

## ***Interactive comment on “Trends in soil solution dissolved organic carbon (DOC) concentrations across European forests” by M. Camino-Serrano et al.***

**M. Camino-Serrano et al.**

elisabeth.pannatier@wsl.ch

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### 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).

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We agree that a quantitative description of the concentrations of DOC is missing. In the revised version, we will add a table 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<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Al<sup>3+</sup> and Fe<sup>2+</sup>). The information will be separated on collector type, soil layer and forest type, as for Table 1 in submitted manuscript.

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.

Before deciding to use the standardized trend slopes, we tested whether there was a relation between the DOC Sen slopes and the median DOC concentrations, and we saw that a priori there was no such a relationship (Figure 1).

This Figure 1 will be included in Supplementary Material in order to support the discussion of the relation between the relative slopes and the DOC concentrations. Moreover, we will use the information gained from the new table with median DOC concentrations (Comment 1) to discuss the possible effect that DOC concentration levels may have, i.e., exaggerating the DOC trends at low DOC levels, such as may occur in the subsoil.

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

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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?

Indeed, the fact that we used the standardized terms (rslope) implies that the rslope may be identical 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. Although the actual change in DOC concentration with depth is normally more limited than that of the example taken in this comment. However, in our opinion, the detected trends in mineral soils are not less important because DOC concentrations are lower. In fact, we decided to use the standardized slopes to be able to compare trends amongst sites, independently of the absolute DOC concentrations. Furthermore, standardizing the slopes allows 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 initial DOC concentrations of the site.

Actually, both relative and absolute slopes will give different information: as mentioned, with the absolute slope we can see the real magnitude and significance of the trend, but it does not allow for comparison among sites or horizons. Consequently, as we were interested in whether there is a general DOC trend and in the intercomparison among sites at European scale, we decided that using the relative slope was more consistent. It is however possible that the large statistical trends in deep mineral soils are a result of this phenomenon (see Figure 1 below) and in the revised manuscript we will test for it.

Finally, we would like to highlight that the statistical analyses (LMM, SMK and PMK) were done on the absolute value and were then transformed to facilitate the interpreta-

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tion. Thus, the fact that we express the resulting trend in relative terms can influence our interpretation but has no influence on the statistical test itself (carried out on the absolute values of DOC). In order to provide all the information to the reader, we will add the median DOC concentration in the table reporting the trends. A more detailed discussion on this issue (relative/absolute slopes) will be added in the revised manuscript.

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):

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. We could add this conclusion in the discussion section (chapter 4.1.1.) in the revised manuscript.

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.

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

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compare trends among sites and soil layers (see answer to comment 3). However, it is true that a discussion on the effects of this choice is missing. We will mention the potential exaggeration of the effects of trends in low DOC-concentration soil horizons in the discussion of the revised manuscript.

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?

We will rework the discussion in the revised manuscript. 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 can add an explanation of this. We will also describe if the trends occur at low and high DOC concentrations based on the new table (See Comment 1). Finally, the initial DOC concentration seems not to influence the trend strength and direction and this will be added in the text.

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).

We agree with this comment and the title of chapter 4.1.1. will be changed to "Evaluation

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tion of non-significant trends" in the revised manuscript. Some speculative sentences will be deleted and the discussion mentioned in reply to comment 4 will be added.

### 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, but we suggest to add some text and references on the importance of riparian zones and peat lands.

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 159-160), 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.

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

Table 2 below clearly explains where these numbers came from, as it seemed to be confusing throughout the manuscript. This table will be included in the revised manuscript (in Supplementary Material).

Thus, both 436 and 529 were correct, but they referred 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 will change the number in Figure 1 for consistency.

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, the same pH ranges were used for all the soil horizons and as a consequence we have more organic soil horizons in the Low pH class (Table 3).

Since the manuscript contains too many figures (also suggested by referee 2), we suggest to move Figure 9 to Supplementary Material. We still find this result as potentially important, and by moving the graph to Supplementary Material we can refer to it through the text, but it will not be part of the manuscript. When discussing the graph, the issue of the bias towards organic and upper mineral soil horizons in the Low pH class will be discussed.

Sites were classified according to soil solution pH, and thus the revised text will be corrected.

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) and for our classification (Lines 219-222), we used mean values of deposition for this period. In the revised manuscript, this will be mentioned in the text.

âĂć 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.

## C7

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

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

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 <sup>-1</sup>), 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.

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 (see response to detailed comment 3): 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 will be clarified in the text of the revised manuscript.

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

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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<sup>-1</sup> yr<sup>-1</sup> for the organic layer versus 0.03 below 80 cm). This is a natural consequence of lower DOC concentrations in deep soils. This issue will be commented in the paragraph in lines 324-332 in the revised manuscript.

10. Lines 360-361: "...we found evidence. . .". The rslope=f(mean TF SO<sub>4</sub> deposition) relations in Figure 9 are no evidence, however, they show a relatively strong indication ( $r^2=0.288$ ) on that the SO<sub>4</sub> deposition may tangibly affect the rslope values in acidic soils. Rephrase the sentence.

In the revised manuscript, the sentence will be rephrased to "However, our results point out to a control of soil acidity on the SO<sub>42-</sub> deposition effect on the trends of DOC in soil solution (Fig. 9)." Figure 9 will be moved to Supplementary Material.

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 1 below), we do 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 suggest to remove the GDA analysis from the manuscript (Fig. 10 and Table 4 in submitted manuscript) to shorten the paper (see answers to comments from referee 2).

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

This will be corrected in the revised manuscript.

13. Line 536: Again the total number of observations (n=174) does not match the  
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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 321-322 in submitted manuscript). In the revised manuscript, this will be added in the text in line 536 for clarification.

14. Lines 645-647: "We found evidence that soil pH determines the response of trends of DOC in soil solution to SO<sub>42-</sub> 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. Therefore, to check the influence of mixing soil layers, we re-did the SEMs models (Figure 11 in submitted 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 11A, 11B and 11C, 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.

In the revised manuscript, this statement will be rephrased as "We found that the response of trends of DOC in soil solution to SO<sub>4</sub><sup>2-</sup> deposition depends on soil pH" and the issue of the bias towards organic horizons at Low pH class will be discussed (see answer to detailed comment 4).

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.

We agree that we should focus the conclusions more on the large local variation instead of the regional processes. This will be changed in the conclusions of the revised manuscript. We will also stress the differences between the DOC trends found in the organic vs mineral layers and the information gained from the influence of DOC concentration levels in the DOC trends will be added. However, we think that we cannot describe the influences by different drivers/processes based on our results without being too speculative for a 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. 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. 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? 4. Table 4, Legend: What do you

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mean with ". . .during the last years. . ."? Explain. 5. Figure 2: Weight\_P is missing on the X-axis 6. Figure 3, legend: Explain boxplots (c.f. Figure 6) and "n" in figure. 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. 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. 9. Figure 9: In the legend, define which soil layers the data points refer to. 10. Figure 10: Use the same scales on the XY-axes in Figure A and B. 11. Figure 11: In the legend change from (>15 kg N ha<sup>-1</sup> yr<sup>-1</sup>) to (<15 kg N ha<sup>-1</sup> yr<sup>-1</sup>)

All these Tables and Figures will be corrected accordingly to these comments.

#### Comments on Supplementary material

1. S2: For the GDA analysis, it is unclear whether the "Weighed positive" and "Weighed negative" trends are included. Clarify.

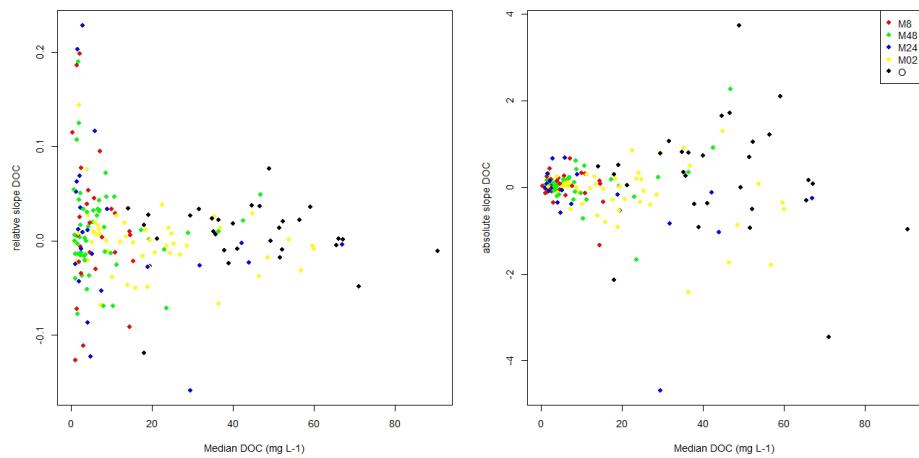
For the GDA analysis, the classes Weighted positive and Weighted negative are not included. This will be clarified in the revised version.

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 will be clarified in the revised version.

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

This figure will be re-done.



**Fig. 1.** Figure 1. Left: Standardize trends (relative slope DOC) versus median DOC concentrations. Right: Absolute trends (absolute slope DOC) versus median DOC concentrations. The different colors represent

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

**Fig. 2.** Table 1. Comparison significant positive, negative and non-significant at  $p<0.05$  and  $p<0.01$ .

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

**Fig. 3.** Table 2. Summary of number of time series used in the study

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

**Fig. 4.** Table 3. Number of cases at high and low pH classified by organic layer.

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