

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

### Anonymous Referee #1

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### Dear editor,

This manuscript deals with DOC trends in soil water at different soil horizons in European forests. The statistical analyzes were mainly performed on data from a subset of sites from the ICP Forests level II plots. Based on 436 soil water time series (number uncertain, see below) from 118 plots (Figure 1), DOC concentration trends at the European level were evaluated with linear mixed-effects models (LMM). A second analysis was performed after removing time series with breakpoints determined with the Breaks For Additive Seasonal and Trend (BFAST) algorithm. The remaining data set included 191 time series (number uncertain, see below) from 97 plots. Different statistical non-parametric methods including Seasonal Mann Kendal (SMK) and Partial

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Mann Kendall (PMK) were used on each time series without breakpoints to evaluate monotonic trends and to test influence of precipitation as a co-variable, respectively. The same types of analyses were performed on other soil solution chemical parameters and on precipitation and temperature. Two multivariate statistical methods were used (General Discriminant Analysis [GDA] and Structural Equation Models [SEM]) to identify the main factors co-varying with the differences in DOC trends among the selected plots.

The presented work is of great scientific interest and well suitable for publishing in BG. The manuscript is well written, technically sound (see below for some comments) and well organized. However, the data presented are not allowing for comparisons with other soil water DOC investigations. There is a lack of quantitative data on real DOC concentrations and trends. Hence, the manuscript needs a major revision before it can be published in BG.

## 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).

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?

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?

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.

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.

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?

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 dis-

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cussions on factors affecting trend analysis including what you have found related to comment 4 (see above).

## 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.

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?

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

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!

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

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

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.

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.

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.

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.

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)?

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

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.

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  $4.2 \le pH \le 5$  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.

15. In the conclusions, I would suggest that you stress the large local variation re-

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lated 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.

Comments on tables and figures

1. Table 1: In the legend, information on how  $0.05 \le p \le 0.1$  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 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-1 yr-1) to (<15 kg N ha-1 yr-1)

# Comments on Supplementary material

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

2. S2: For the SEM analysis, it is unclear whether the analyses are performed on SEN slopes or rslopes. Clarify.

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

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