed. The individual trend analyses confirmed the
471 increasing trend under the organic layer (Table 1), while more heterogeneous trends in the
472 mineral soil were found, which is in line with previous findings (Borken et al., 2011; Evans et
473 al., 2012; Hruška et al., 2009; Löfgren and Zetterberg, 2011; Sawicka et al., 2016;
474 Vanguelova et al., 2010). This difference has been attributed to different processes affecting
475 DOC in the organic layer and top mineral soil and in the subsoil. External factors such as acid
476 deposition may have a more direct effect in the organic layer where interaction between DOC
477 and mineral phases is less important compared to deeper layers of the mineral soil (Fröberg et
478 al., 2006). However, DOC measurements are not available for all depths at each site,
479 complicating the comparison of trends across soil depth intervals. Hence, the depth-effect on
480 trends in soil solution DOC cannot be consistently addressed within this study (see
481 Supplementary material, Fig. S1, Fig. S2).

482 Finally, the direction of the trends in soil solution DOC concentrations did not follow a clear
483 regional pattern across Europe (Fig. 3 and 4) and even contrasted with other soil solution
484 parameters that showed widespread trends over Europe, such as decreasing SO_4^{2-} and
485 increasing pH. This finding indicates that effects of environmental controls on soil solution
486 DOC concentrations may differ depending on local factors like soil type (e.g., soil acidity,
487 texture) as well as site and stand characteristics (e.g., tree growth or acidification history).
488 Thus, the trends in DOC in soil solution appear to be an outcome of interactions between
489 controls acting at local and regional scales.

490 In order to compare soil solution DOC trends among sites, trends of DOC concentrations are
491 always expressed in relative trends (% yr^{-1}). By using the relative trends, we removed the
492 effect of the median DOC concentration at the "plot-depth" combination and, consequently,
493 the results do not reflect the actual magnitude of the trend, but their importance in relation
494 with the median DOC concentration at the "plot-depth" combination. It implies that the
495 interpretation of our results was done only in relative terms (see Supplementary Material,
496 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 and 7). .

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. 3,4 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.

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. 7). 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.

561 Similar to our observation for soil solution DOC, decreasing SO_4^{2-} deposition has been linked

562 to increasing surface water DOC (Evans et al., 2006; Monteith et al., 2007; Oulehle and

563 Hruska, 2009). Sulphate deposition triggers soil acidification and a subsequent release of Al^{3+}

564 in acid soils. The amount of Al^{3+} is negatively related to soil solution DOC due to two

565 plausible mechanisms: 1) The released Al^{3+} can build complexes with organic molecules,

566 enhancing DOC precipitation and, in turn, suppressing DOC solubility, thereby decreasing

567 DOC concentrations in soil solution (de Wit et al., 2001; Tipping and Woof, 1991;

568 Vanguelova et al., 2010), and 2) at higher levels of soil solution Al^{3+} in combination with low

569 pH, DOC production through SOM decomposition decreases due to toxicity of Al^{3+} to soil

570 organisms (Mulder et al., 2001). Consequently, when SO_4^{2-} deposition is lower, increases of

571 soil solution DOC concentration could be expected (Fig. 7A, B). Finally, an indirect effect of

572 plant response to nutrient-limited acidified soil could also contribute to the trend in soil

573 solution DOC by changes to plant belowground C allocation (Vicca et al., 2012) (see Sect.

574 4.2.1.).

575 Nevertheless, increasing DOC soil solution concentration as a result of decreasing SO_4^{2-}

576 deposition occurred only at sites with low or medium mean N deposition. Therefore, our

577 results indicate that the response of DOC to changes in atmospheric deposition seems to be

578 controlled by the past and present inorganic N deposition loads (Clark et al., 2010; Evans et

579 al., 2012; Tian and Niu, 2015). It suggests that the mechanisms of recovery from SO_4^{2-}

580 deposition and acidification take place only in low and medium N deposition areas, as has

581 been observed for inorganic N deposition effects (de Vries et al., 2009). In high inorganic N

582 deposition areas, it is likely that impacts of N-induced acidification on forest health and soil

583 condition lead to more DOC leaching, even though SO_4^{2-} deposition has been decreasing.

584 Therefore, the hypothesis of recovery from acidity cannot fully explain overall soil solution

585 DOC trends in Europe, as was also previously suggested in local or national studies of long-

586 term trends in soil solution DOC (Löfgren et al., 2010; Stutter et al., 2011; Ukonmaanaho et

587 al., 2014; Verstraeten et al., 2014). Collinearity between SO_4^{2-} deposition and inorganic N

588 deposition was low (variance inflation factor <3) for both the mean values and temporal

589 trends. We therefore assumed that the proposed response of DOC to the decline in SO_4^{2-}

590 deposition in low to medium N areas is not confounded by simultaneous changes in SO_4^{2-} and

591 NO_3^- deposition, even more so because the statistical models account for the covariation in

592 SO_4^{2-} and NO_3^- deposition (Figure 7). Nonetheless, as SO_4^{2-} and NO_3^- deposition are

593   generally decreasing across Europe (Figure 8), concomitant changes in NO_3^- deposition may

594   still have somewhat confounded the attribution of DOC changes solely to SO_4^{2-} deposition.

595   Ultimately, internal soil processes control the final concentration of DOC in the soil solution.

596   The solubility and biological production and consumption of DOC are regulated by pH, ionic

597   strength of the soil solution and the presence of Al^{3+} and Fe (Bolan et al., 2011; De Wit et al.,

598   2007; Schwesig et al., 2003). These conditions are modulated by changes in atmospheric

599   deposition but not uniformly across sites: soils differ in acid-buffering capacity (Tian and

600   Niu, 2015), and the response of DOC concentrations to changes in SO_4^{2-} deposition will thus

601   be a function of the initial soil acidification and buffer range (Fig. 7). Finally, modifications

602   of soil properties induced by changes in atmospheric deposition are probably an order of

603   magnitude lower than the spatial variation of these soil properties across sites, making it

604   difficult to isolate controlling factors on the final observed response of soil solution DOC at

605   continental scale (Clark et al., 2010; Stutter et al., 2011).

606   In conclusion, our results confirm the long-term trends of DOC in soil solution as a

607   consequence of the interactions between local (soil properties, forest growth), and regional

608   (atmospheric deposition) controls acting at different temporal scales. However, further work

609   is needed to quantify the role of each mechanism underlying the final response of soil

610   solution DOC to environmental controls. We recommend that particular attention should be

611   paid to the biological controls (e.g., net primary production, root exudates or litterfall and

612   canopy infestations) on long-term trends in soil solution DOC, which remains poorly

613   understood.

4.3   Link between DOC trends in soil and streams

615   An underlying question is how DOC trends in soil solution relate to DOC trends in stream

616   waters. Several studies have pointed out recovery from acidification as a cause for increasing

617   trends in DOC concentrations in surface waters (Dawson et al., 2009; Evans et al., 2012;

618   Monteith et al., 2007; Skjelkvåle et al., 2003). Overall, our results point to a noticeable

619   increasing trend in DOC in the organic layer of forest soils, which is qualitatively consistent

620   with the increasing trends found in stream waters and in line with positive DOC trends

621   reported for the soil organic layer or at maximum 10 cm depth of the mineral soil in Europe

622   (Borken et al., 2011; Hruška et al., 2009; Vanguelova et al., 2010). DOC from the organic

623   layer may be transferred to surface waters via hydrologic shortcuts during storm events, when

624 shallow lateral flow paths are activated. On the other hand, trends in different soil layers
625 along the mineral soil were more variable and responded to other soil internal processes.

626 It is currently difficult to link long-term dynamics in soil and surface water DOC. Large scale
627 processes become more important than local factors when looking at DOC trends in surface
628 waters (Lepistö et al., 2014), while the opposite seems to apply for soil solution DOC trends.
629 Furthermore, stream water DOC mainly reflects the processes occurring in areas with a high
630 hydraulic connectivity in the catchment, such as peat soils or floodplains, which normally
631 yield most of the DOC (Ledesma et al., 2016; Löfgren and Zetterberg, 2011). Further
632 monitoring studies in forest soils with high hydraulic connectivity to streams are needed to be
633 able to link dynamics of DOC in forest soil with dynamics of DOC in stream waters.

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

5   Conclusions

645 Different monotonic long-term trends of soil solution DOC have been found across European
646 forests at plot scale, with the majority of the trends for specific plots and depths not being
647 statistically significant (40%), followed by significantly positive (35%) and significantly
648 negative trends (25%). The distribution of the trends did not follow a specific regional
649 pattern. A multivariate analysis revealed a negative relation between long-term trends in soil
650 solution DOC and mean SO_4^{2-} deposition and a positive relation to mean NO_3^- deposition.
651 While the hypothesis of increasing trends of DOC due to reductions of SO_4^{2-} deposition could
652 be confirmed in low to medium N deposition areas, there was no significant relationship with
653 SO_4^{2-} deposition in high N deposition areas. There was evidence that an overall increasing
654 trend of DOC concentrations occurred in the organic layers and, to a lesser extent, in the deep
655 mineral soil. However, trends in the different mineral soil horizons were highly

656 heterogeneous, indicating that internal soil processes control the final response of DOC in
657 soil solution. Although correlative, our results suggest that there is no single mechanism
658 responsible for soil solution DOC trends operating at large scale across Europe but that
659 interactions between controls operating at local (soil properties, site and stand characteristics)
660 and regional (atmospheric deposition changes) scales are taking place.

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References

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

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

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

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

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

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

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

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

705   Camino-Serrano, M., Gielen, B., Luyssaert, S., Ciais, P., Vicca, S., Guenet, B., De Vos, B.,
706   Cools, N., Ahrens, B., Arain, M. A., Borken, W., Clarke, N., Clarkson, B., Cummins, T.,
707   Don, A., Pannatier, E. G., Laudon, H., Moore, T., Nieminen, T. M., Nilsson, M. B., Peichl,
708   M., Schwendenmann, L., Siemens, J., and Janssens, I.: Linking variability in soil solution
709   dissolved organic carbon to climate, soil type, and vegetation type, Global Biogeochem Cy,
710   28, 497-509, 2014.

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

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

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

719   Dawson, J. J. C., Malcolm, I. A., Middlemas, S. J., Tetzlaff, D., and Soulsby, C.: Is the
720   Composition of Dissolved Organic Carbon Changing in Upland Acidic Streams?, Environ Sci
721   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.

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

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

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

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

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

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

774 Haaland, S., Hongve, D., Laudon, H., Riise, G., and Vogt, R. D.: Quantifying the Drivers of
775 the Increasing Colored Organic Matter in Boreal Surface Waters, Environ Sci Technol, 44,
776 2975-2980, 2010.

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

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

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

785 Haylock, M. R., Hofstra, N., Tank, A. M. G. K., Klok, E. J., Jones, P. D., and New, M.: A
786 European daily high-resolution gridded data set of surface temperature and precipitation for
787 1950-2006, J Geophys Res-Atmos, 113, 2008.

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

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

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

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

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

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

806 Kvaalen, H., Solberg, S., Clarke, N., Torp, T., and Aamlid, D.: Time series study of
807 concentrations of SO42- and H+ in precipitation and soil waters in Norway, Environ Pollut,
808 117, 215-224, 2002.

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

811 Ledesma, J. L. J., Futter, M. N., Laudon, H., Evans, C. D., and Kohler, S. J.: Boreal forest
812 riparian zones regulate stream sulfate and dissolved organic carbon, Sci Total Environ, 560,
813 110-122, 2016.

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

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

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

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

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

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

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

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

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

836 Moffat, A. J., Kvaalen, H., Solberg, S., and Clarke, N.: Temporal trends in throughfall and
837 soil water chemistry at three Norwegian forests, 1986-1997, Forest Ecol Manag, 168, 15-28,
838 2002.

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

843 Mulder, J., De Wit, H. A., Boonen, H. W. J., and Bakken, L. R.: Increased levels of
844 aluminium in forest soils: Effects on the stores of soil organic carbon, Water Air Soil Poll,
845 130, 989-994, 2001.

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

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

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

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

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

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

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

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

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

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

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

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

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

884 Sebestyen, S. D., Boyer, E. W., and Shanley, J. B.: Responses of stream nitrate and DOC
885 loadings to hydrological forcing and climate change in an upland forest of the northeastern
886 United States, J Geophys Res-Biogeo, 114, 2009.

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

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

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

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

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

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

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

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

906 Tranvik, L. J. and Jansson, M.: Climate change - Terrestrial export of organic carbon, Nature,
907 415, 861-862, 2002.

908 Ukonmaanaho, L., Starr, M., Lindroos, A. J., and Nieminen, T. M.: Long-term changes in
909 acidity and DOC in throughfall and soil water in Finnish forests, Environ Monit Assess, 186,
910 7733-7752, 2014.

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

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

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

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

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

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

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

934 Waldner, P., Marchetto, A., Thimonier, A., Schmitt, M., Rogora, M., Granke, O., Mues, V.,
935 Hansen, K., Karlsson, G. P., Zlindra, D., Clarke, N., Verstraeten, A., Lazdins, A.,
936 Schimming, C., Iacoban, C., Lindroos, A. J., Vanguelova, E., Benham, S., Meesenburg, H.,
937 Nicolas, M., Kowalska, A., Apuhtin, V., Napa, U., Lachmanova, Z., Kristoefel, F., Bleeker,
938 A., Ingerslev, M., Vesterdal, L., Molina, J., Fischer, U., Seidling, W., Jonard, M., O'Dea, P.,
939 Johnson, J., Fischer, R., and Lorenz, M.: Detection of temporal trends in atmospheric
940 deposition of inorganic nitrogen and sulphate to forests in Europe, Atmos Environ, 95, 363-
941 374, 2014.

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

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

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

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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

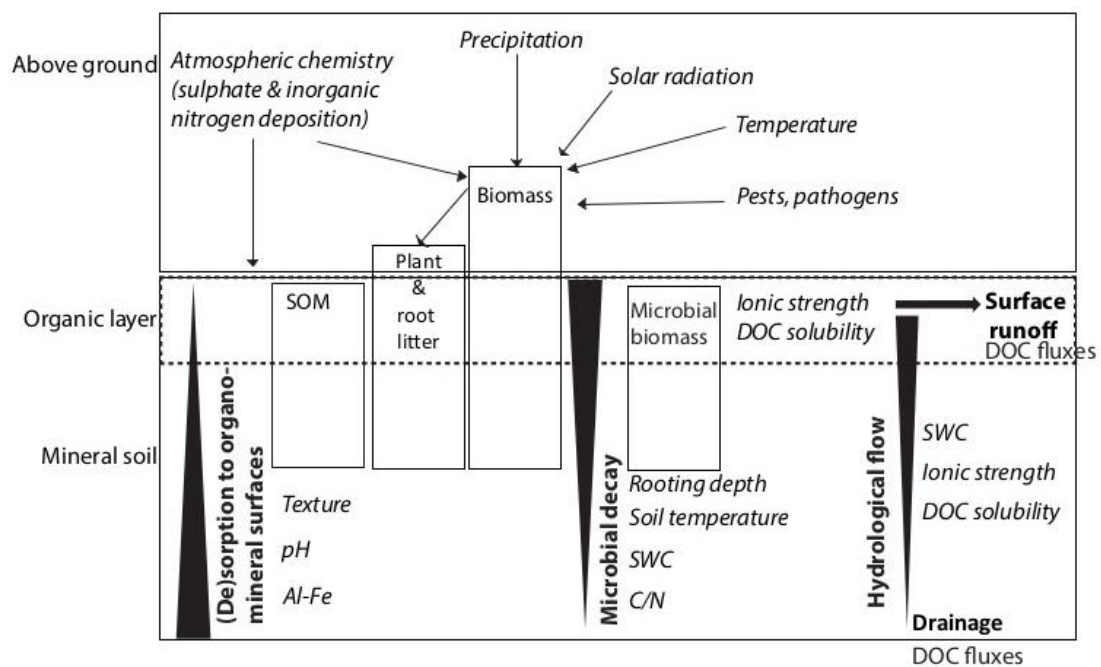
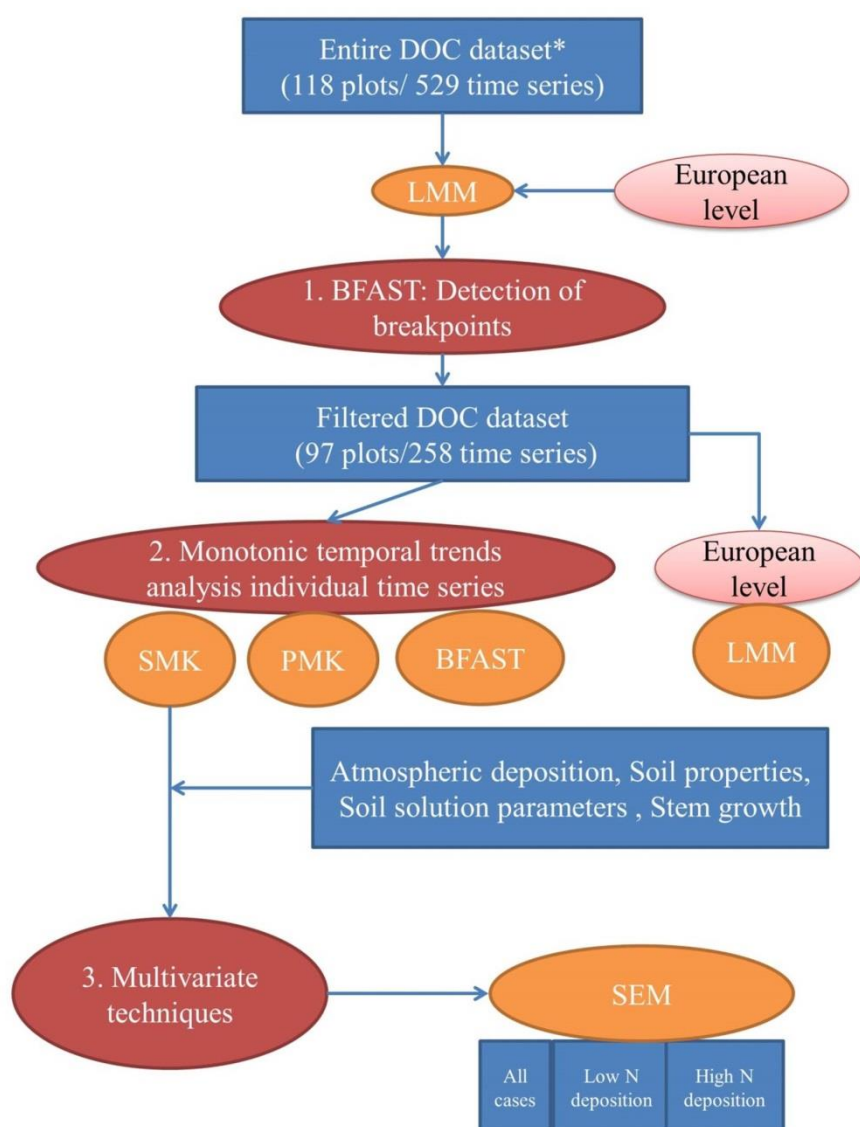



Figure 1. Schematic diagram illustrating the main sources (in boxes) of dissolved organic carbon (DOC) and the main processes (in bold) and factors (in italics) controlling DOC.

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

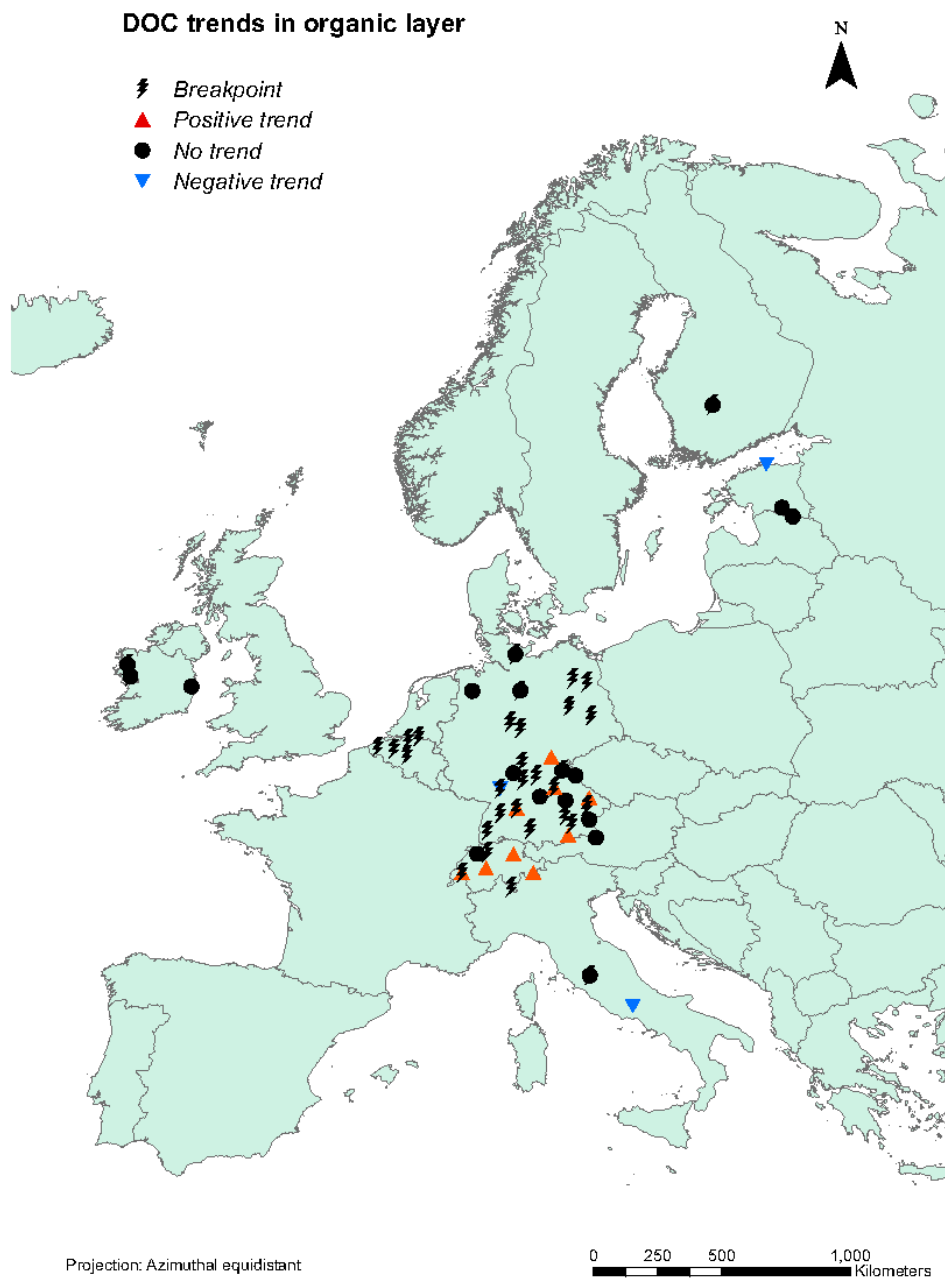



Figure 3. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

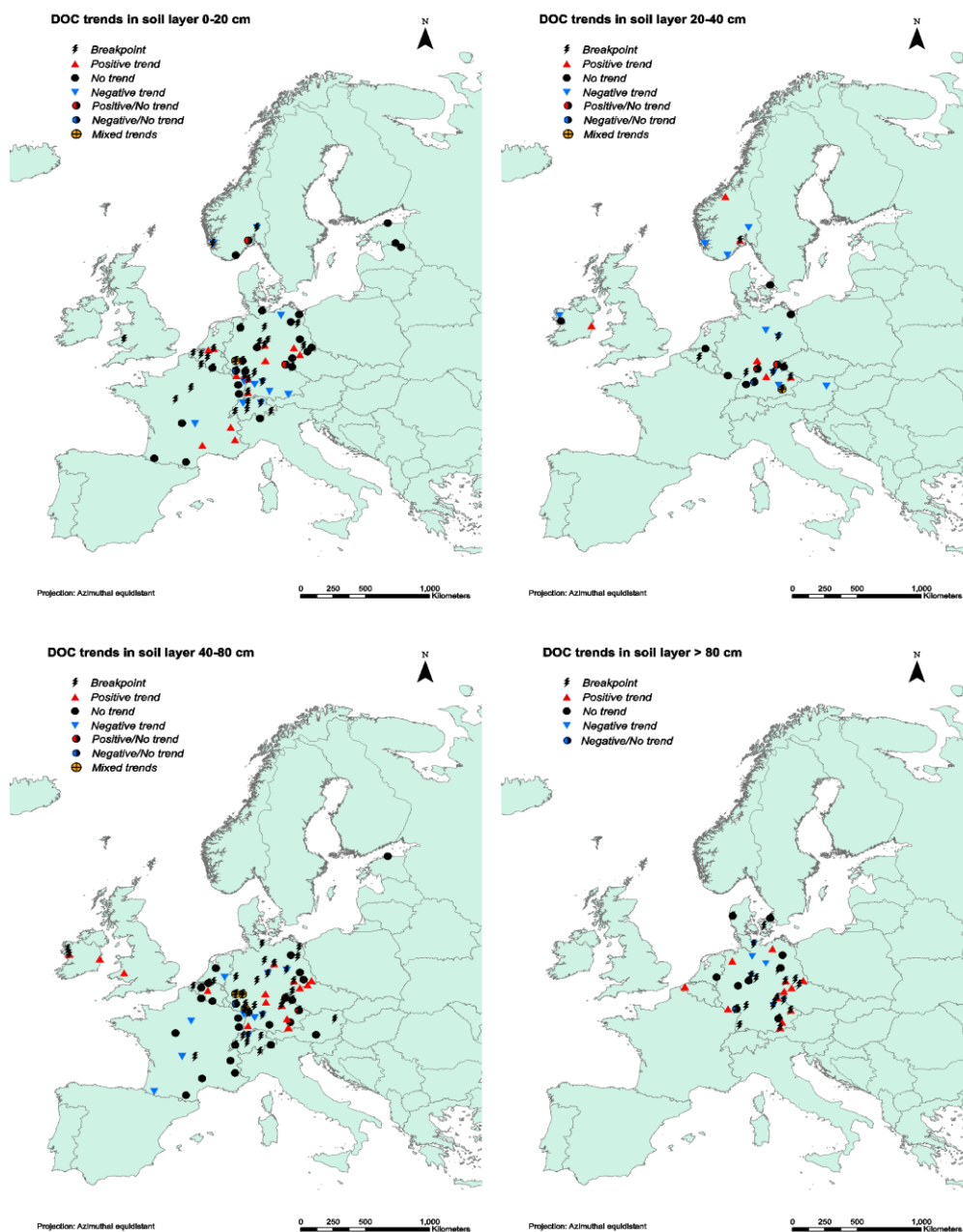



Figure 4. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0–20 cm), b) intermediate (20–40 cm), c) subsoil (40–80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1991 to 2011.

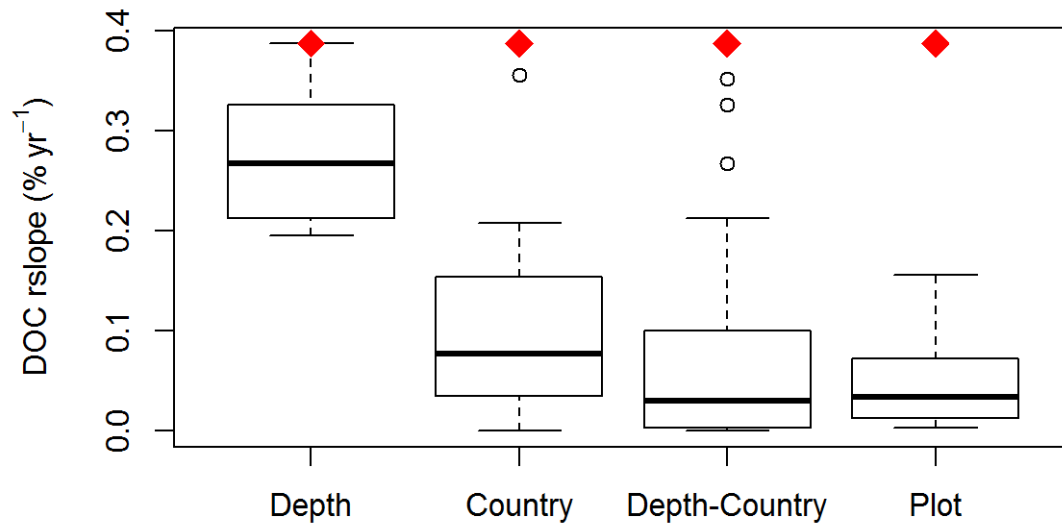



Figure 5. Range of relative trend slopes (max-min) for trends of DOC concentration in soil solution within each 1) depth interval, 2) country, 3) depth interval per country, and 4) plot. The boxplots show the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers) and higher values (circles). The red diamond marks the maximum range of slopes in soil solution DOC trends in the entire dataset.

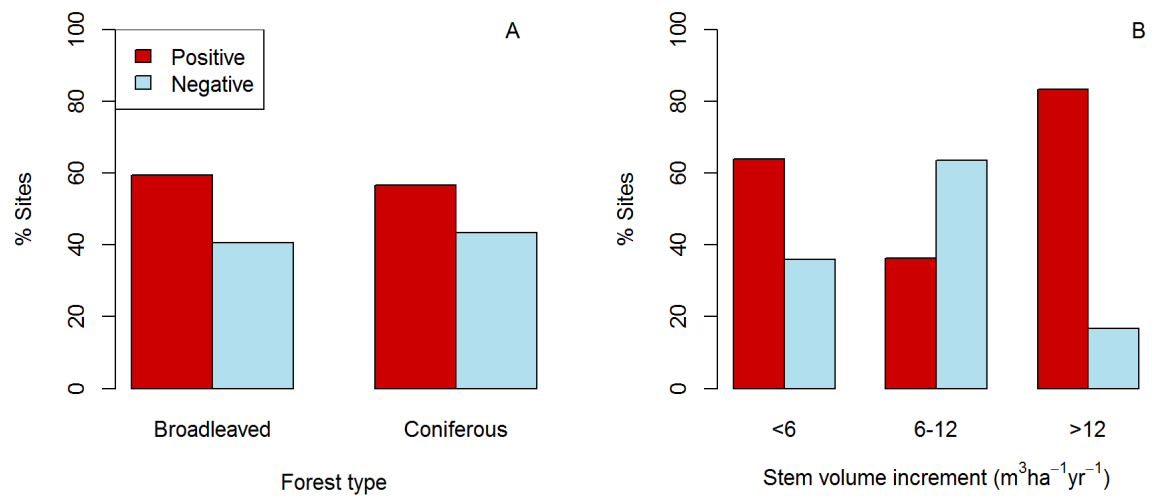



Figure 6. Percentage of occurrence of positive and negative trends of DOC concentration in soil solution separated by A) forest type and B) stem volume increment (m^3 ha^{-1} yr^{-1}).

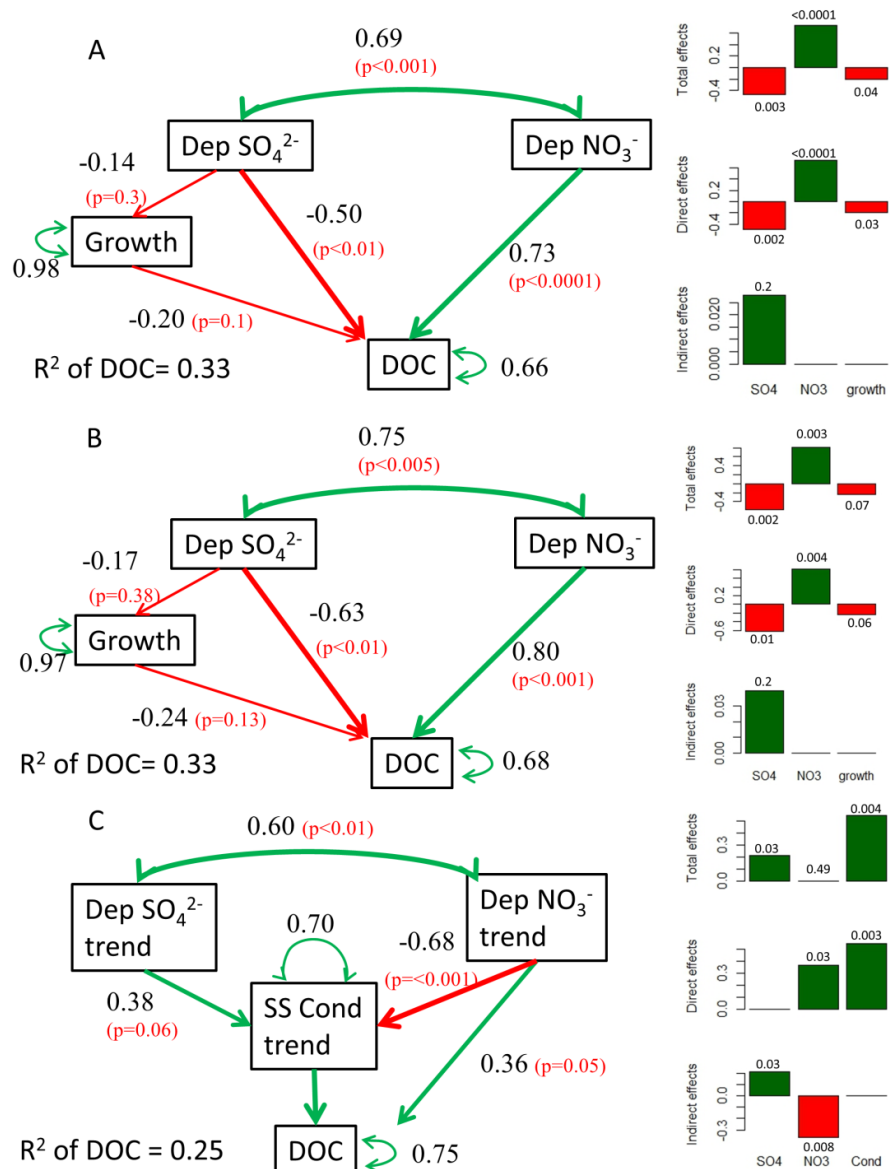



Figure 7. Diagrams of the structural equation models (SEM) that best explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium throughfall inorganic N deposition (< 15 kg N ha^{-1} yr^{-1}), and C) cases with high throughfall inorganic N deposition (>15 kg N ha^{-1} yr^{-1}) with mean or trends in annual SO$_4^{2-}$ and NO$_3^-$ deposition (% 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.

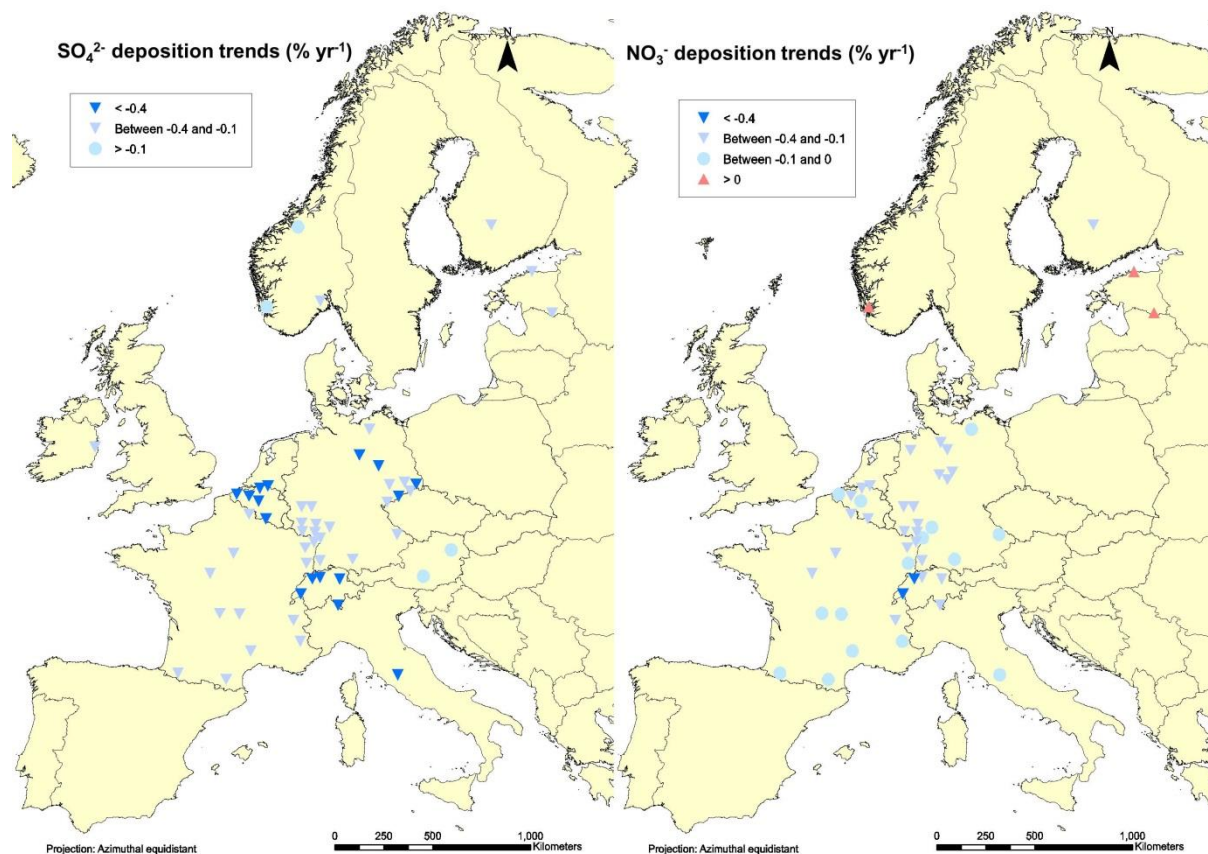



Figure 8. Temporal trends in a) throughfall SO_4^{2-} deposition and b) throughfall NO_3^- deposition at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span from 1999 to 2010.