Answers to Referee 1

General comments

1. In the manuscript and supplement, there is no information on the soil solution chemistry at the studied plots. A quantitative description of the concentrations of DOC and other relevant water chemical parameters is missing. This information could be given in tables and figures in manuscript and supplementary materials, describing e.g. median values, 25- and 75-percentiles and number of observations or in boxplots. The information should be available separated on collector type and soil layer (cf. Table 1) for all classes used in the assessment (forest type, soil type, soil pH, N and S depositions).

We agree that a quantitative description of the concentrations of DOC is missing. We have added tables to the Supplementary Material with the median values, 25- and 75- percentiles and number of observations of DOC, and other water chemical parameters: pH, conductivity, Ca, Mg, SO_4^{2-}, NO_3^-, Al^{3+}(Tables S4 to S11, pages 21-27 in the Supplementary Material of the revised manuscript). The information is separated on collector type, soil layer and forest type, as for Table 1 in submitted manuscript.

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2. The above information should be used for assessing how the standardized trends (rslope) are affected by the median concentrations (see comment 3) and for defining whether the statistically significant rslope trends in the filtered data (LMM, SMK and PMK) are found over the entire DOC concentration range or within certain intervals. Additionally, what does the statistically significant rslope trends correspond to in DOC concentration trends? Are they quantitatively large or not?

To determine whether the absolute trend in DOC is quantitatively large or not from an ecological perspective, we used the median DOC as a reference. That is, we calculated the relative (standardized) trend slope dividing the absolute trend slope by the median DOC level. Nevertheless, since the aim of this paper is to understand the soil solution DOC trends at European level, being able to compare them among sites and soil depths, we discussed the results from a relative point of view. The quantification of the DOC trends at individual plots are, however, beyond the scope of this study.

In Supplementary Material of the revised manuscript we have added a new figure (Figure S5, page 20), showing the effect of the median DOC levels on the relative and absolute trend slopes. We saw that, a priori, there was no relationship between median DOC concentrations and DOC trend slopes. This Figure was also useful to support the discussion about the potential effect that our decision of using the standardized slopes may have, i.e., exaggerating the DOC trends at low DOC levels, such as may occur in the subsoil (see Comment 3).

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3. The trends are reported in standardized terms (rslope), which means that the slope (Sen slope) of each time series was divided by the median concentration over the studied period. This implies that the rslope-value can be identical regardless of the DOC concentration level. Hence, rslope will be 0.1 if you have a trend of 0.2 mg DOC yr-1 and a median DOC concentration of 2 mg l-1 at one plot-soil depth as well as if the trend is 5 mg DOC yr-1 at 50 mg DOC l-1 at another plot-soil depth. The significance of the latter example is of course much larger than in the former. Are e.g. the statistical trends in deep mineral soils (Table 1, layer M8) a result of this phenomenon?

We used the standardized slopes instead of the absolute trend slopes for our analysis in order to remove the effect that the DOC concentration levels have on the absolute DOC trends. Standardizing the slopes allows us for comparisons in trends among soil layers, which have very different DOC values. Otherwise, using the absolute trends will introduce a bias when we try to explain the DOC trends with other parameters, because the trend slope will be highly dependent on the median DOC concentrations of the site.

It is indeed true that by standardizing the slopes (rslopes), we may have identical DOC trend slopes for two sites with very different mean DOC concentrations. It is also true that DOC concentration decreases with depth and is therefore lower in the deep mineral soil than in the upper mineral soil. However, in our opinion, the detected trends in mineral soils are not less important because DOC concentrations are lower. In fact, as previously commented, we decided to use the standardized slopes to be able to compare trends amongst sites, independently of the absolute DOC concentrations.

Nevertheless, expressing the trend slopes in relative terms influence the magnitude and thus can affect our interpretation of the results but has no influence on the significance and direction of the trends, as the statistical analyses (LMM, SMK and PMK) were done on the absolute value and were then transformed to facilitate the interpretation. Thus, the standardization of the slopes did not affect the statistical tests itself (carried out on the absolute values of DOC).

To address this issue of the absolute versus relative DOC trend slopes, we have added a new section in Supplementary Material with a more detailed discussion on it (pages 18-20 in Supplementary Material of the revised version).

Moreover, in order to provide all the information to the reader, we have added the median DOC concentration in the table reporting the trends in the revised manuscript (Table 1).

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4. Evaluating hundreds of time series may introduce random effects affecting the number of statistically significant trends. The theoretical and if possible quantitative implication of this (false positive and false negative trends) should be discussed.

To check how robust the significant tests are we did an extra test (not included in the manuscript). We considered the trend tests to be significant at the 0.01 level, instead of 0.05, and compared the number of significant and non-significant trends (Table 1):

Table 1. Comparison significant positive, negative and non-significant at $p<0.05$ and $p<0.01$.

	Significant positive	Significant negative	Non-significant
p<0.05	91	63	104
p<0.01	70	50	138

We can see that, at the 0.05 level, out of the 258 tests, we would expect to see a significance just by chance (type I error) in 13 cases, so about 6-7 in positive and about 6-7 in negative direction. As we detected many more trends in both direction, most of the significant results are not a type I error but are genuine effects. Moreover, the fact that we found many trends in both positive and negative direction implies that patterns vary across Europe, an argument that also stands if we test at the 0.01 level. Therefore, we believe that we can trust that the conclusions based on trends at 0.05 level are correct.

Finally, the results from the Linear Mixed Models (LMM), also presented in the manuscript (Table 1 in submitted manuscript), are not subject to this issue.

We have added this discussion in section 4.1.1.of the revised manuscript (lines 421-428).

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5. Using relative data in multivariate statistical models like GDA, may cause biased results strongly exaggerating the effects of trends in low DOC-concentration soil horizons. A discussion on the latter is missing.

We decided to use relative data in the multivariate statistical models to be able to compare trends among sites and soil layers (see answer to comment 3). Although it is not ideal, soil layers had to be mixed to compute the multivariate statistical analysis due to lack of data. We acknowledged this limitation of our study in a section of the Supplementary Material (pages 13-14). However, it is true that a discussion on the effects of this choice is missing. This discussion has been added in Supplementary Material in the revised manuscript, with mention to the potential exaggeration of the effects of trends in low DOC-concentration soil horizons (page 18-20 in Supplementary Material of the revised version).

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6. Throughout the manuscript, the information gained from comments 1-3 should be commented where relevant. The information is especially important for the results and discussions dealing with the directions and controls on soil solution temporal trends (Chapters 3.1 and 4.2) partly based on the GDA and SEM results. Are the indicated effects quantitatively important, do they occur both at low and high DOC concentrations in soil solution and has the DOC concentration level any influence on the trend strength and direction?

The controls on soil solution DOC trends have been discussed from a relative point of view, as we focused on explaining the high heterogeneity of DOC trends found across Europe, instead of the quantification of the trends at local scale. We have added an explanatory sentence at the end of Section 4.1.3 (lines 487-493 in revised manuscript), but, to avoid making the manuscript even longer, a more detailed explanation on the use of relative versus absolute slopes and the effect of DOC concentration levels has been added in Supplementary Material (pages 18-20). We decided to add this information in Supplementary Material because the main issue raised by referee number 2 was to synthesize the paper to clarify the message, and we also believe that adding more information to the main manuscript will make it more difficult to understand.

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7. The title of chapter 4.1.1 as well as some of the text are obscure. The number of non-significant trends is determined by the data and the statistical methods used. The authors themselves have selected data after quality check and chosen the statistical methods including probabilities to accept or reject trends. By speculating on whether the non-significant trends are real or not, the authors seem to reject their own data and methods? Change title and remove these speculations, but keep the general discussions on factors affecting trend analysis including what you have found related to comment 4 (see above).

In this section, we do not aim to reject our own data and methods, but to discuss potential (and unavoidable) limitations of the methods selected, such as the length of the time series, or the strength of the trends in the time series of our dataset. However, we agree that this section needed to be reformulated and the title of chapter 4.1.1. has been changed to “Evaluation of the trend analysis techniques”, the last paragraph has been deleted and the discussion mentioned in reply to comment 4 has been added in the revised manuscript (lines 421-428).

Detailed comments

1. Lines 71-81: Riparian zones and peat lands, the most important DOC sources for surface waters are not referred to. Add some text and references.

In the introduction, we focused on forest soils because our study deals only with forest soils. We believe that adding text and references on the importance of riparian zones and peat lands will just extend the introduction and probably interrupt the flow of the text.

2. Line 205: ". . .more than 60 observations of soil solution DOC of individual or groups of collectors". What do the 60 observations refer to? Individual or groups of collectors? If the latter, was it pooled composite samples?

As mentioned previously in the manuscript (line 164-165), in some countries, samples from these replicates were pooled before analyses or averaged prior to data transmission. Therefore, we selected time series with more than 60 observations from individual or groups of collectors, when the samples were pooled before analysis or prior to data transmission.

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3. Line 209: In Figure 1, the number is 436 time series instead of 529. Which figure is the correct one?

Both 436 and 529 are correct numbers, but they refer to different stages of the study: 529 in the number of time series for the entire dataset and 436 is the number of time series after aggregating per plot-soil depth combinations. In the revised manuscript, we have changed the number in Figure 1 for consistency (from 436 to 529). Moreover, a table clearly explaining where the different numbers of time series come from has been added in Supplementary Material (Table S2, pages 11-12 in Supplementary Material), as it seemed to be confusing throughout the manuscript.

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4. Line 218: Did you use the same pH ranges for all soil horizons? If so, you may have a bias towards organic and upper mineral soil horizons in the Low pH class. Additionally it is not clear whether it is soil pH as stated in text or in soil solution as stated in Figure 9? Clarify!

Yes, we used the same pH ranges for all the soil horizons and as a consequence we have more organic soil horizons in the Low pH class (Table 1).

Table 1. Number of cases at high and low pH classified by organic layer.

	High pH	Low pH
O	7	14
M02	15	13
M24	9	3
M48	21	6
M8	9	6

Since the manuscript contains too many figures (also suggested by referee number 2), we have moved Figure 9 from the manuscript. Even though we still find this result as potentially important, we think that the main message of the manuscript will be clearer by focusing only in the results from the SEM. Figure 9 was a supplementary figure to confirm that the response of DOC to environmental factors was a function of site deposition and acidification status.

Finally, sites were classified according to soil solution pH, and thus the revised text has been corrected (lines 224-225).

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5. Lines 219-222: From which time period do the S and N depositions originate? Is it median values or. . .?

S and N deposition data covers the period 1999-2010 (Waldner et al., 2014). This have been mentioned in the text of the revised manuscript (lines 183-184). For our classification, we used mean values of deposition for this period (Lines 225-229).

- 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.

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6. Line 276: Add p-value to "…overall positive trend…". p<0.05 or p<0.10??

The p-value ($p<0.05$) has been added in the text referring to this overall positive trend in the organic layer.

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7. Lines 296-301 and Table 2. In the last sentence, it is stated that trends computed with SMK and PMK agreed well. However, at soil depth M24 the two methods results in very different rslopes (Table 2) both as regards directions and values. Comment on this and present a possible explanation.

We have checked for these results and the difference in the rslopes between SMK and PMK originates from the difference in sites available for computing the SMK and the PMK. There are two extra sites for which SMK tests were performed, but not the PMK. These two extra sites show a positive trend (1.1 and 2 % yr -1), creating the difference in the median value at M24 between the two methods (Table 2 in submitted manuscript). However, when using exactly the same set of sites, the trend did not differ between the two methods.

Nevertheless, Table 2 was removed from the manuscript and the text dealing with the comparison between methods was moved to Supplementary Material, as it is a rather technical information. The above explanation has been commented in this new section of the Supplementary Material (page 17).

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8. Lines 309-311: nNS-trends=104, nP-trends=91 and nN-trends=63 makes up a total of 258 time series, which corresponds to the value in Supplementary materials. However, the number of monotonic trends is 191 according to Figure 1. Correct where appropriate.

The numbers 258 and 191 correspond to different observations: 258 is the number of time series with less than 60 observations and more than 10 years, while 191 refers to the same time series, but after aggregation per plot-depth combination. This has been clarified in the revised Supplementary Material (Table S2).

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9. Lines 324-332 and Table 2: There are increased rslope values towards deeper mineral soil horizons. Is this a result of lower soil solution DOC concentrations (cf. general comment 3) and thereby very small DOC trends in absolute numbers? The rslope values in the O-horizon, generally showing high DOC concentrations, are close to those found for M8, indicating large DOC trends if statistically significant (N or P). Comment on this.

We have checked the median values of the absolute DOC slopes and absolute trends in the organic horizons are indeed higher than in mineral soils (0.33 mg L^{-1} yr^{-1} for the organic layer versus 0.03 below 80 cm). This is a natural consequence of lower DOC concentrations in deep soils. This issue has been commented in the new section added to the Supplementary Material (pages 18-20), where also a table comparing relative versus absolute DOC trend slopes has been added (Table S3).

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10. Lines 360-361: ". . .we found evidence. . .". The rslope=f(mean TF SO4 deposition) relations in Figure 9 are no evidence, however, they show a relatively strong indication (r2=0.288) on that the SO4 deposition may tangibly affect the rslope values in acidic soils. Rephrase the sentence.

In order to shorten the manuscript, Figure 9 has been removed from the manuscript and consequently the mentioned sentence has been deleted.

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11. Lines 367-372: Complement the GDA analysis with the DOC concentrations as an independent continuous variable and comment on the results. Is DOC concentration an important variable for explaining the variation (cf. general comment 3)?

As we did not find a relationship between median DOC concentrations and absolute or relative slopes (see Figure S5 in the revised Supplementary Material), we did not see necessary to include DOC as a variable in the GDA. Introducing an additional variable would lower the robustness of the analysis. Moreover, we have removed the GDA analysis (Figure 10) from the manuscript to simplify the message, since results from the GDA are used just to support our findings from the SEM.

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12. Line 414: A bracket in front of Fig. 11A is missing.

When re-writing the discussion, this paragraph has been deleted.

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13. Line 536: Again the total number of observations (n=174) does not match the number (n=191) stated in Figure 1. In the methods chapter, it may be wise to further explain the different number of observations occurring in different analysis and why so.

191 is the total number of time series aggregated per plot and soil layer, 174 of this 191 time series show positive, negative or non-significant trends. The rest of plot/soil depth combinations (17) correspond to the plots that 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) (lines 312-315 in submitted manuscript).

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14. Lines 645-647: "We found evidence that soil pH determines the response of trends of DOC in soil solution to SO42- deposition. . .". This statement is not correct. What you have found is a relation between relative slopes of DOC and S-deposition in very acidic soils with a pH<4.2 in soil solution, but not in non-acid soils with a pH>5 (Figure 9). The multivariate analyses do not show that as stated. The relation in soils with 4.2_pH_5 is not shown or discussed in the text. Additionally, the statement refers to the entire soil column, but I suppose that the low pH in soil solution (pH<4.2) is primarily found in O-horizons and upper mineral soils. Rephrase the statement.

We did not show the relation in soils with intermediate pH (between 4.2 and 5) to avoid introducing more information, as the manuscript is already dense in statistical analysis, number of figures and tables.

Regarding the fact that the statement refers to the entire soil column, we could not do the statistical analysis separately for the different soil layers due to a lack of data (see explanation in Supplementary Material, pages 13-14). Therefore, to check the influence of mixing soil layers, we re-did the SEMs models (Figure 6 in the revised manuscript) with horizon type (organic versus mineral) as an explanatory variable. For the model obtained for 1) all the cases, 2) for low and medium nitrogen deposition and 3) for high nitrogen deposition (Figure 6A, 6B and 6C, respectively), the variable "depth" (organic vs mineral) was not significantly correlated with DOC slopes (p =0.85, p=0.34 and p=0.56). Based on this test, horizon type does not appear to play a role in explaining the differences between the trend slopes of DOC and, thus we trusted the findings from the SEMs even when mixing soil layers.

The statement "We found evidence that soil pH determines the response of trends of DOC in soil solution to SO42- deposition. . ." has been removed from the conclusions in the revised manuscript.

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15. In the conclusions, I would suggest that you stress the large local variation related to a multitude of factors and discuss the regional processes in a more humble way, supported by your results. I also suggest that you describe the differences found between DOC trends in organic and mineral soil layers and possible influences by different drivers/processes. Finally, if there is any relation between DOC concentration level and DOC trends (levels or directions), this should be stressed.

Part of the conclusion has been rephrased to stress the differences found between DOC trends in organic and mineral soil layers, however, we cannot describe the influences by different drivers/processes based on our results without being too speculative for a conclusion. We think that the importance of the local variation related to several factors is discussed in the last sentence. Finally, there was no finding regarding the relation between DOC concentration level and DOC trends that should be stressed in the conclusion.

Comments on tables and figures

1. Table 1: In the legend, information on how 0.05_p_0.1 is indicated is missing (italics?). In the table, there is a mess among grey, bold and italic figures. Related to the SMK results, the number zero is sometimes missing.
The legend of Figure 1 has been completed and the table corrected.

2. Table 2:The different statistical methods do not always show the same direction on rslope for all soil layers (BFAST M02 and PMK M24 are negative). This should be commented on in the text.
Table 2 was removed from the manuscript, but this issue has been commented on in the Supplementary Material (see detailed comment 7)

3. Table 3. Change name on slope to rslope in column headings and explain in legend. Which year(s) do the S and N depositions data refer to?
Table 3 has been corrected accordingly.

4. Table 4, Legend: What do you mean with ". . .during the last years. . ."? Explain.
Table 4 has been removed from the manuscript to shorten the paper.

5. Figure 2: Weight_P is missing on the X-axis
Figure 2 has been corrected and moved to Supplementary Material (now Figure S4).

6. Figure 3, legend: Explain boxplots (c.f. Figure 6) and "n" in figure.
Figure 3 has been removed from the manuscript to shorten the paper.

7. Figure 7: Defining that the trends refer to DOC is missing in the legend. The Y-axis is too short in Figure 7C and perhaps also in the others. Maximum values on the Y-axis seem to be very close to the observed maximum numbers.
Figure 7 has been modified in the revised version and corrected where appropriate.

8. Figure 8. Define whether it is natural logarithms or 10-logarithms on the X-axis. The X-axis is too short in Figure 8B.

Figure 8 has been removed from the manuscript to shorten the paper.

9. Figure 9: In the legend, define which soil layers the data points refer to.
Figure 9 has also been removed from the manuscript.

10. Figure 10: Use the same scales on the XY-axes in Figure A and B.
Figure 10 has been removed from the manuscript.

11. Figure 11: In the legend change from (>15 kg N ha-1 yr-1) to (<15 kg N ha-1 yr-1)
Figure 11 has been corrected.

Comments on Supplementary material
1. S2: For the GDA analysis, it is unclear whether the "Weighed positive" and "Weighed negative" trends are included. Clarify.
The GDA analysis has been omitted in the revised manuscript (see response to Detailed comment 11).

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2. S2: For the SEM analysis, it is unclear whether the analyses are performed on SEN slopes or rslopes. Clarify.
The SEM analyses were performed on the relative slopes (rslopes): this has been clarified in the revised version.

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3. Figure S1: The legend box hides some bars.

Figure S1 has been re-done.

Answers to Referee 2

Referee 2: However, saying that this article is not very clear is litotes. The abstract and introduction are rather well written. However, the result and discussion sections are extremely hard to read, the number of figures and tables is not tenable (I counted 27 items, figures+tables) and the usefulness of numerous statistical analyses is not convincing since they provide similar results and conclusions. I think that an effort of synthesis is necessary to simplify messages and prevent a dilution of important results with accessory observations. For example, at the end of the reading of your manuscript, I was not able to say whether sulphate depositions increase or decrease soil solution DOC content. In your abstract, it is suggested that DOC concentrations and sulphate depositions are positively linked, a statement which is then contradicted in the manuscript (e.g. L412-413 but L348-349).

We agree that the manuscript includes many statistical approaches and we understand that this might confuse the reader. This approach diversity comes from the large community of scientists involved in the study by providing data and scientific input. Concerning the temporal analyses of DOC concentrations, we decided to show results from the different statistical methods (LMM, seasonal and partial Mann Kendall) because the approaches are complementary. Each method has pros and cons. This allowed us to show that DOC concentrations have increased during the observation period overall in coniferous forests in the organic layers. However, at individual plots and depths, DOC concentrations did not show any consistent temporal trend (increase, decrease or no change). We could also show that there was no geographical pattern either.

Therefore, we have shorten the manuscript mainly by synthesizing the multivariate analyses. We have removed four figures (Fig, 3, Fig 8, Fig. 9, Fig. 10), parts of Figure 7 (7A, 7B), and one table (Table 4). Moreover, we have shorten the most technical part of the results by removing Table 2 and Fig. 2. This has not changed the conclusions of the manuscript, but made the discussion more concise. In the revised manuscript, in Figure 7 (now Figure 5), we focused only on the relationships between the temporal trends of DOC concentrations, forest types and classes of stem volume increment (proxy for forest productivity). The relationships between trends in DOC concentrations and SO4 and NO3 throughfall deposition are now explored only in Figure 6 to avoid confusion. The comparison among trend analysis techniques is now in the Supplementary Material of the revised manuscript. We believe that this reduction of the number of tables and figures will improve the readability of the manuscript.

Referee 2: Moreover, it would be useful to create a figure summarizing the main chemical reactions and biological processes controlling soil solution DOC content

Our results come from an exploratory statistical approach (and not deterministic) of a large European dataset and we are afraid that it would be preposterous at this stage to build a model based on such a variety of local (e.g. soil properties) and regional (e.g. atmospheric deposition) factors. The only alternative we can think of is to include a figure based on the numerous mechanistic models proposed in the literature, but it will increase the number of figures and will not provide with novel information.

Referee 2: More fundamentally, I am not sure that the measurement of soil solution DOC provides an accurate estimate of the amount of DOC flowing out of terrestrial ecosystems (and supply of DOC to surface water). The leaching of DOC happens at specific moments of the year depending on hydric balance (precipitationevapotranspiration), soil type, plant activity etc. I am even sure that the DOC soil solution concentration can be inversely related to DOC leaching in some conditions. Just an example: soil solution DOC concentration is higher in summer than in winter, but DOC leaching only occurs in winter in France. This issue could explain why the present study fails to show clear overall trend in soil solution DOC at individual plot and soil depths. A warming-induced change of ecosystem water balance could also contribute to changes in DOC content in soil solution and surface water. Therefore, I suggest to present (in manuscript or in supplementary materials) the volume of water *harvested in lysimeters or calculations of theoretical water balance (precipication-evapotranspiration).*

We agree with the referee that we did not assess DOC fluxes flowing out from forest soils.
Our time series analysis aimed to detect long-term changes of DOC concentrations that are not due to seasonal effects or dilution-concentration effects caused by fluctuations in soil water content. Therefore, we decided to apply both Seasonal Mann Kendall and Partial Mann Kendall using precipitation as a co-variable to remove the seasonality and dilution-concentration effects. This method allowed us to detect significant monotonic changes (increase or decrease) of DOC concentrations over a period of 10 years at least. Studies having shown temporal changes of DOC in surface waters also reported concentrations rather than fluxes (e.g. Worral & Burt 2004, Evans et al. 2005, Monteith et al. 2007, Dawson et al. 2009, all cited in the manuscript).

Using water volume collected by lysimeters to assess water fluxes was not possible, because these data were available since 2011 only. In addition, the volume collected by tension lysimeters depends on the suction applied to the system.
To assess water fluxes at different soil depths, we would need to model the water balance at 118 forest sites, which is very challenging, since many input parameters (meteorology, soil, vegetation) would be required. This was beyond the scope of this study. A simple estimate based on the difference between precipitation and evapotranspiration, would add a substantial uncertainty to the calculation of DOC fluxes and therefore detecting long-term changes of DOC fluxes would be even more difficult. Because of large variations in soil water fluxes (e.g. Borken et al. 2011, Verstraeten et al. 2014, Meesenburg et al. 2016), it is more difficult to detect long-term trends of fluxes than long-term trends of concentrations in soil solution. Since most times series of DOC concentrations in soil solution do not indicate any long-term trend in our dataset, the chance of finding long-term changes in DOC fluxes are even lower.

- Borken, W., Ahrens, B., Schulz, C., & Zimmermann, L. (2011). Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils. *Global change biology*, *17*(7), 2428-2443.
- Meesenburg, H., Ahrends, B., Fleck, S., Wagner, M., Fortmann, H., Scheler, B., ... & Meiwes, K. J. (2016). Long-term changes of ecosystem services at Solling, Germany: Recovery from acidification, but increasing nitrogen saturation?. *Ecological Indicators, 65,* 103–112
- Verstraeten, A., De Vos, B., Neirynck, J., Roskams, P., & Hens, M. (2014). Impact of air-borne or canopy-derived dissolved organic carbon (DOC) on forest soil solution DOC in Flanders, Belgium. Atmospheric Environment, 83, 155-165

Referee 2: I am not really convinced by the relevance of removing the breakpoints. These breakpoints are not necessary the result of site disturbances (change of sensors etc) but could result from sudden change of atmospheric chemical composition or ecosystem functionning.

Monotonicity of time series is generally assumed when analyzing DOC data for temporal trends (Filella and Rodriguez-Murillo, 2014). However, it is rarely statistically tested and, thus, potential abrupt changes in the time series may be overlooked. This issue becomes important in temporal trend analysis since a breakpoint may cause changes in the direction of the trend and could lead us, for example, to classify a time series as constant, when in reality we may have averaged out separate periods with significant changes (de Jong et al., 2013). On the other hand, breakpoints may erroneously induce the detection of a significant trend in long-term time series due to artifacts (see Supplementary Material).The aim of our study is to analyze monotonic trends related to factors that have been measured within the ICP Forests database. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints.

We agree that removing breakpoints using the BFAST technique may remove time series that show abrupt changes not only due to artifacts (collector replacement, etc.,), but also due to natural causes (meteorological conditions, extreme events), forest management (changes in soil condition, thinning, etc.), sudden change of atmospheric chemical composition or ecosystem functionning. Nevertheless, many breakpoints are the consequence of technical issues or even inconsistencies in the database. The ICP Forests soil solution dataset has a great potential for analysis of large scale trends, but at the same time it may also contains some inconsistencies. The BFAST analysis proved to be effective at removing breakpoints caused by some dataset errors and thus the most defective time series were left out.

Although the investigation of the potential causes of the abrupt changes (breakpoints) in the individual time series can indeed provide a very valuable information, we do not count with the site-level information necessary for that purpose. To attribute the different causes of the breakpoints at site scale, we would need information of the management and climate history at each particular site, which is not available at the time of writing the present manuscript. Consequently, we cannot be sure of the origin of each breakpoint, and thus we decided to leave out all the time series showing abrupt changes to avoid erroneous detections of significant trends. Moreover, in this way, we are confident that the trends found in the time series that we analyzed are not a consequence of local factors. The alternative is to study each time series individually to identify the local (or regional) factors causing abrupt changes at plot scale, and this task is beyond the scope of this study, but is a very interesting topic to be addressed in a follow-up paper.

- Filella, M. and Rodriguez-Murillo, J. C.: Long-term Trends of Organic Carbon Concentrations in Freshwaters: Strengths and Weaknesses of Existing Evidence, Water-Sui, 6, 1360-1418, 2014.
- de Jong, R., Verbesselt, J., Zeileis, A., and Schaepman, M. E.: Shifts in Global Vegetation Activity Trends, Remote Sens-Basel, 5, 1117-1133, 2013.

Referee 2: The terminology used in the manuscript is often not clear. The term "trend" is vague and does not specifically refer to change with time. The terms "trend slope", "trend direction" and "relative trend slope" are even more difficult to understand.

To avoid any confusion about the term "trend", we have added a sentence in the Method section explaining the different temporal components of time series analyses (lines 231-232 in the revised manuscript).

We have also added some explanations on the terms "trend slope" and "relative trend slope" in the Method section (lines 268-270 in the revised manuscript). The term "trend direction" now appear only once in the manuscript and it has been clarified (line 316 in the revised manuscript).

Referee 2: The terms"depositions" and "troughfall" are interchangeably used, I suggest you to use only one of the two terms.

We used throughfall deposition of sulfate and inorganic nitrogen, except in Table 3 where bulk deposition was provided for three sites because throughfall deposition was not available. This was marked by an asterisk in the table. To avoid any confusion, we have reviewed the whole manuscript and used only "throughfall deposition" or "deposition" in the text.

Referee 2: The term "fertile soil" is weak and, as usual, does not refer to measurable variable. The fact that tree growth is high does not necessary mean that the soil is fertile. The tree growth is often linked to forest dynamics and age (tree growth of old forests is typically slow irrespective of soil *characteristics; tree growth after forest disturbance (drought events, storm etc) is typically high because tree mortality allows the recruitment of seedling with fast growth rate).*

We agree with the referee that tree growth is not necessarily related to soil fertility. Consequently, we have reformulated chapter 4.2.1. to show that this chapter aims to discuss the relationship between forest productivity (in our case only stem growth is available as a proxy for forest productivity) and DOC in soil solution. A number of other factors such as climate, soil water availability, soil fertility, tree age and competition between neighboring trees can influence tree growth too. We have shorten this section and clearly speculated about the relationship between soil fertility and DOC in soil solution. This is an interesting topic to be investigated in the future, but it is beyond the scope of this paper.

Most relevant changes made in the manuscript

1. The number of Tables and Figures has been reduced to improve clarity of the manuscript: Tables 2 and 4 and Fig. 2, Fig, 3, Fig. 7A, 7B, Fig 8, Fig. 9 and Fig. 10 has been deleted.

2. The comparison between methods (Section 3.2.1.) has been moved to Supplementary Material: Fig. 2 is now Fig. S4 (pages 16-17 of the Supplementary Material).

3. New tables have been added to the Supplementary Material with the median values, 25- and 75-percentiles and number of observations of DOC, and other water chemical parameters: pH, conductivity, Ca, Mg, SO_4^{2-}, NO_3^-, Al_3^+(Tables S4 to S11, pages 21-27 of the Supplementary Material).

3. A new section has been added to Supplementary Material titled: "Implications of using standardized DOC slopes versus absolute DOC slopes.". In this section, issues raised by reviewer number 1 concerning the use of the relative (standardized) slope and the effect of the median DOC on the DOC trends are discussed (pages 18-20 of the Supplementary Material). A new table (Table S3) and figure (Fig. S5) has been added to support this discussion.

4. Clarification of the number of time series used in the study: a table summarizing the number of time series used has been added to Supplementary material (Table S2) and two sentences has been added in the manuscript (lines 247-248 and 264-265).

5. The entire discussion has been rewritten to improve clarity, and more specifically:

5.1. Title and content of Section 4.1.1., discussing the trend detection methodology, has been changed. We have added a discussion on the potential multiple testing effect (lines 421-428).

5.2. Section 4.2.1, dealing with the discussion of the effect of stem growth on the DOC trends has been reformulated (lines 496-521).

6. The text and figures has been corrected according to the detailed comments from reviewer number 1.

7. The term "trend", "trend slope" and "relative trend slope" has been clarified in the text (lines 231-232, 268-270).

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

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Abstract

Dissolved organic carbon (DOC) in surface waters~~soil solution~~ is connected to DOC in ~~surface waters~~soil solution through hydrological ~~flows~~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~~ recovery~~. The objectives of this study were therefore to understand the long-term trends of soil solution DOC from a

large number of European forests (ICP Forests Level II plots) and determine their main physico-chemical and biological controls. We applied trend analysis at two levels: 1) to the entire European dataset and 2) to the individual time series and related trends with plot characteristics, i.e., soil and vegetation properties, soil solution chemistry and atmospheric deposition loads. Analyses of the entire dataset showed an overall increasing trend in DOC concentrations in the organic layers, but, at individual plots and depths, there was no clear overall trend in soil solution DOC. The rate change of~~ across Europe with temporal slopes of~~ soil solution DOC ranged~~ing~~ 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 ~~decreasing~~ 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~~N poorer forests~~, in agreement with observations in surface waters, this was not the case in ~~N richer forests~~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 ~~ecosystem soil solutions~~ mirror those observed in ~~surface waters~~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 due to land use changes were detected in areas where increasing DOC trends have been observed (Monteith et al., 2007).

Recent focus was mainly on decreasing acidifying deposition as an explanatory factor for DOC increases in surface waters in Europe and North America by means of decreasing ionic strength (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 nNorthern Belgium (Sawicka et al., 2016; Vanguelova et al., 2010; Verstraeten et al., 2014), it is not consistent with observed ttrends in soil solution DOC concentrations measured inreported 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 ofgoverning 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) wereare 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 wais 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 hypothesized that temporal trends in soil solution DOC willould also be positive, but with trends varying locally depending on plot characteristics. We further investigated whether plot characteristics, specifically climate, inorganic N and SO_4^{2-} deposition loads, forest type, soil properties, and changes in soil solution chemistry can explain differences across sites in DOC trends.

2 Materials and Methods

2.1 Data description

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

Soil water was usually collected fortnightly or monthly, although for some plots sampling periods with sufficient soil water for collection were scarce, especially in prolonged dry periods or in winter due to snow and ice. After collection, the samples were filtered through a 0.45 μm membrane filter, stored below 4 °C and then analyzed for DOC, together with other soil solution chemical properties (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{-2}, total dissolved Al, total dissolved Fe, pH, electrical conductivity). 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~~ S1~~, Table S1).

Soil properties, open field bulk deposition and throughfall ~~atmospheric~~ deposition of NO_3^-, NH_4^+, and SO_4^{2-}, are measured at the same plots as well as ~~meteorological variables and~~ stem volume increment~~ were also measured at the plots~~. 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 as not available, it wasthey were gap-filled with ICP Forests precipitation values gained by deposition measurements where available (open field bulk deposition or throughfall deposition).

2.2 Data preparation

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

The plots were classified according to their forest type (broadleaved/coniferous dominated), soil type (World Reference Base, ~~Reference Soil Group~~ (WRB 2006)), their stem growth (slow, < 6 m^3 ha^{-1} yr^{-1}, intermediate, 6–12 m^3 ha^{-1} yr^{-1}; and fast, > 12 m^3 ha^{-1} yr^{-1}), and soil 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 ~~of each individual time series~~. While the first analysis allows an evaluation of the overall trend in soil solution DOC at a continental scale, the second analysis indicates whether the observed large scale trends are occurring at local scales as well, and tests whether local trends in DOC can be attributed to certain driver variables.

Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution DOC concentration at the European scale (Fig. 1). For these models, the selected 529 time series were used. For the trend analysis of individual time series, however, we focused on the ~~investigation of the potential~~ long-term trends in soil solution DOC at European forests that show monotonicity. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010; 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~~ S2.2.~~) ~~(Fig. 1)~~. 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. ~~When the different trends at the same plot-soil depth combination were either P and NS, or N and NS, it was marked as "Weighted positive" and "Weighted negative" to indicate that there was potential predominant direction of the trend but with less significance.~~ 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, ~~two multivariate statistical analyses were performed, General Discriminant Analysis (GDA) and~~ 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 ~~, to investigate the main factors explaining differences in DOC trends~~ among the selected plots (Fig. 1). ~~To test whether the influence of~~

stem growth and soil solution chemistry was related to the effect of SO_4^{2-} and/or NO_3^- deposition on soil solution DOC, we applied SEM to determine the capacity of these variables in explaining variability in the slope of DOC trends. We evaluated the influence of both the annual mean (kg ha^{-1} yr^{-1}) and the trends (% yr^{-1}) in deposition and soil solution parameters.. All the statistical analyses were performed in R software version 3.1.2 (R Core Team, 2014) using the "rkt" (Marchetto et al., 2013), "bfast01" (de Jong et al., 2013) and "sem" (Fox et al., 2013) packages, except for the GDA that was performed using Statistica 8.0 (StatSoft, Inc. Tule, Oklahoma, USA) and the LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA). More detailed information on the statistical methods used can be found in Supplementary material S2.

3 Results

3.1 Soil solution DOC trends at European scale

First, temporal trends in DOC were analyzed for all the European DOC data pooled together by means of LMM models to test for the presence of overall trends. A significantly increasing DOC trend ($p < 0.05$) in soil solution collected with zero-tension lysimeters in the organic layer was observed mainly under coniferous forest plots (Table 1). Similarly, a significantly increasing DOC trend ($p < 0.05$) in DOC for soil solution collected with tension lysimeters was found in deep mineral horizon soil (> 80 cm) for all sites, but 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 horizons 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 including showing breakpoints (see Sect. 3.2), 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

3.3 Comparison of methods of individual trend analysis

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

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

~~3.6~~3.2 ~~**For virtually all plots, including precipitation as a co-variable in the PMK test gave the same result as the SMK test, which indicates that precipitation (through dilution or concentration effects) did not affect the DOC concentration trends. Dilution/concentration effect was only detected in four plots (Supplementary material S1, Table S1).**~~

~~**3.6.1 Soil solution DOC concentration trends using the SMK test**~~

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~~emporal~~ 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~~2~~). There was, thus, no uniform trend in soil solution DOC in forests across a large part of Europe. ~~Although a slight tendency of increasing trends in central and decreasing trends in north and south Europe was observed (Fig. 3), the uneven number of analyzed time series for each country (few in Austria, Italy or Finland and many in Germany) made it difficult to draw firm conclusions about the spatial pattern of the trends in soil solution DOC concentrations in Europe.~~ Furthermore, the regional trend differences were inconsistent when looking at different soil depth intervals separately (Fig. 2~~4~~ and 3~~5~~), 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~~6~~). We found consistent within-plot trends only for 50 out of the 97 sites. Moreover, some plots even showed different trends (P, N or NS) in DOC within the same depth interval, which was the case for 17 plot-depth combinations (16 in Germany and one in Norway), evidencing a high small-scale plot heterogeneity.

Trend directions (P, N or NS) often differed among depths. For instance, in the organic layer, we found mainly non-significant trends and, ~~when~~ 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~~2~~). Nevertheless, it is important to note that a statistical test of whether there was a real difference in DOC trends between depths was not possible as the set of plots differed between the different soil depth intervals. However, a visual comparison of trends for the few plots in which trends were evaluated for more than three soil depths showed that~~, at first sight,~~ there was no apparent difference in DOC trends between soil depths (Supplementary material~~ S3~~, 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 ~~direction and slopes of the~~ soil solution DOC trends

~~3.6.2~~3.3.1 Effects of vegetation, soil and climate

There was ~~A stratification of the forests into broadleaved and coniferous forest revealed~~ no direct effect of forest type (broadleaved vs. coniferous) on the direction of the statistically significant trends in soil solution DOC (Fig. 5~~7~~A~~C~~). 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 ~~less than~~ 6 $m^3\ ha^{-1}\ yr^{-1}$ over the study period, whereas decreasing DOC trends were more common in ~~often associated with~~ 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. 5~~7~~B~~D~~). 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 $m^3\ ha^{-1}\ yr^{-1}$).

~~Mean annual throughfall SO_4^{2-} and inorganic N deposition both had a significant effect on the direction of the trends in soil solution DOC (Fig. 7A, 7B). Increasing trends were more frequent in forests with high or medium inorganic N deposition than in forests with low inorganic N deposition where only decreasing trends were found ($\chi^2(2, N = 57) = 9.58$, $p =$ 0.008). Correspondingly, the probability of positive trends in soil solution DOC was higher at~~

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

~~Regarding the soil properties~~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~~3~~). It is remarkable that trends in soil solution pH, Mg^{2+} and Ca^{2+} concentrations were similar across plots with both positive and negative DOC trends. Soil solution pH increased distinctly in almost all the sites, while Ca^{2+} and Mg^{2+} decreased markedly (Table 2~~3~~).

~~However, we found evidence that soil acidity controlled the SO_4^{2-} deposition effect on the trends of DOC in soil solution (Fig. 9). In very acid soils, a higher mean SO_4^{2-} deposition enhanced the temporal increase in soil solution DOC, while in less acid soils, there was no significant effect of mean SO_4^{2-} on DOC trends.~~ Finally, no significant correlations were found between trends in temperature or precipitation and trends in soil solution DOC, with the exception of a positive correlation between trends in soil solution DOC in the soil depth interval 20-40 cm and the~~n increasing~~ trend in temperature ~~in the soil depth interval 20-40 cm~~ (r = 0.47, p = 0.03).

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

~~To test whether the influence of stem growth and soil solution chemistry was related to the effect of SO_4^{2-} and/or NO_3^- deposition on soil solution DOC, we applied SEM to determine the capacity of these variables in explaining variability in the slope of DOC trends. We~~

~~evaluated the influence of both the annual mean (kg ha^{-1} yr^{-1}) and the trends (% yr^{-1}) in deposition and soil solution parameters.~~

~~3.6.3~~3.3.2 Effects of mean and trends in atmospheric~~mean~~ deposition and soil solution parameters

Analyzing different models that could explain the DOC trends using the overall dataset indicated both direct and indirect effects of the annual mean SO_4^{2-} and NO_3^- throughfall atmospheric deposition on the trend slopes of DOC ~~trends~~. The Structural Equation Model accounted for 32.7% of the variance in DOC trend slopes (Fig. 6~~11~~A). According to ~~T~~this model, lower mean throughfall SO_4^{2-} deposition resulted in increasing trend slopes of DOC in soil solution ~~identified a significantly negative direct effect of SO_4^{2-} deposition on trends in soil solution DOC~~. On the other hand, higher mean throughfall NO_3^- deposition resulted in increasing ~~had a significantly positive direct effect on~~ trend slopes of DOC ~~trends~~ (Fig. 6~~11~~A). 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. 6~~11~~B). Lower ~~M~~mean SO_4^{2-} deposition again resulted in a significant increase in ~~had a significant negative effect on DOC~~ trend slopes, while increasing NO_3^- deposition resulted in increasing DOC trend slopes.~~had a significantly positive effect.~~ 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.

Effects of trends in deposition and soil solution parameters

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

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

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

4 Discussion

4.1 Trend analysis of soil solution DOC in Europe

4.1.1 ~~Are the many non-significant trends real~~Evaluation of the trend analysis techniques~~?~~

A substantial proportion (40%) of times series did not indicate any significant trend in ~~Non-significant trends dominated the~~ site-level DOC concentrations across the ICP Forests network. Measurement precision, strength of the trend, and the choice of the method may all affect trend detection (Sulkava et al., 2005; Waldner et al., 2014). Evidently, strong trends are easier to detect than weak trends. To detect a weak trend, either very long time series or very accurate and precise 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).

~~By filtering out the time series with breakpoints and removing outliers, we improved the overall quality of the data, and thus~~ 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 ~~factual~~ real and not a result of a multiple testing effect. ~~at a 0.05 significance level.~~

~~Nevertheless, we found a majority of non-significant trends. For these cases, we cannot state with certainty that DOC did not change over time: it might be that the trend was not strong enough to be detected, or that the data quality was insufficient for the period length available for the trend analysis (more than 9 years in all the cases). For example, the mixed-effects models detected a positive trend in the organic layer, and while many of the individual time series measured in the organic layer also showed a positive trend, most were classified as non-significant trends (Fig. 4). This probably led to an underestimation of trends that separately might not be strong enough to be detected by the individual trend analysis but combined with the other European data these sites may contribute to an overall trend of increasing DOC concentrations in soils of European forests. (Marchetto et al., 2013; Waldner et al., 2014)Anyway,~~

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

4.1.2 Analysis of breakpoints in the time series

Soil solution DOC time series measured with lysimeters are subject to possible interruptions of monotonicity, which is manifested by breakpoints. For instance, installation effect, collector replacement, local forest management, disturbance by small animals, or by single or repeated canopy insect infestations may disrupt DOC concentrations through abrupt soil disturbances and/or enhanced ~~throughfall chemical~~ input 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 ~~not available~~lacking for the majority of Level II plots, which hinders assigning observed breakpoints to~~selection of individual monotonic time series based on~~ specific site conditions. The BFAST analysis allowed us to filter out time series affected by local disturbances (natural or artefacts) from the dataset and to solely retain time series ~~that represented~~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~~ (Fig. 2)~~ that might be caused by local factors not directly explaining the long-term monotonic trends in DOC and thus complicating or confounding the trend analysis (Clark et al., 2010).

In view of these results, we recommend that testing for monotonicity of the individual time series is a necessary first step in this type of analyses and that the breakpoint analysis is an appropriate tool to filter large datasets prior to analyzing the long-term temporal trends in DOC concentrations. It is worth mentioning that, 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, ~~since our main goal was to study general monotonic trends, we did not focus on finding the direct causes of breakpoints in time series. F~~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~~6~~). This high small-scale variability in soil solution DOC makes it difficult to draw conclusions about long-term DOC trends from individual site measurements, particularly in plots with heterogeneous soil and site conditions (Löfgren et al., 2010).

The trends in soil solution DOC also varied across soil depth intervals. The mixed-effect models suggested an increasing trend in soil solution DOC concentration in the organic layer, and an increasing trend in soil solution DOC concentration under 80 cm depth only when the entire dataset (with breakpoints) was analyzed. The individual trend analyses ~~seemed to~~ 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 shallow soils~~ and in the subsoil. External factors such as acid deposition may have a more direct effect in the organic layer where interaction between DOC and mineral phases is less important compared to deeper layers of the mineral soil (Fröberg et al., 2006). However, DOC measurements are not available for all depths at each site, complicating the comparison of trends across soil depth intervals. Hence, the depth-effect on trends in soil solution DOC cannot be consistently addressed within this study (see Supplementary material, Fig. S1, Fig. S2~~-S3~~).

Finally, the direction of the trends in soil solution DOC concentrations did not follow a clear regional pattern across Europe (Fig. 2~~-4~~ and 3~~5~~) and even contrasted with other soil solution parameters that showed widespread trends over Europe, such as decreasing SO_4^{2-} and increasing pH. This finding indicates that effects of environmental controls on soil solution DOC concentrations may differ depending on local factors like soil type (e.g., soil acidity, 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

~~4.3~~4.2 Controls on soil solution DOC temporal trends

~~4.3.1~~4.2.1 Vegetation

Biological controls on DOC production and consumption, like net primary production (NPP)~~stem growth~~, operating at site or catchment level, are particularly important when studying soil solution as plant-derived carbon is the main source of DOC (Harrison et al., 2008). Stem growth was available as a proxy for NPP only for 53 sites and was calculated as the increment between inventories carried out every five years. ~~, and as such no annual growth estimates were available. Nevertheless,~~ Similarly to what has been found for peatlands (Billett et al., 2010; Dinsmore et al., 2013), the results ~~our results~~ suggest that vegetation growth is an important driver of DOC temporal dynamics in forests.~~, as reported for peatlands (Billett et al., 2010; Dinsmore et al., 2013)~~. Differences in DOC temporal trends across all soil depths were ~~not~~ strongly related to ~~forest type but to~~ stem growth, ~~:~~ with~~more fertile~~more productive plots, as indicated by higher stem volume increment (6-12 m^3 ha^{-1} yr^{-1}), more often exhibiting ~~exhibited more often~~ decreasing trends in DOC (Fig. 5~~7~~ and 6~~11~~). .

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~~deposition~~ ~~are then possibly~~

response tomay result from reduced C allocation to the belowground nutrient acquisition system (Vicca et al., 2012), hence, reducing an important source of belowground DOC.

It is well-established that N-enrichment favors the above-ground tissue production (as indicated by a higher stem volume increment) in forests (Janssens et al., 2010; Vicca et al., 2012) at the expense of C allocation to the root system, hence, reducing an important source of belowground DOC. On the other hand, forests with higher production would also have higher aboveground litterfall (Hansen et al., 2009), providing a higher input of labile carbon as a source for DOC leaching. Nevertheless, fertile forests may exhibit a higher microbial use efficiency, which may lead to proportionally more DOC being consumed, i.e., less DOC remaining in soil solution (Manzoni et al., 2012). Also, compared to vigorously growing forests with dense canopies, slower forest growth with less dense canopies have less interception and higher soil water input, which could stimulate litter decomposition and thus DOC production.

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.Finally, forest growth might indirectly affect DOC trends through changes in soil solution chemistry (via cation uptake) (Vanguelova et al., 2007), but our data did not allow to test these pathways and thus the DOC response to vegetation uptake remains hypothetical..

4.3.24.2.2 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 largelygreatly, with increases, decreases, as well as steady states being observed across respectively 56, 41 and 77 time series in European forests (Fig. 24 and 35). 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. we observed a switch in the direction of the DOC trends according to the mean SO_4^{2-} and inorganic N deposition levels (Fig. 7 and 8), with increasing soil solution DOC trends occurring more often in plots with high N and, to a lesser extent, SO_4^{2-} deposition. REMOVE?This suggests an interaction between the deposition load and the mechanisms underlying the temporal change of soil solution DOC.

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 NO_3^-, (Fig. 6). DOC concentration in the soil solution is predominantly decreasing (Fig. 8A and 10) REMOVE? and in these forests, we showed that decreasing trends in SO_4^{2-} deposition coincided with increasing trends in soil solution DOC (Fig. S3). The role of atmospheric 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 affectincrease 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, ~~therefore~~ 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. ~~11~~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).

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

Ultimately, internal soil processes control the final concentration of DOC in the soil solution. The solubility and biological production and consumption of DOC are regulated by pH, ionic strength of the soil solution and the presence of Al^{3+} and Fe (Bolan et al., 2011; De Wit et al., 2007; Schwesig et al., 2003). These conditions are modulated by changes in atmospheric deposition but not uniformly across sites: soils differ in acid-buffering capacity (Tian and Niu, 2015), and the response of DOC concentrations to changes in SO_4^{2-} deposition will thus be a function of the initial soil acidification and buffer range (~~F~~Fig. ~~9 and 11~~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, the response of DOC to changes in atmospheric deposition seems to be controlled by the past and present N deposition loads and acidification of soils (Clark et al., 2010; Evans et al., 2012; Tian and Niu, 2015). It suggests that the mechanisms of recovery from SO_4^{2-} deposition and acidification take place only in non-N-saturated forests, as it has been observed for N deposition effects (de Vries et al., 2009). In high N deposition areas, it is likely that impacts of N-induced acidification on forest health and soil condition lead to more DOC leaching, even though SO_4^{2-} deposition has been decreasing. Therefore, soil solution DOC concentrations responded as expected to changes in acid deposition, particularly in non N-saturated sites but the hypothesis of recovery from acidity cannot fully explain overall trends in Europe, as was also previously suggested in local or national studies of long-term trends in soil solution DOC (Löfgren et al., 2010; Stutter et al., 2011; Ukonmaanaho et al., 2014; Verstraeten et al., 2014).~~

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

~~4.4~~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, ~~while there was also evidence of increasing trends in the deep mineral horizon (> 80 cm),~~ trends ~~at~~in different~~-~~ soil ~~horizons~~ layers along the mineral soil were more variable and responded to other soil internal processes.

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

5 Conclusions

Different monotonic long-term trends of soil solution DOC have been found across European forests at plot scale, with the majority of the trends for specific plots and depths not being statistically significant (40%), followed by significantly positive (35%) and significantly negative trends (25%). The distribution of the trends did not follow a specific regional pattern. ~~There was evidence that an overall increasing trend occurred in the organic layers~~

~~and, to a lesser extent, in the deep mineral soil, however, there is less agreement on the trends found in different soil horizons along the mineral soils.~~

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

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Table 1. Temporal trends of DOC concentrations obtained with the linear mixed models (LMM) built for different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints) and the Seasonal Mann Kendal tests (SMK). The table shows the 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 ($0.05<p<0.1$). ~~and the LMMs for which a significant trend ($p<0.05$) was detected are in bold.~~ (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm/ TL: tension lysimeter, ZTL: zero-tension lysimeter/ n.s.: no significant.)

In broadleaved and coniferous forests:

Collector type	Layer	[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	*0.0782*	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 (±3.98)	13	22	11
	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. Median relative trend (rslope in % yr^{-1}) of DOC concentrations and interquartile range of rslope and number of time series with statistically significant ($p < 0.05$) positive (P) and negative (N) trends and with non-significant (NS) trends of DOC using the seasonal Mann-Kendall test (SMK), the partial Mann-Kendall test (PMK) and the Breaks For Additive Seasonal and Trend test (BFAST). (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm.)

Soil depth	**SMK**				**PMK**			
	rslope	**N**	**NS**	**P**	**rslope**	**N**	**NS**	**P**
O	1.18 (±3.37)	4	19	9	1.0 (±3.44)	4	18	9
M02	0.04 (±3.41)	17	32	22	0.10 (±3.29)	16	33	21
M24	0.61 (±8.62)	11	12	11	-0.03 (±8.97)	10	11	11
M48	1.01 (±4.79)	23	32	33	0.77 (±4.75)	22	31	33
M8	1.18 (±9.39)	8	9	16	1.01 (±8.48)	8	11	14

Table 23. 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 Ttrend slopess (rslope) -in soil solution pH, Ca^{2+} and Mg^{2+} concentrations were calculated using the Sseasonal Mann-Kendall test.

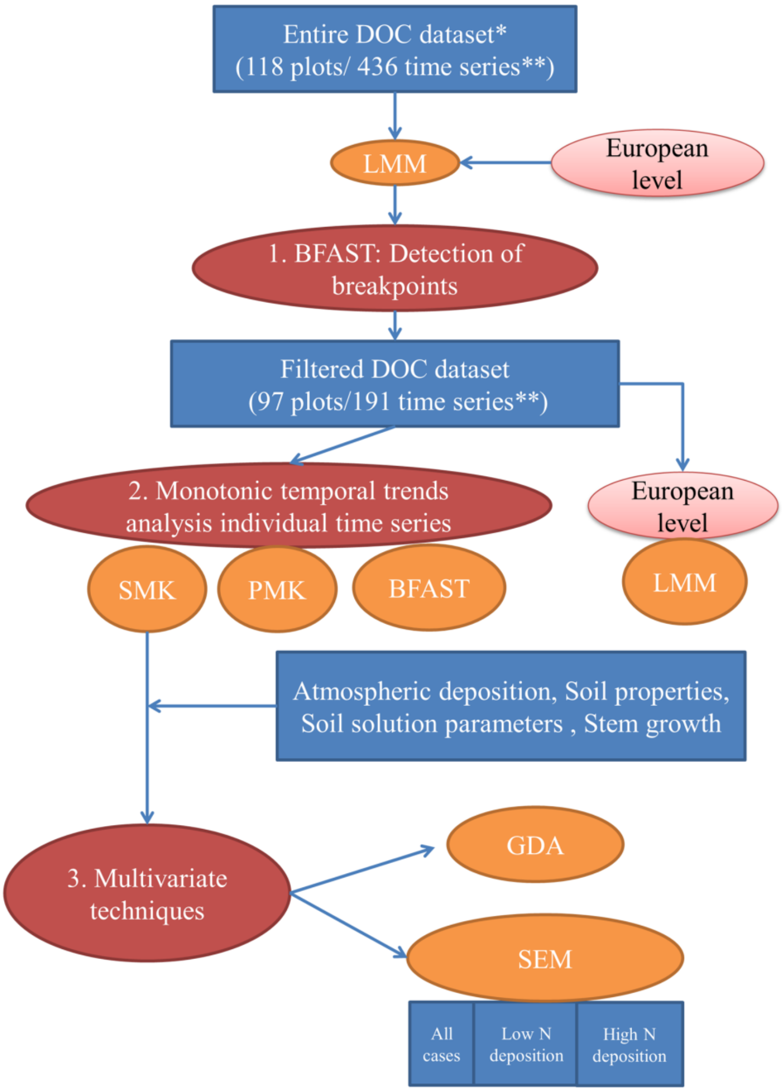
Code Plot	Trend	Soil Type (WRB)	Clay (%)	C/N	pH	CEC ($cmol_+ kg^{-1}$)	MAP (mm)	MAT (°C)	N depos. (kg N ha^{-1} yr^{-1})	SO_4^{2-} deposition (kg S ha^{-1} yr^{-1})	rslope pH (%yr^{-1})	rslope Ca^{2+} (% yr^{-1})	rslope Mg^{2+} (% yr^{-1})
France (code = 1)													
30	N	Cambic Podzol	3.79	16.8	3.96	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

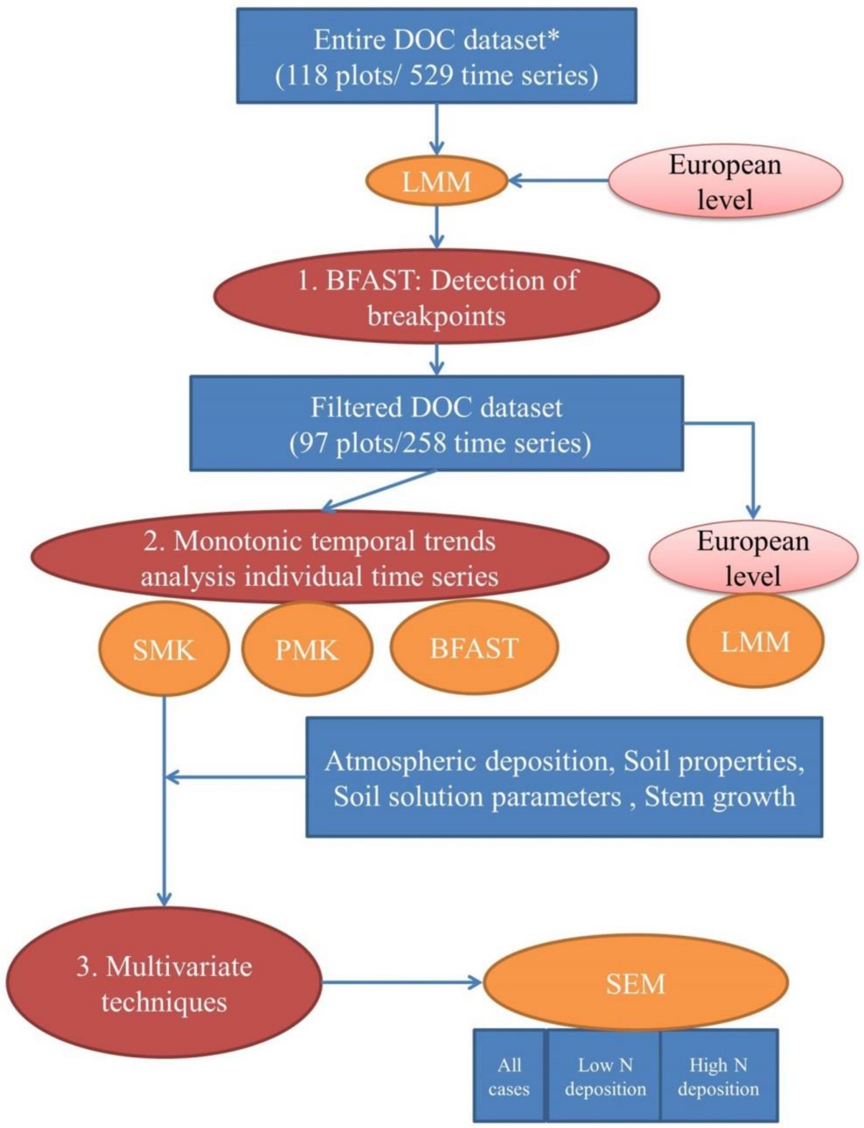
Table 4. Statistics (Wilks' Lambda and p value) of the General Discriminant Analysis among groups of plot-soil depth combinations with different trend in DOC during the last years conducted with 10 different soil solution and deposition variables as independent continuous variables and soil depth as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

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



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

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



* 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.

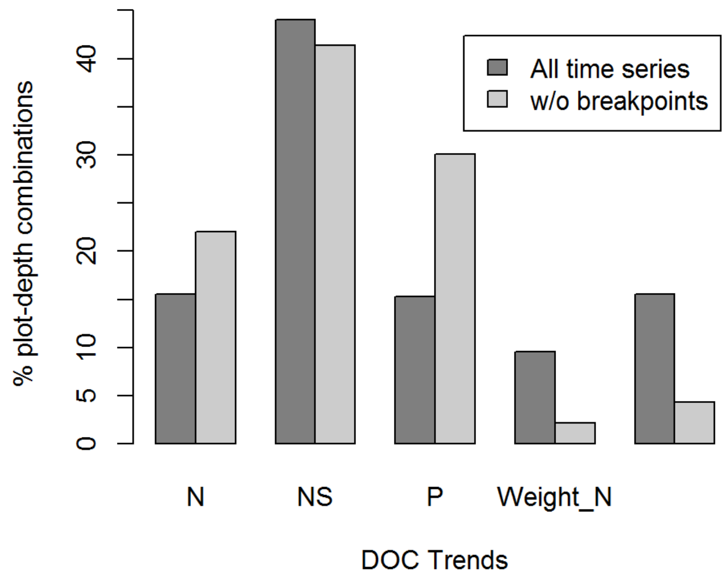
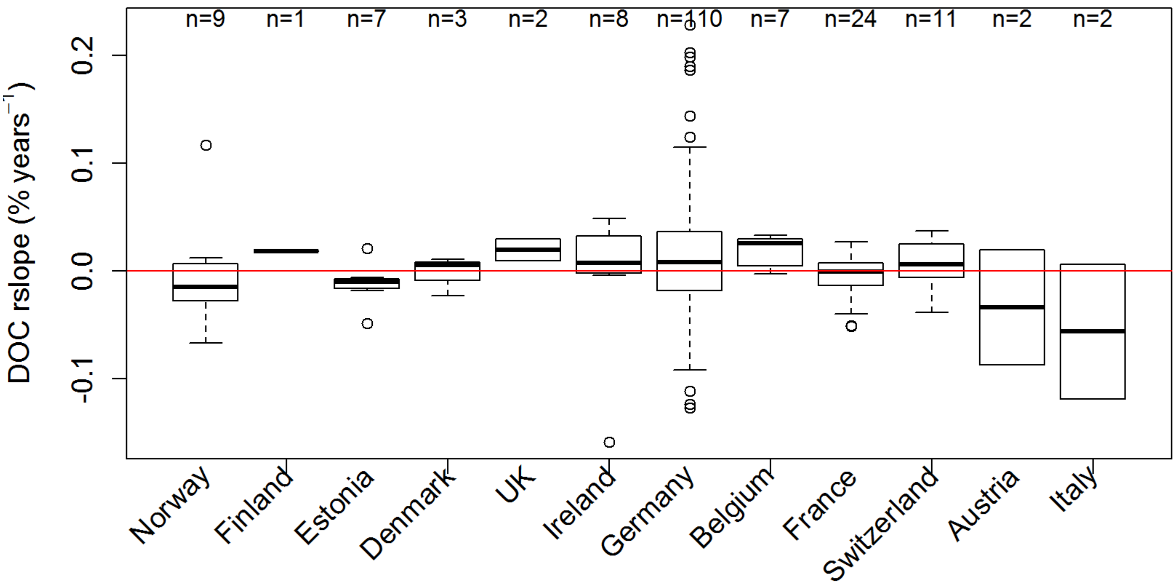


Figure 2. Percentage of plot-soil depth combinations for which negative (N), non-significant (NS), positive (P), negative and non-significant (Weight_N) and positive and non-significant (Weight_P) trends of DOC concentrations were found using SMK (seasonal Mann-Kendall) tests when 1) all the 436 time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



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

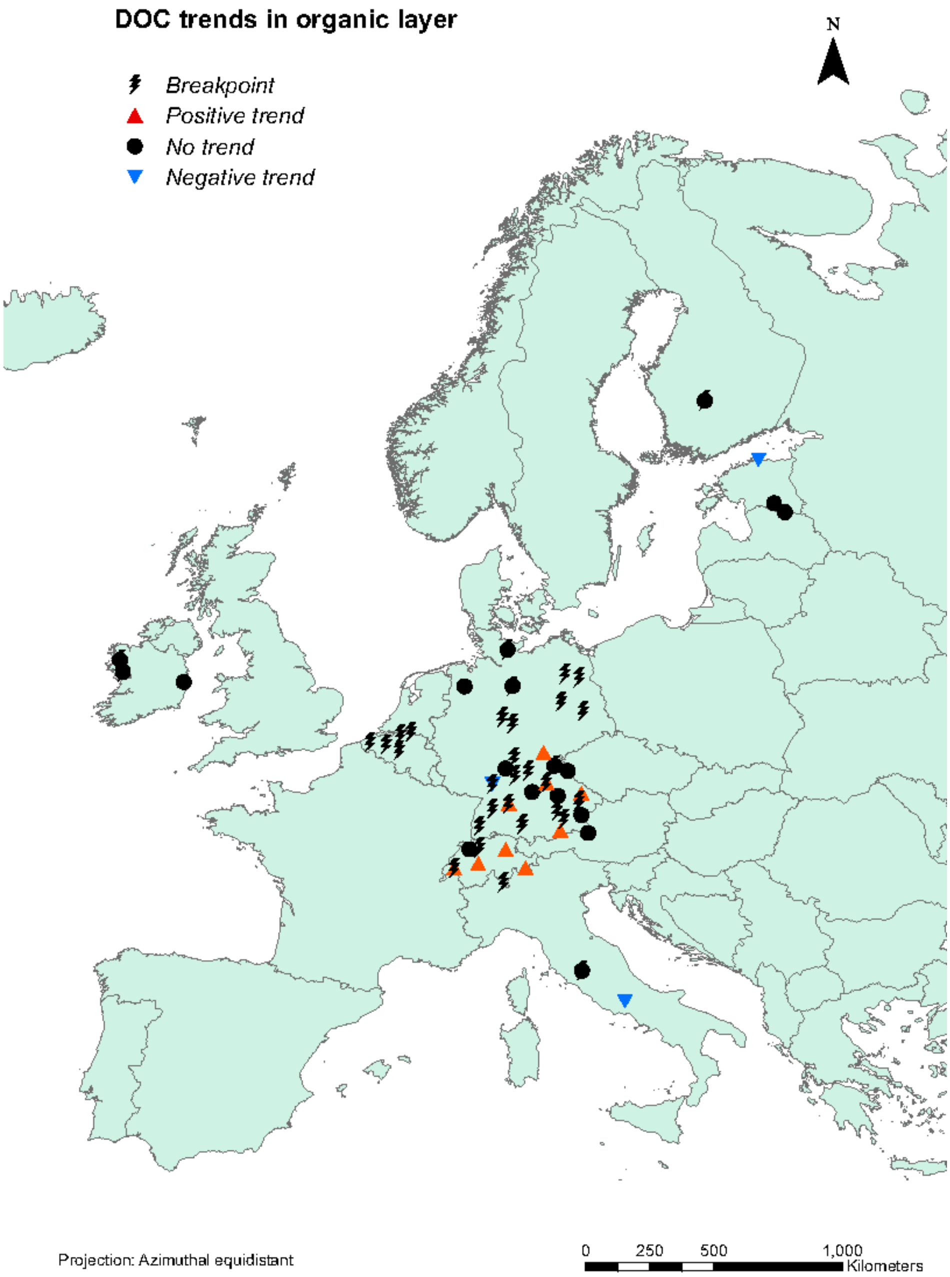


Figure 42. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the Sseasonal Mann-Kendall test. Data span from 1991 to 2011.

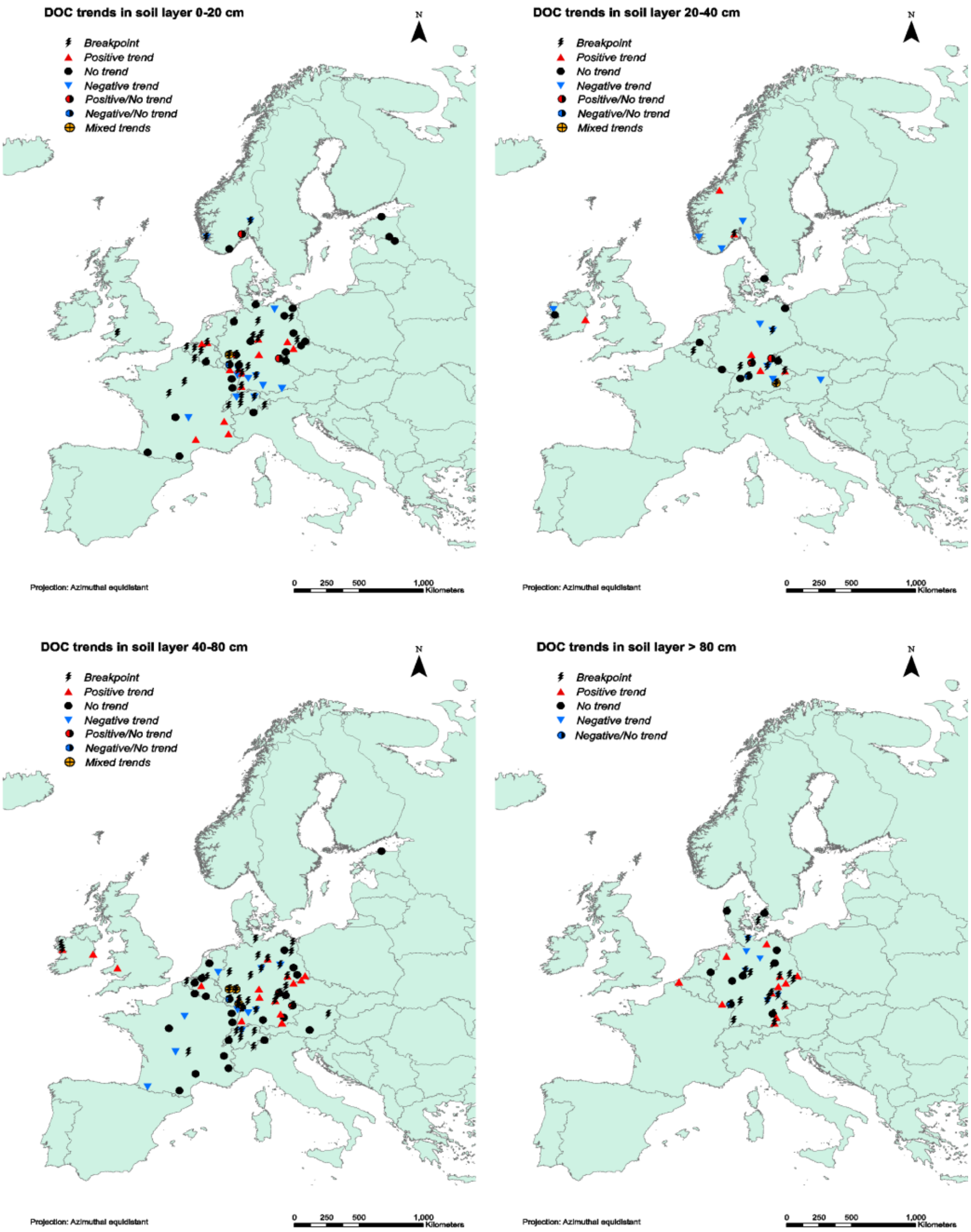
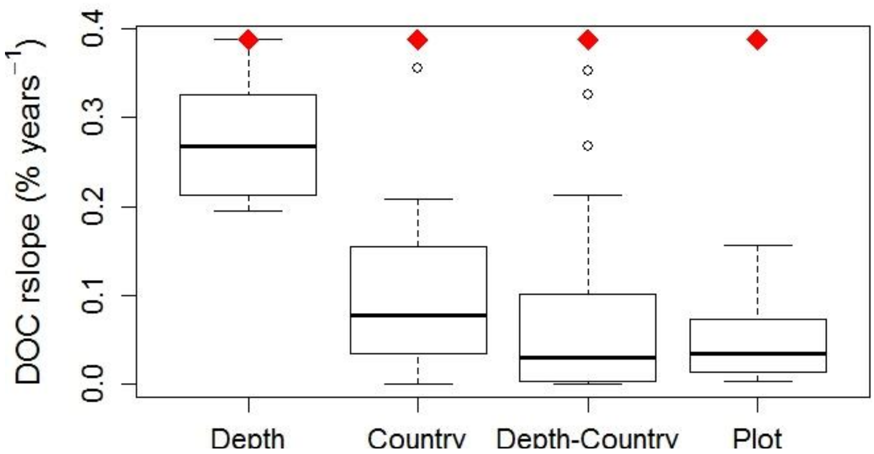


Figure ~~5~~3. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0–20 cm), b) intermediate (20–40 cm), c) subsoil (40–80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the S~~s~~easonal Mann-Kendall test. Data span from 1991 to 2011.



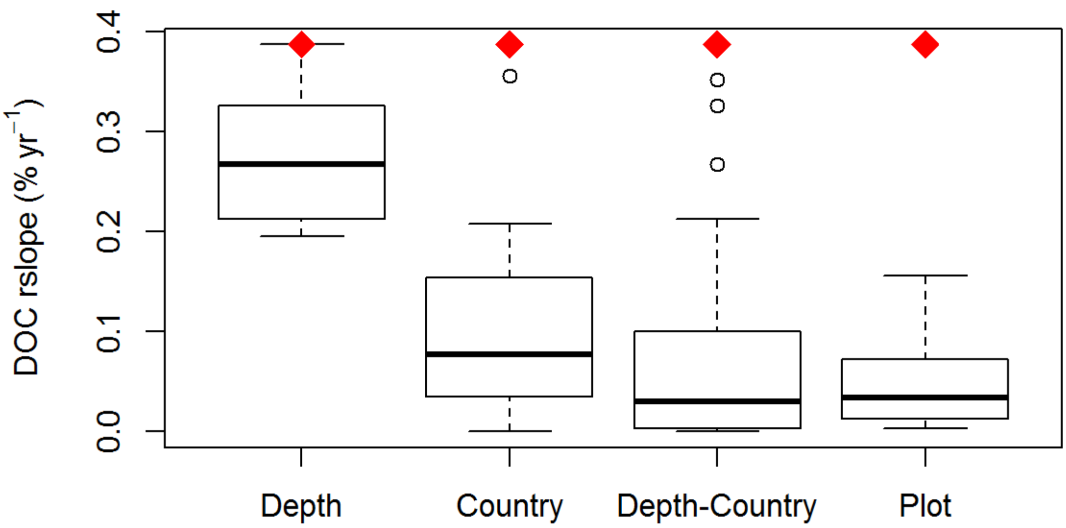
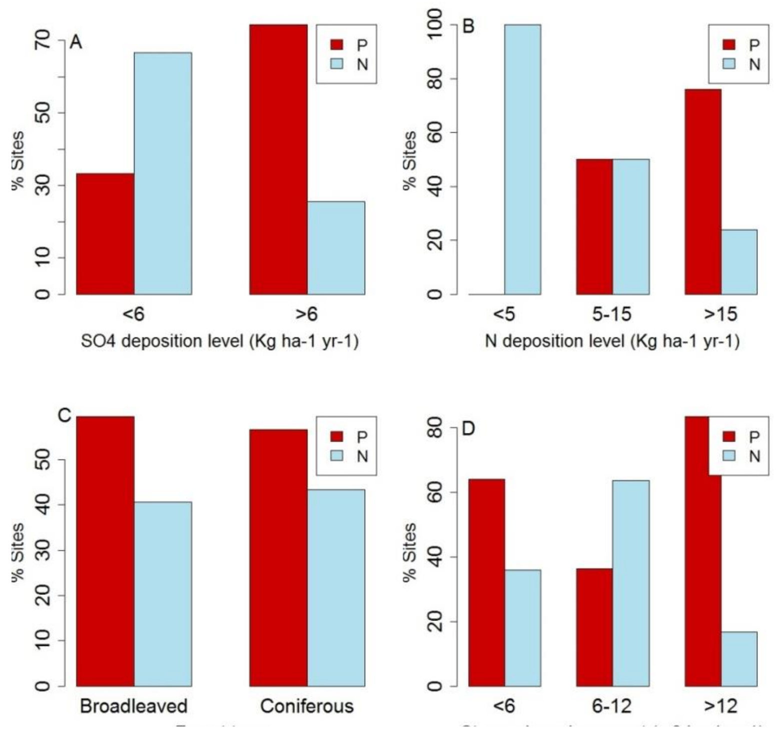


Figure 64. Range of relative trend slopes (max-min) for trends of DOC concentration in soil solution within each 1) depth interval, 2) country, 3) depth interval per country, and 4) plot. The boxplots show the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers) and higher values (circles). The red diamond marks the maximum range of slopes in soil solution DOC trends in the entire dataset.



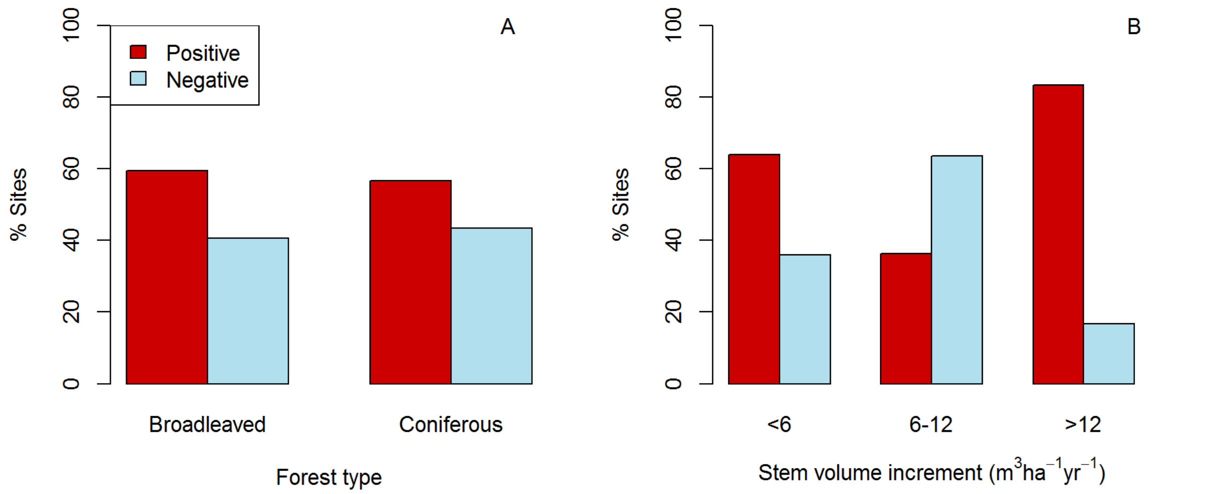
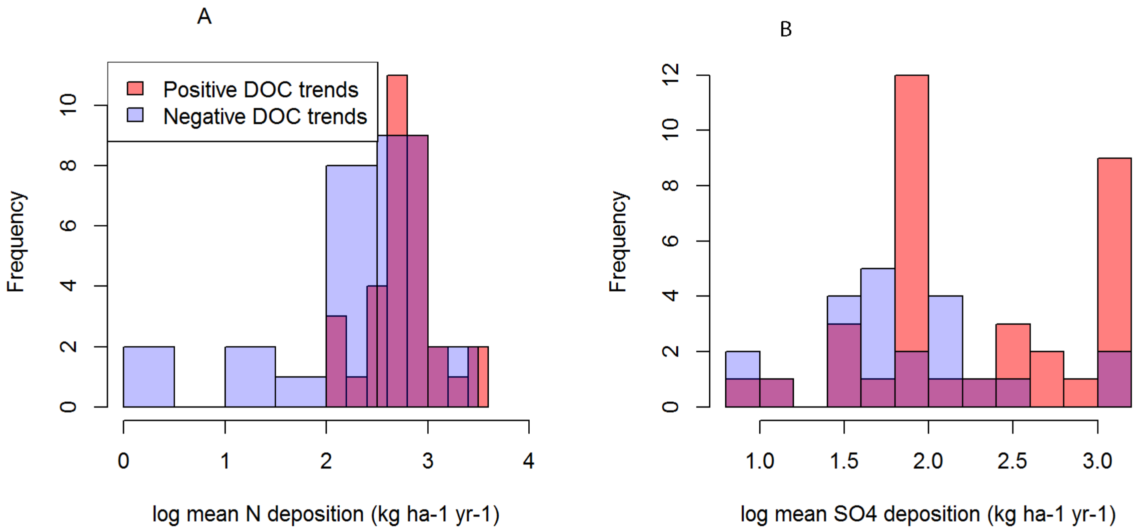


Figure ~~7~~5. Percentage of occurrence of positive and negative trends of DOC concentration in soil solution separated by A) ~~throughfall SO_4^{2-} deposition level (kg S ha^{-1} yr^{-1}), B) throughfall inorganic N deposition level (kg N ha^{-1} yr^{-1}), C)~~ forest type and B~~D~~) stem volume increment (m^3 ha^{-1} yr^{-1}).



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

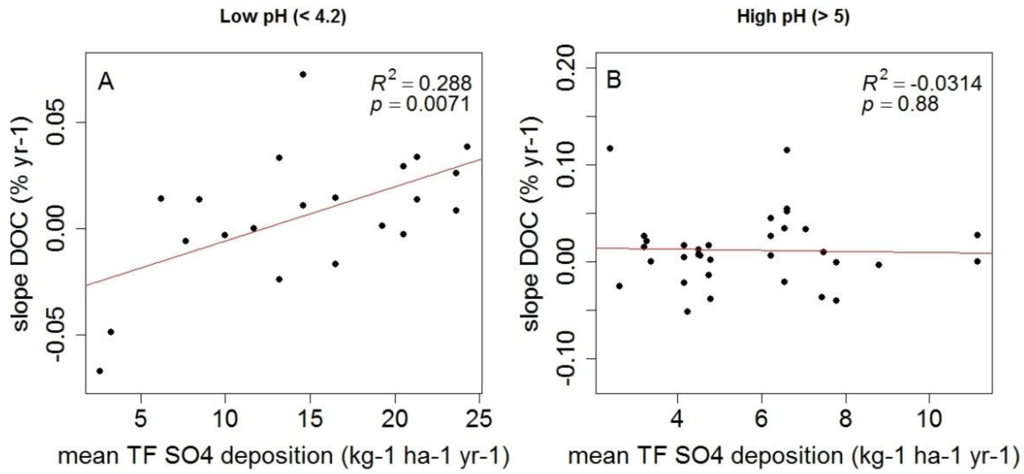
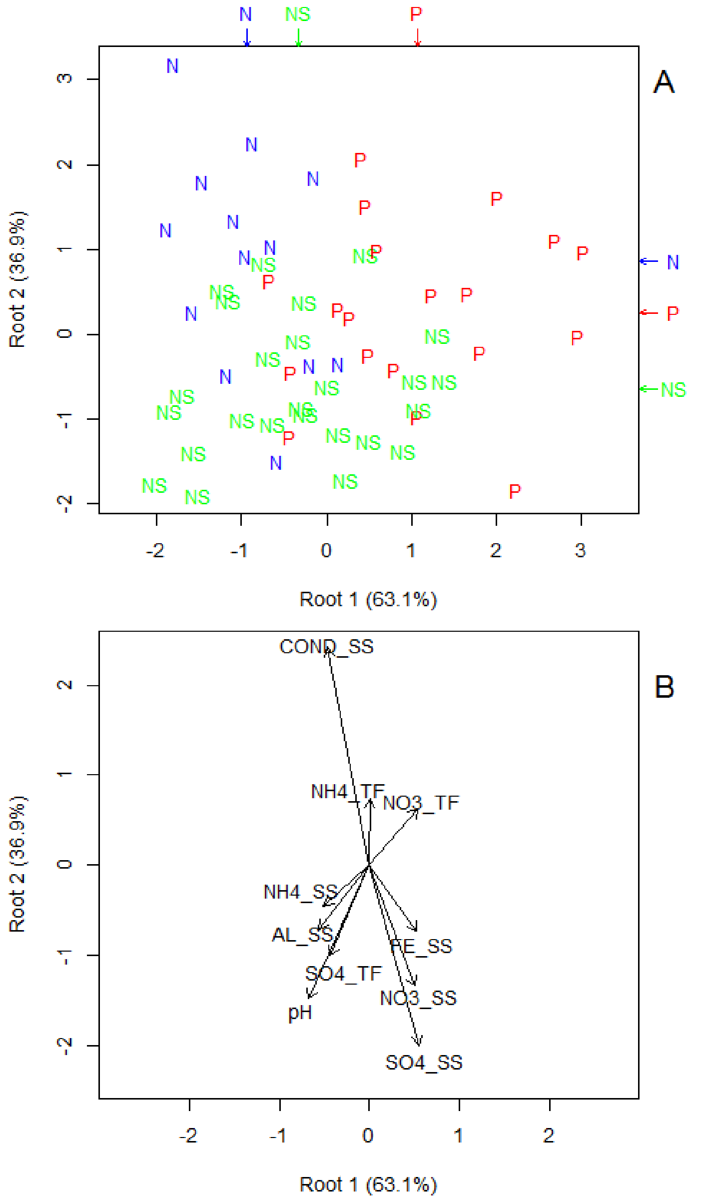


Figure 9. Relationship between mean throughfall SO_4^{2-} deposition and relative slopes of DOC for very acid soils (pH in soil solution < 4.2) (left) and non-acid soils (pH in soil solution > 5) (right).



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

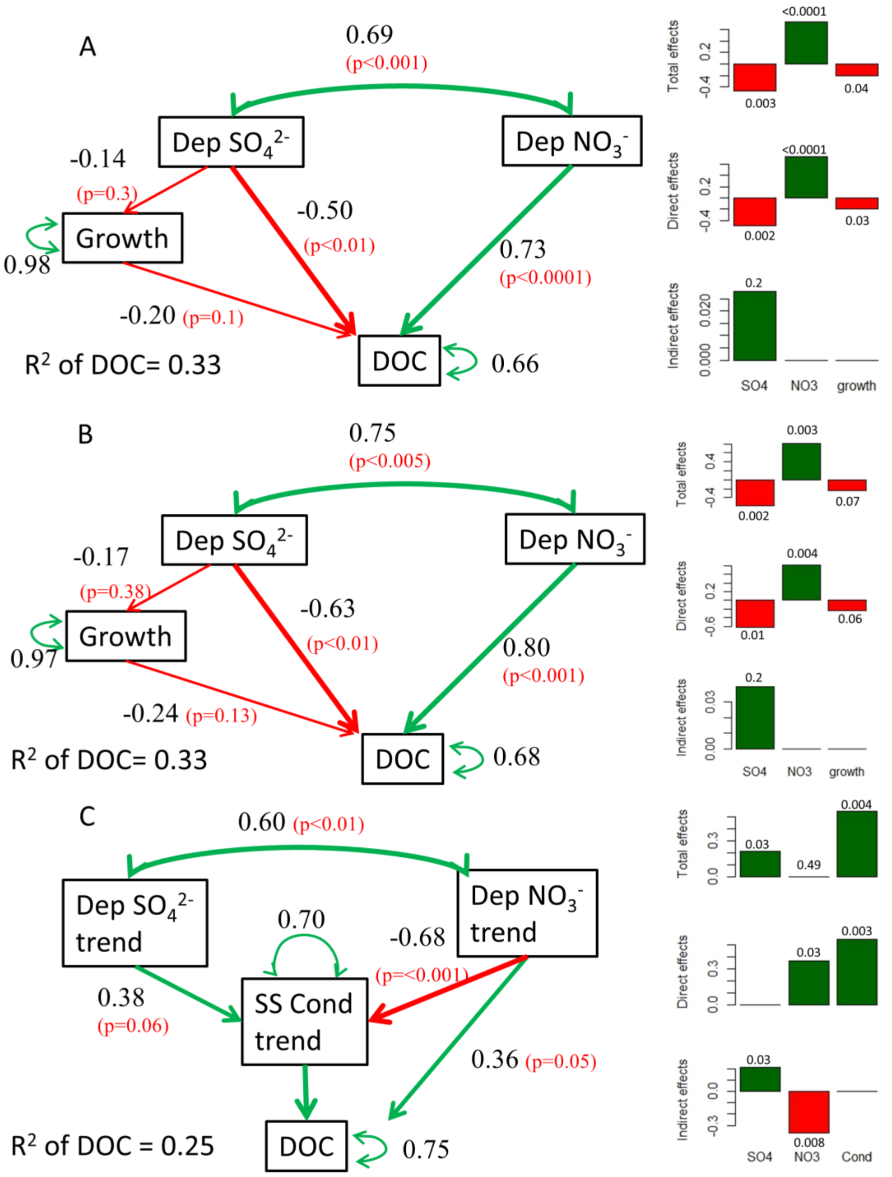


Figure ~~11~~6. Diagrams of the structural equation models (SEM) that best explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium throughfall inorganic N deposition (<~~>~~ 15 kg N ha^{-1} yr^{-1}), and C) cases 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.

Supplementary material for

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

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~~Supplementary material S1. List of~~ ICP Forests Level II plots data used for the trend analysis

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

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

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Belgium	2_16	1999	2011	ZTL/TL	*Quercus robur*	NS		**Formatted:** Font: Italic
Belgium	2_21	1999	2011	ZTL/TL	*Fagus sylvatica*	P		**Formatted:** Font: Italic
Germany	4_101	1996	2011	TL	*Fagus sylvatica*	NS/N		**Formatted:** Font: Italic
Germany	4_301	1997	2011	TL	*Fagus sylvatica*	NS		**Formatted:** Font: Italic
Germany	4_302	1997	2011		*Picea abies*	BP		**Formatted:** Font: Italic
Germany	4_303	1998	2011	TL	*Picea abies*	N		**Formatted:** Font: Italic
Germany	4_304	1998	2011	TL	*Fagus sylvatica*	N		**Formatted:** Font: Italic
Germany	4_305	1998	2011		*Picea abies*	BP		**Formatted:** Font: Italic
Germany	4_306	1996	2011	TL	*Fagus sylvatica*	P		**Formatted:** Font: Italic
Germany	4_307	1996	2011	TL	*Pinus sylvestris*	NS/P	depth=-2.5, coll=3	**Formatted:** Font: Italic
Germany	4_308	1993	2011	TL	*Quercus robur*	N		**Formatted:** Font: Italic
Germany	4_502	1998	2011	TL	*Quercus robur*	N/NS		**Formatted:** Font: Italic
Germany	4_503	1997	2011		*Fagus sylvatica*	BP		**Formatted:** Font: Italic
Germany	4_506	1997	2011	TL	*Picea abies*	NS		**Formatted:** Font: Italic
Germany	4_603	1998	2005		*Fagus sylvatica*	Lack data		**Formatted:** Font: Italic
Germany	4_604	1998	2001		*Fagus sylvatica*	Lack data		**Formatted:** Font: Italic
Germany	4_605	1998	2005		*Fagus sylvatica*	Lack data		**Formatted:** Font: Italic
Germany	4_606	1996	2011	TL	*Fagus sylvatica*	NS		**Formatted:** Font: Italic
Germany	4_607	1998	2010		*Fagus sylvatica*	Lack data		**Formatted:** Font: Italic
Germany	4_701	1996	2011	TL	*Picea abies*	Weight_N		**Formatted:** Font: Italic
Germany	4_702	1996	2011	TL	*Picea abies*			**Formatted:** Font: Italic
Germany	4_703	1996	2011	TL	*Fagus sylvatica*	NS/P		**Formatted:** Font: Italic
Germany	4_704	1996	2011	TL	*Fagus sylvatica*	Weight_P		**Formatted:** Font: Italic
Germany	4_705	1996	2011	TL	*Quercus petraea*	N/Weight_N		**Formatted:** Font: Italic
Germany	4_706	1996	2011	TL	*Quercus robur*	P/Weight_P		**Formatted:** Font: Italic
Germany	4_707	1996	2011	TL	*Pinus sylvestris*	P		**Formatted:** Font: Italic
Germany	4_802	1997	2011	TL	*Picea abies*	N		**Formatted:** Font: Italic
Germany	4_806	1997	2011	TL	*Picea abies*	P		**Formatted:** Font: Italic

Germany	4_808	1997	2011	TL	*Picea abies*	N/NS	
Germany	4_809	1997	2010	TL	*Picea abies*	N/NS	
Germany	4_812	1997	2011	TL	*Picea abies*	P/N/Weight_N	
Germany	4_901	1996	2011	ZTL/TL	*Pinus sylvestris*	P/N	
Germany	4_902	1996	2011	ZTL/TL	*Picea abies*	NS	
Germany	4_903	1998	2011	ZTL/TL	*Fagus sylvatica*	P	
Germany	4_904	1996	2011	ZTL/TL	*Larix decidua*	NS	
Germany	4_905	1996	2011	ZTL/TL	*Pinus sylvestris*	P/NS	
Germany	4_906	1996	2011	ZTL/TL	*Picea abies*	NS/P	
Germany	4_907	1996	2006		*Fagus sylvatica*	Lack data/BP	
Germany	4_908	1996	2011	ZTL/TL	*Picea abies*	NS/N	
Germany	4_909	1996	2011	ZTL/TL	*Picea abies*	NS/Weight_P/P	depth=-1.2, coll=15
Germany	4_910	1996	2006		*Quercus robur*	Lack data/BP	
Germany	4_911	1996	2011	ZTL/TL	*Fagus sylvatica*	P/Weight_P	
Germany	4_912	1996	2006		*Pinus sylvestris*	Lack data/BP	
Germany	4_913	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4_914	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4_915	1996	2006		*Fagus sylvatica*	Lack data	
Germany	4_916	1996	2006		*Picea abies*	Lack data	
Germany	4_917	1996	2006		*Picea abies*	Lack data	
Germany	4_918	1996	2006		*Pinus sylvestris*	Lack data	
Germany	4_919	1996	2011	ZTL/TL	*Fagus sylvatica*	N/P/NS	
Germany	4_920	1998	2011	ZTL/TL	*Picea abies*	P	
Germany	4_921	1997	2011	ZTL/TL	*Quercus petraea*	P/Weight_P	
Germany	4_922	1997	2011	ZTL/TL	*Picea abies*	P/N	depth=-0.5, coll=6
Germany	4_1001	1998	2011	TL	*Quercus robur*	P/NS	
Germany	4_1201	2001	2007		*Pinus sylvestris*	Lack data	
Germany	4_1202	2001	2011	TL	*Pinus sylvestris*	NS	

Germany	4_1203	2000	2011		*Pinus sylvestris*	BP	
Germany	4_1204	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1205	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1206	2000	2007		*Pinus sylvestris*	Lack data	
Germany	4_1302	1998	2011	TL	*Fagus sylvatica*	N/P	
Germany	4_1303	1997	2011	TL	*Pinus sylvestris*	NS	
Germany	4_1401	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1402	1996	2012	TL	*Picea abies*	P	
Germany	4_1403	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1404	1996	2012	TL	*Picea abies*	NS/P	
Germany	4_1405	1996	2012	TL	*Pinus sylvestris*	NS	
Germany	4_1406	1996	2011	TL	*Quercus petraea*	P	
Germany	4_1501	1998	2011	TL	*Pinus sylvestris*	N/P	
Germany	4_1502	1998	2011	TL	*Pinus sylvestris*	N	
Germany	4_1605	2007	2011		*Picea abies*	Lack data	
Germany	4_1606	2007	2011		*Fagus sylvatica*	Lack data	
Germany	4_1607	2007	2011		*Pinus sylvestris*	Lack data	
Germany	4_1608				*Quercus petraea*	Lack data	
Germany	4_1609				*Abies alba*	Lack data	
Italy	5_1	1999	2011	ZTL	*Fagus sylvatica*	N	
Italy	5_9	1999	2011	ZTL	*Quercus cerris*	NS	
UK	6_512	2004	2011		*Quercus robur*	Lack data	
UK	6_517	2002	2010		*Quercus robur*	Lack data	
UK	6_715	2002	2011	TL	*Pinus sylvestris*	NS	
UK	6_716	2002	2009		*Pinus sylvestris*	Lack data	
UK	6_919	2004	2011		*Picea sichensis*	Lack data	

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UK	6_920				*Picea sichensis*	Lack data	
UK	6_922	1997	2011	TL	*Picea sichensis*	P	
Ireland	7_1	1991	2000	ZTL/TL	*Picea sichensis*	P/NS	
Ireland	7_10	1991	2011	ZTL and others/ TL	*Picea sichensis*	NS/P	
Ireland	7_11	1991	2011	ZTL/TL	*Quercus petraea*	N/NS	
Denmark	8_11	1996	2011	TL	*Picea abies*	NS	
Denmark	8_34	1997	2011	TL	*Fagus sylvatica*	NS	
Denmark	8_74	2002	2012		*Fagus sylvatica*	Lack data/BP	
Denmark	8_85	2003	2011		*Quercus robur*	Lack data	
Greece	9_3					Lack data	
Greece	9_4					Lack data	
Sweden	13_1301	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_1403	1996	2006		*Picea abies*	Lack data	
Sweden	13_5201	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5202	1996	2006		*Picea abies*	Lack data	
Sweden	13_5401	1996	2006		*Picea abies*	Lack data	
Sweden	13_5501	1996	2006		*Picea abies*	Lack data	
Sweden	13_5502	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5601	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5602	1996	2006		*Picea abies*	Lack data	
Sweden	13_5603	1996	2006		*Picea abies*	Lack data	
Sweden	13_5701	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_5702	1996	2006		*Picea abies*	Lack data	
Sweden	13_5703	1996	2006		*Picea abies*	Lack data	
Sweden	13_5801	1996	2006		*Pinus sylvestris*	Lack data	

Sweden	13_6001	1996	2006		*Fagus sylvatica*	Lack data	
Sweden	13_6002	1996	2006		*Quercus robur*	Lack data	
Sweden	13_6003	1996	2006		*Picea abies*	Lack data	
Sweden	13_6102	1996	2006		*Fagus sylvatica*	Lack data	
Sweden	13_6103	1996	2006		*Picea abies*	Lack data	
Sweden	13_6301	2000	2006		*Fagus sylvatica*	Lack data	
Sweden	13_6302	1996	2006		*Picea abies*	Lack data	
Sweden	13_6401	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6501	1996	2006		*Picea abies*	Lack data	
Sweden	13_6503	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6507	1996	2006		*Picea abies*	Lack data	
Sweden	13_6601	1996	2006		*Picea abies*	Lack data	
Sweden	13_6702	1996	2006		*Picea abies*	Lack data	
Sweden	13_6703	1996	2006		*Picea abies*	Lack data	
Sweden	13_6802	1996	2006		*Picea abies*	Lack data	
Sweden	13_6803	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_6901	1996	2006		*Picea abies*	Lack data	
Sweden	13_7402	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_7404	1996	2006		*Picea abies*	Lack data	
Sweden	13_7501	1996	2006		*Pinus sylvestris*	Lack data	
Sweden	13_7502	1996	2006		*Picea abies*	Lack data	
Austria	14_9	1997	2010	TL	*Fagus sylvatica*	N	
Austria	14_16	2001	2010	TL	*Picea abies*	NS	
Finland	15_1	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_3	1998	2011		*Picea abies*	Lack data	
Finland	15_5	1997	2011		*Picea abies*	Lack data	
Finland	15_6	1997	2011		*Pinus sylvestris*	Lack data	

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Finland	15_11	1997	2011	ZTL	*Picea abies*	NS	
Finland	15_16	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_17	1998	2011		*Picea abies*	Lack data	
Finland	15_19	1999	2011		*Picea abies*	Lack data	
Finland	15_20	1998	2011		*Pinus sylvestris*	Lack data	
Finland	15_21	2000	2010		*Picea abies*	Lack data	
Finland	15_23	1998	2010		*Picea abies*	Lack data	
Switzerland	50_2	1999	2012	ZTL/TL	*Picea abies*	P	
Switzerland	50_3	1999	2012	Mix collector type one	*Fagus sylvatica*	N/NS	
Switzerland	50_4	1999	2011	ZTL/TL	*Pinus cembra*	NS/P	
Switzerland	50_8	1999	2012	ZTL/TL	*Fagus sylvatica*	NS/P	
Switzerland	50_12	1999	2012	ZTL/TL	*Quercus cerris*	NS	
Switzerland	50_15	1999	2011	ZTL/TL	*Abies alba*	N	
Switzerland	50_16	1999	2012	Mix collector type one	*Fagus sylvatica*	N/P	
Norway	55_1	1996	2011	ZTL/TL	*Picea abies*	NS/N	
Norway	55_9	1996	2011	TL	*Picea abies*	P/Weight_P	
Norway	55_14	1996	2011	TL	*Picea abies*	N	
Norway	55_18	1999	2010	TL	*Pinus sylvestris*	P	
Norway	55_19	1998	2011	TL	*Picea abies*	N	
Czech Republic	58_521	2006	2011		*Picea abies*	Lack data	
Czech Republic	58_2015	2006	2011		*Fagus sylvatica*	Lack data	
Czech Republic	58_2361	2006	2011		*Quercus fruticosa*	Lack data	
Estonia	59_2	1999	2011	ZTL	*Pinus sylvestris*	NS/N	
Estonia	59_3	1999	2011	ZTL	*Pinus sylvestris*	NS	
Estonia	59_7	2002	2011	ZTL	*Pinus sylvestris*	NS	

~~Supplementary material S2.~~ Description of the statistical methods

1) Overall trend analysis at European scale

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

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

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

2) Trend analysis of individual time series

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

On the other hand, breakpoints may erroneously induce the detection of a significant trend in long-term time series due to artifacts.

For these reasons, we focused on the investigation of the potential long-term trends in soil solution DOC at European forests that show monotonicity. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010). When a breakpoint was detected in a time series, there were two possibilities: first, one of the segments (before or after the detected breakpoint) was longer than 9 years, and, in this case, only the longest segment was used for the subsequent analysis of monotonic trends; second, the breakpoint split the time series in two segments shorter than 9 years and then the time series was not used for the analysis of monotonic trends. We used a length threshold of 9 years, which is the minimum time series length recommended for long-term trend analysis (Libiseller and Grimvall, 2002; Waldner et al., 2014). In total, 258 time series from 97 plots were selected for analysis of monotonic trends (Table S2). No clear pattern could be observed in the distribution of time series of DOC with breakpoints, which appeared to occur randomly across the study plots (Figs. 3~~4~~ and 4~~5~~).

Monotonic trend analyses were carried out using the Seasonal Mann Kendall (SMK) test for monthly DOC concentrations (Hirsch et al., 1982; Marchetto et al., 2013). Partial Mann Kendall (PMK) test was also used to test the influence of monthly precipitation as a co-variable, i.e., to test if the trend detection might be due to a DOC dilution/concentration effect (Libiseller and Grimvall, 2002). For the SMK and PMK tests, the trend slopes were estimated following Sen (1968), as the median of all the slopes determined by all pairs of sample points. The SMK and PMK account for seasonality of the time series by computing the test on each of the seasons (in our case months) separately. The resulting slopes were also tested against the slopes calculated by BFAST. Finally, the individual slopes calculated according to Sen (1968) for each time series using the SMK or PMK method were standardized by dividing them by the median DOC concentration over the sampling period to avoid the influence of the magnitude of DOC concentration in the between-site comparison. The resulting standardized slopes (relative slopes) were used for the subsequent statistical analysis.

For this study, five depth intervals were considered: the organic layer (0 cm), topsoil (0-20 cm), intermediate (20-40 cm), subsoil (40-80 cm) and deep subsoil (> 80 cm). The slopes of each time series were then aggregated to a unique slope per depth interval in each plot (hereafter called "plot-soil depth combination") and classified by the direction of the trend as significantly positive (P, $p < 0.05$), significantly negative (N, $p < 0.05$) and not significant (NS, $p \geq 0.05$). When there was more than one collector per depth class, the median of the slopes was used when the direction of the trend (P, N or NS) was similar. When the different trends at the same plot-soil depth combination were either P and NS, or N and NS, it was marked as "Weighted positive" and "Weighted negative". The five plot-soil depth combinations for which the calculated slopes showed opposite trend directions were discarded. All aggregated trend slopes came from time series measured using the same collector type. After aggregation per plot-depth combinations, 191 trend slopes from 97 plots were available for analysis (Table S2).

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

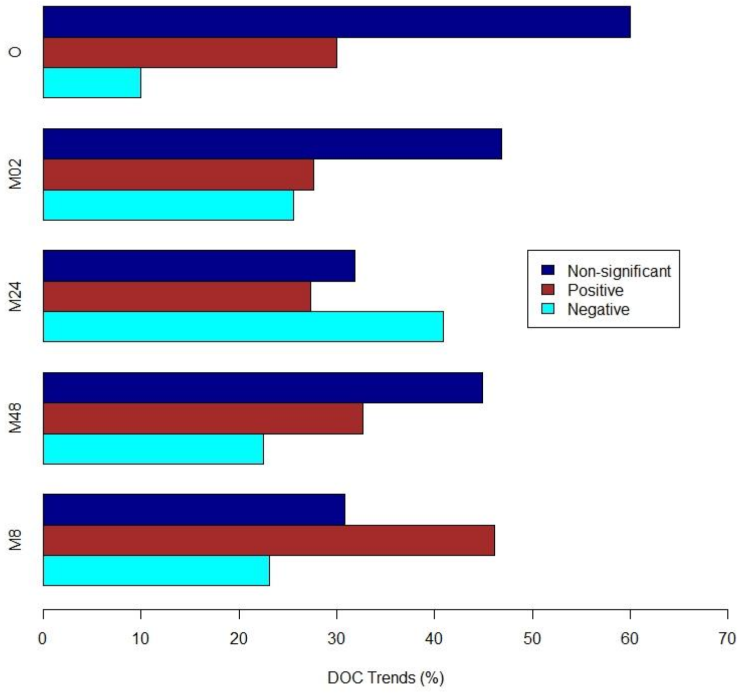
Finally, we performed a multivariate statistical analysies to investigate the main factors explaining differences in DOC trends among the selected plots. Firstly, we used General Discriminant Analysis (GDA) (Raamsdonk et al., 2001) to determine the importance of soil solution and deposition variables in the separation of groups with different trend classes (P, N, NS) in DOC. We also accounted for the part of the variance due to the different soil layers (depth interval) as an independent categorical variable. Secondly, wWe applied Structural Equation Models (SEM) to test whether deposition variables had an effect (direct, indirect or total) on DOC the relative trends slopes of DOC through different pathways (Grace et al., 2010). For the SEMs, we assumed that there is no effect of soil depth on the DOC trends (see next section in Supplementary Material S3). We applied three SEM models: 1) for all the slopes in DOC, 2) only for the forests with low or medium total N deposition, and, 3) only for the forests with high total N deposition. For each case, we searched for the most parsimonious adequate model using the Akaike information criterion (AIC) and R^2. The significance level (p value) of the total, direct and indirect effects were calculated using the bootstrap (with 1200 repetitions) technique (Davison et al., 1986). Dependent variables were log-transformed to improve normality of the continuous variables and then standardized before performing the GDA and SEMs. All the statistical analyses were performed in R software version 3.1.2 (R Core Team, 2014) using the "rkt" (Marchetto et al., 2013), "bfast01" (de Jong et al., 2013) and "sem" (Fox et al., 2013) packages, except for ~~the GDA that was performed using Statistica 6.0 (StatSoft, Inc. Tule, Oklahoma, USA) and t~~the LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA).

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

	Entire dataset	Without breakpoints
All time series	1480 (173 plots)	--
Time series >60 observations and > 10 years	529	258
Aggregated plot-depth combinations	436	191
Plots	118	97

Supplementary material S3. Depth effect on the individual trends in soil solution DOC

Trends in soil solution from different soil depth intervals were mixed for the Pearson's chi-squared test performed for Fig. ure 56 and the Structural Equation Models (SEM) (Fig.ure 611), as the number of cases available for each depth will beare insufficient to compute the statistics if we separate per soil depth interval. To check if the trends calculated at different depths were actually independent from the soil depth interval, we performed a Pearson's chi-squared test and found that the differences in trends among soil depth intervals were not statistically significant $\chi^2(8, N = 174) = 10.94$, $p = 0.21$) (Fig. S1). Therefore, we assumed that there is no difference in trends among soil depth layers and performed the subsequent statistical analysis mixing the trends from different soil depths.



O
M02
M24
M48
M8
Non-significant
Positive
Negative
0
10
20
30
40
50
60
70
DOC Trends (%)

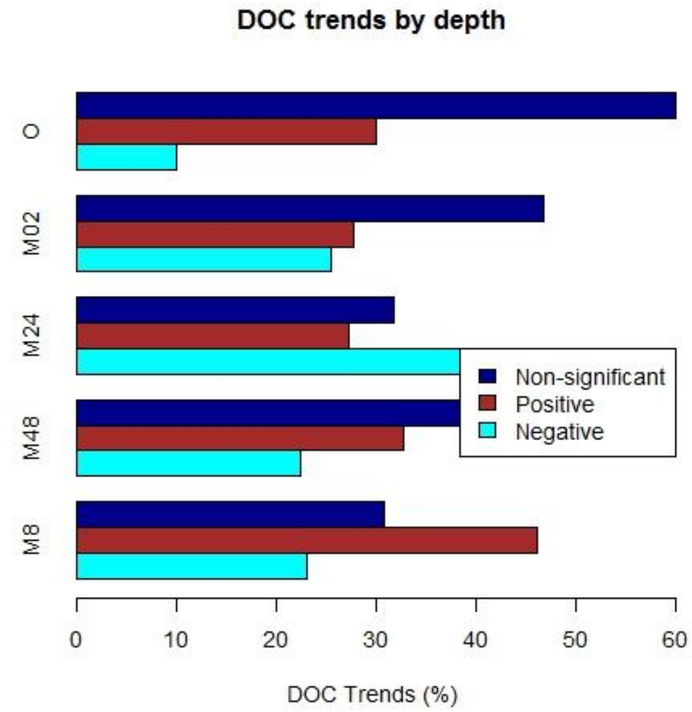


Figure S1. Percentage of non-significant, positive and negative trends per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm).

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

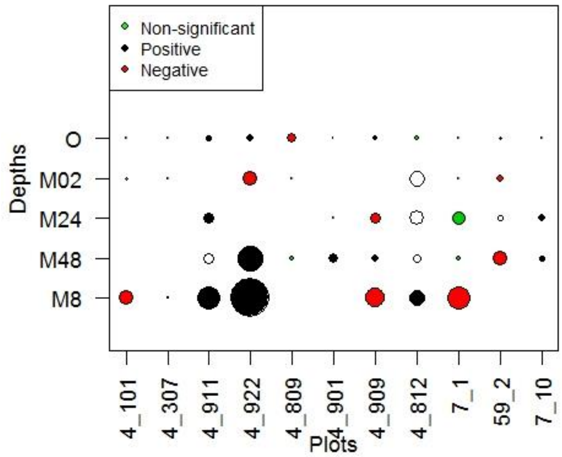


Figure S2. Direction of the trend (non-significant, positive and negative) per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm) for the 11 plots with DOC measured at least at 3 soil depth intervals including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

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

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

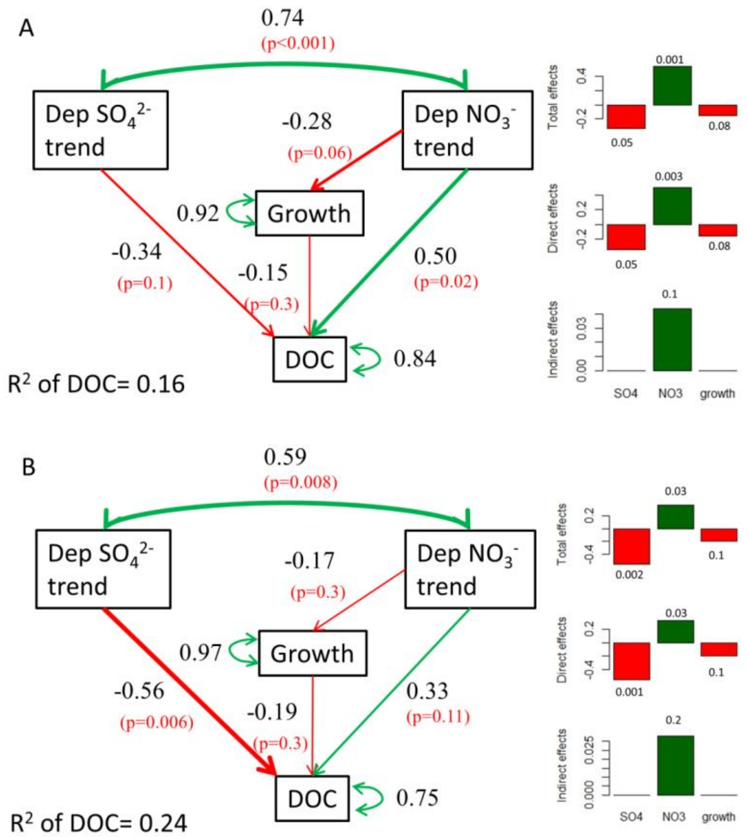


Figure S3. Diagram of the structural equation model (SEM) that best explains the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases and B) cases with low or medium inorganic N deposition, with trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) with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

Comparison of methods of individual trend analysis

We applied the BFAST analysis to select the monotonic time series in order to assure that the overall detected trends were not influenced by breakpoints in the time series. Time series with breakpoints represented more than 50% of the total time series aggregated by soil depth interval (245 out of 436). In total, 191 plot-soil depth combinations from 97 plots were analyzed after filtering out the time series showing breakpoints and 94% of the analyzed plot-depth combinations showed consistent trends among replicates collected at the same depth. In contrast, when also considering the time series with breakpoints, the trends calculated for plot-depth combinations agreed only in 75% of the cases implying that the proportion of contradictory trends within plot-depth combinations increased from 6% in the dataset without breakpoints to 25% in the entire dataset (Fig. S4). For both datasets, the majority of the trends were not statistically significant (44% and 41%, for the dataset with and without breakpoints, respectively). In other words, filtering the time series for breakpoints reduced the within-plot variability, while most of the plots showed similar aggregated trends per plot-depth combinations. For this reason, the results discussed in this paper correspond only to the trends of monotonic (breakpoint filtered) time series of soil solution DOC concentrations.

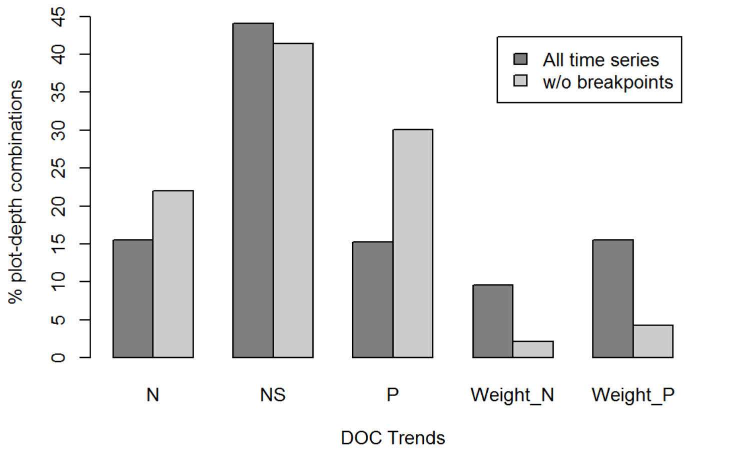


Figure S4. Percentage of plot-soil depth combinations for which negative (N), non-significant (NS), positive (P), negative and non-significant (Weight_N) and positive and non-significant (Weight_P) trends of DOC concentrations were found using SMK (seasonal Mann-Kendall) tests when 1) all the 436 time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

There was a good agreement between results using the three methods: BFAST, SMK, and PMK. The direction and significance of the trend agreed for 84.5% of the time series analyzed. For the majority of the remaining time series for which the trends did not agree, BFAST did not detect a trend when SMK and PMK did, thus, the latter two methods seemed more sensitive for trend detection than BFAST. Trends computed with SMK and PMK agreed well. The direction of the trend for SMK and PMK only differed for the intermediate soil layer (20-40 cm), as a result of the two extra sites for which SMK tests were performed, but not the PMK, that showed a marked positive trend (1.1 and 2 % yr^{-1}). However, when using exactly the same set of sites, the trend did not differ between the two methods.

Implications of using standardized DOC slopes versus absolute DOC slopes.

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

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

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

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

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

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

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

Table S3. Comparison of median relative trend slope (rslope in % yr-1) and absolute trend slope (abs slope in mg L^{-1} yr^{-1}) of DOC concentrations in soil solution and their interquartile range using the Seasonal Mann-Kendall test (SMK). (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm.)

Soil depth	rslope (% yr^{-1})	abs slope (mg L^{-1} yr^{-1})
O	1.18 (±3.37)	0.32 (±1.2)
M02	0.04 (±3.41)	0.008 (±0.52)
M24	0.61 (±8.62)	0.025 (±0.48)
M48	1.01 (±4.79)	0.013 (±0.22)
M8	1.18 (±9.39)	0.032 (±0.31)

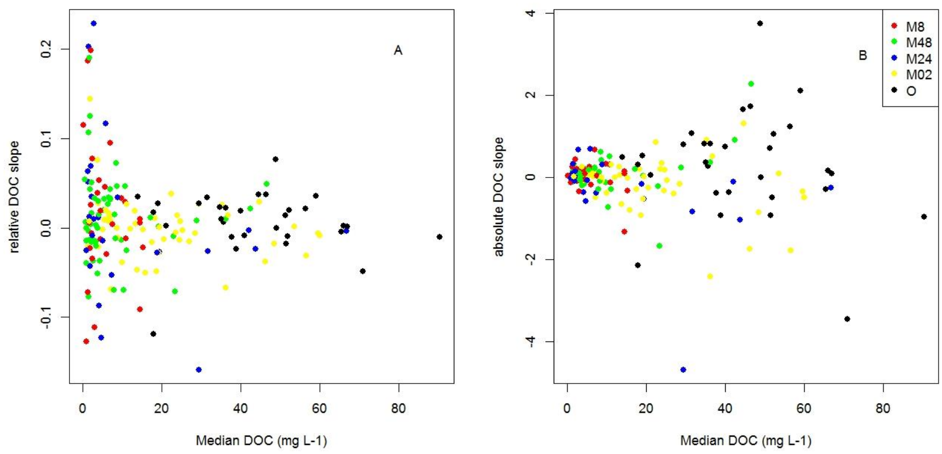


Figure S5. A) Standardized trends (relative DOC slope) versus median DOC concentrations. B) Absolute trends (absolute slope DOC) versus median DOC concentrations. The different colors represent the different soil layers.

Supplementary material S4. Structural equation model with trends in SO_4^{2-} and NO_3^- deposition

The same structural equation models (SEM) represented in Figure 11 were performed using the trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) instead of the mean values of SO_4^{2-} and NO_3^- throughfall deposition (kg ha^{-1} yr^{-1}) (Figure S3). The SEMs for all the cases and for cases with low and medium N deposition are shown in Figure S3.

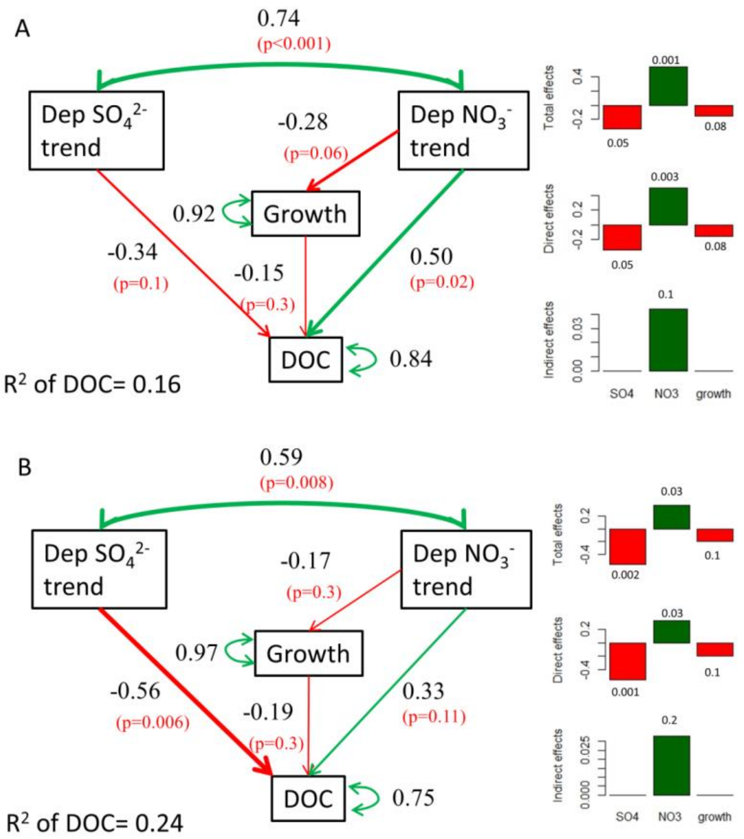


Figure S3. Diagram of the structural equation model (SEM) that best explains the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases and B) cases with low or medium N deposition, with trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) with direct effects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

~~effects.~~**Information on the soil solution chemistry at the studied ICP Forests Level II plots**

Table S4. Median soil solution DOC concentrations (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

Table S5. Median soil solution pH, 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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		WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
		median pH	25% percentile	75% percentile	n	median pH	25% percentile	75% percentile	n
Broadleaved									
TL	O	3.9	3.8	4.1	636	3.90	3.80	4.10	518
	M02	4.5	4.2	5.2	8346	4.60	4.20	6.2	3322
	M24	6.3	4.9	7.1	2482	6.10	4.90	6.7	993
	M48	5.1	4.5	6.7	10496	5.10	4.40	6.5	5162
	M8	6.4	4.6	7.8	4228	4.50	4.30	6.46	2115
ZTL	O	5.30	4.40	6.30	4026	5.30	4.30	6.60	2025
	M02	6.15	5.00	7.6	608	5.00	4.80	5.75	227
	M24	4.70	4.50	5	93	0.00	0.00	0	0
	M48	8.30	8.20	8.4	426	5.20	5.10	5.3	108
	M8	8.20	8.00	8.3	34	0.00	0.00	0	0
Coniferous									
TL	O	4.00	3.80	4.40	2496	3.80	3.60	4.00	726
	M02	4.30	4.00	4.7	10634	4.30	4.00	4.7	6930
	M24	4.60	4.30	5	4739	4.60	4.30	4.8	2849
	M48	4.50	4.30	4.9	13596	4.50	4.20	4.9	7462
	M8	4.57	4.30	6.4	4837	4.48	4.29	4.7	1660
ZTL	O	4.02	3.80	4.60	4038	4.00	3.80	4.80	2839
	M02	4.40	4.10	4.9	2412	4.80	4.53	5.3	254
	M24	4.90	4.50	5.4	551	0.00	0.00	0	0
	M48	4.80	4.10	5.1	225	4.40	4.27	4.9	319
	M8	4.70	4.60	4.8	84	0.00	0.00	0	0

Table S6. Median soil solution conductivity (µS cm^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

	M8	148.50	61.63	305.75	3006	133.00	59.00	210	1736
ZTL	O	71.00	48.00	110.00	2750	70.00	46.60	111.00	1489
	M02	63.35	34.00	86.775	608	28.20	19.10	51.05	227
	M24	44.00	28.00	56	93	0.00	0.00	0	0
	M48	282.00	254.00	318	425	19.30	16.38	25.325	108
	M8	485.50	446.50	539.75	34	0.00	0.00	0	0
Coniferous									
TL	O	77.00	56.00	124.00	2425	85.00	65.00	155.00	725
	M02	58.00	31.00	92	9222	61.00	33.00	105.5	5699
	M24	50.00	30.00	97	2954	56.00	31.00	111	1715
	M48	56.00	37.00	94	10270	56.00	37.20	99	6658
	M8	104.00	55.00	207.75	2850	120.50	66.00	259	1118
ZTL	O	65.30	45.00	104.00	2296	64.00	42.30	106.00	1537
	M02	39.20	25.00	59	2627	27.00	20.08	41.1	228
	M24	32.00	21.00	57.95	615	0.00	0.00	0	0
	M48	39.05	28.00	150.5	214	95.85	46.48	155.5	290
	M8	50.00	31.75	69.25	84	0.00	0.00	0	0

Table S7. Median soil solution Ca (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

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

Table S8. Median soil solution Mg (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

	M02	0.37	0.20	0.616	2773	0.49	0.38	0.6375	262
	M24	0.44	0.25	0.927	644	0.00	0.00	0	0
	M48	0.76	0.49	3.725	227	0.55	0.35	0.91	321
	M8	0.85	0.37	1.3425	84	0.00	0.00	0	0

Table S9. Median soil solution S-SO_4^{2-} (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

Table S10. Median soil solution N-NO_3^- (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

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

Table S11. Median soil solution Al (mg L^{-1}), 25% and 75% percentiles and number of observations (n) for the different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints).

-	-	WITH BREAKPOINTS				WITHOUT BREAKPOINTS			
-	-	media	25%	75%	n	median	25%	75%	n

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

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