

Biogeosciences Discuss., author comment AC2
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Reply on RC2

Clara Romero González-Quijano et al.

Author comment on "Dissolved organic matter signatures in urban surface waters: spatio-temporal patterns and drivers" by Clara Romero González-Quijano et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-340-AC2>, 2022

General Comments

González-Quijano et al.'s manuscript seeks to understand how dissolved organic matter (DOM) pools are structured in an urban ecosystem. The manuscript further describes how well DOM quality relates to conventional water quality monitoring measurements and asks if DOM would be a useful indicator of water quality. The study used three different approaches to characterize the organic matter pool. I think the manuscript would be of interest to a broad audience and provides a useful and complex dataset. The results did well at describing the main multidimensional patterns in the data without focusing too heavily on individual data specifics. I think the multivariate approach used in the paper has merits, but I think adjustments to the approach would be useful. First, the trace organic compounds (TrOC) PCA overcomplicated the manuscript and made it challenging to connection microcontaminant loads with urban pollution. Second, I think the DOM PCA could be focused by reducing the number of variables used and by presenting the parallel factor analysis (PARAFAC) results as percent of Fmax or relative to DOC. I think that both of these changes to the DOM PCA would allow the PCA and RDA to better highlight the data and connections between urban water quality markers. These adjustments will likely also meaningfully influence how DOM optical properties related to mass spectrometry results. Finally, I think the manuscript highlights an important topic, using DOM optical properties as a management tool. The current framing of the manuscript could be altered to better bring out this point. I think the "DOM as a monitoring tool" argument would be strengthened by adding broader statements explaining what makes DOM ideal for management, adding a hypothesis around the RDA between urban pollution drivers, and more fully explaining what basic knowledge is missing. Below I provide more detail around these main points for the author's consideration as well as other specific suggestions

Thank you for these excellent suggestions, which we will consider as follows:

- *We will compute a mean of all the TrOC compounds after standardizing the values to ensure equal weighting. This aggregation is justified by the strongly positive correlations between all TrOCs.*
- *We will slightly reduce the complexity of the PCA by removing obviously redundant variables. This eases the interpretation of the PCA biplot without a major loss of*

information.

- We will present a new PCA using PARAFAC components normalized by DOC, replacing the PCA of the raw PARAFAC data.
- We side with the reviewer that an important implication of our study is the suggestion to develop DOM optical properties for monitoring purposes that complement established approaches. In particular, DOM "fingerprints" could yield valuable information about functional impairment. We will further develop this in the Discussion.

Specific Suggestions

Abstract & manuscript framing – I think the study would be better set up if "basic" was explained in more detail. I am curious to know what connections are missing and how or why this information is needed to better understand DOM composition in urban ecosystems. I think it would be useful if the abstract reconnects the expected high DOM diversity to "filling in the basics"

We will reframe the manuscript and also revise the abstract as suggested:

- Explain that basic information refers to the unknown causal relationships between processes (or functions) in urban settings and their imprints on DOM composition and dynamics.
- Clarify that "high DOM diversity" is expected to result from the putatively high diversity of processes in urban settings, owing to the combination of natural and human-facilitated processes in these environments, both within the aquatic systems and in the watershed that supply much of the DOM.
- Link both aspects to the use of DOM composition for water quality monitoring.

Discussion section 4.3 & manuscript framing – this seems like the main objective of the study and is a valuable argument to be made and supported. I think some of this framing is lost in the methods and results. It would be useful for the reader if perhaps more direct statements of hypotheses were made that connect more traditional water quality measures to the potential use of DOM in water quality monitoring.

We will improve the rationale behind our hypotheses, focusing on the value of monitoring and the use of DOM composition to infer processes, rather than exploring correlations with established water quality measures.

Methods, 2.1 study sites – I think it would be useful to provide the size cutoff for streams vs rivers as was done for lakes and ponds.

Rivers and streams were classified according to a width cutoff of 5 m.

Methods - Given the differences in habitat and the location of primary producers in Rivers, Streams, Ponds, and Lakes, I am not certain CHL should be used as a proxy for trophic state. Benthic algae are often abundant in urban streams. I think CHL should be removed from RDA because I don't think it's a comparable measure of eutrophication between lotic and lentic systems.

Most rivers in Berlin are relatively deep and slow-flowing. In contrast, although streams are also typically slow-flowing, much of their autotrophic biomass could indeed be benthic. This limits the value of chl concentration in the water column as a proxy of eutrophication. However, in the absence of more suitable indicators and because high chl values do indicate high productivity (while the inverse is not necessarily true), we still prefer retaining the variable - along with ammonium, nitrate and total phosphorus concentrations.

Methods - I did not understand what the hypotheses were in RDA around DOM drivers. It was unclear what possible drivers were measured and then how they were applied to see changes in DOM. Perhaps more explanation is needed for readers like me with less experience using RDA and also to strengthen this analysis' connection to using DOM in urban monitoring.

The goal of the RDA was to identify potential drivers of DOM composition and to test whether a series of selected predictors provide useful information on DOM composition. We will expand the RDA paragraph in Methods (formerly lines 181-188) to better explain the rationale behind using the RDA (besides the PCA and the Procrustes test) and the associated hypotheses. We will also clarify the use of the selected predictors.

Methods & Result - There are an impressive number of variables determined in this study. Many of which correlate or are a proxy for the same type of measure. For example, molecular weight is approximated through three optical indices and measured more directly with liquid size-exclusion chromatography. Given the complexity of the manuscript's dataset, it might be easier for the reader if only one variable that measures or estimates a DOM property was used. In my experience, especially given the inherent correlation between DOM characteristics, redundancy of multiple variables targeting the same DOM attribute are not needed. For example, I suggest only using S275-295 or SR as the optical indicator of DOM molecular weight. For comparison, its fine to keep all measures in the appendix but, for the main body of the paper and multivariate analysis, I think it would be easier for the reader to understand the results if only S275-295 or SR was used as the optical indicator of size. One final note: Short slope (S275-295) should be positive (see Fichot & Benner 2012 L&O 57(5):1453).

The very purpose of a PCA is to reduce the number of dimensions in a dataset, so that prior selection of variables is not critically needed, even when variables are redundant. However, highly correlated variables can clutter PCA biplots and could thus hamper discerning clear patterns. Thus, we will remove a small number of strongly correlated and obviously redundant variables for the PCA. This changes the PCA biplot only slightly. We will report the correlations between the discarded variables and the variables that were included (or the principal components) in the appendix.

The sign of the short slope will be corrected.

Methods & Results – I am not certain the TrOC PCA is necessary. The purpose is to show micropollutant load. I worry about the below detection limit impact of ponds on the PCA loadings and scores. It seems like an easier and more straightforward metric that would also show micropollutant load is to sum all TrOCs and report a total TrOC concentration. This way, the reader does not need to remember three different PCAs and use a relative measure of load, when the sum of TrOCs would provide an understandable indicator of micropollutant load.

We will standardize all TrOC concentrations to zero mean and unit variance, compute a mean for each site as an aggregate indicator of pollution by TrOCs, and use this indicator in the RDA analysis. This standardization step ensures equal weightings of the variables. The approach is justified by the strong positive correlations between all TrOCs, which we will show by the (old) PCA results in the appendix.

Methods & Results – I think the DOM PCA would structure better around DOM quality if PARAFAC components were set as percentages of Fmax or relative to DOC rather than RU. RU tends to follow concentration rather than clearly line up to quality measures and I think this is why all PARAFAC components point in the

same direction in the DOM PCA. For example, DOC was significantly higher in streams. The DOM PCA water body type clusters follow fairly well this DOC concentration gradient, with all the PARAFAC components increasing in intensity toward places that had higher DOC. This would make quantity rather than quality the main driving force behind the PCA loadings. I agree that there is some separation of allochthonous to autochthonous sourced DOM along PC1 but the PARAFAC components did not follow the expected pattern based on quality. I am guessing that making the PARAFAC components relative, will cause them to line up much better across the source gradient. Using PARAFAC components as a percent of total Fmax or standardized to DOC (RU/DOC) might also provide better overlap between optical and FT-ICR-MS properties of DOM and help DOM optical estimates of similar compositional properties better align in the PCA space. The last paragraph of the results describes the FT-ICR-MS results clearly and in summarized way the read can understand. However, the PC comparisons don't always match with the optical multivariate space. For example, C6 & C8 are negative on PC1 and positive on PC2 suggesting there is more protein in that quadrant, but the comparison with FT-ICR-MS indicates that N containing compounds are positively related to PC1. Similar conflicts arise with humics. I think the reason for this is the PARAFAC components are being driven by quantity rather than quality. By making PARAFAC relative, then the resulting re-analyzed PCA might track more expectedly with FT-ICR-MS patterns.

We will include a new PCA with the DOC-normalized PARAFAC components, which will reduce the influence of DOC concentration and emphasize instead qualitative differences among DOM from different sites. In the new PCA, three of the PARAFAC components are now distinctly different from the others on the biplot, while the rest of the variables ordinate almost like in the old PCA.

Discussion, around line 320 - These are interesting ideas and useful points. I wonder if the lower B:A in streams reflects that the WWTP degrades DOM and the effluent is highly processed, while in lakes and ponds there is more new production of DOM resulting in a higher index score.

Thank you for the idea. We will add the point to the Discussion.

Figure 1 – I like the style of this figure. I think it shows the sites and results well. For the caption, the reader needs more information. At this stage in the manuscript, it is unclear what variables are included in the PCA scores and what the patterns mean. It would be useful for the reader if a plain language interpretation of each PC axis was given so the reader could quickly understand the pattern

We will expand the caption as follows:

Figure 1 (a) Map of 32 sampling sites in the city of Berlin, including 7 lakes (dark green), 7 ponds (light green), 9 streams (light blue), and 9 rivers (dark blue), including two heavily polluted stream sites and two heavily polluted river sites. (b, c) Scores of a Principal Component Analysis (PCA) of DOM characteristics for all sites sampled in four different seasons. The PCA includes the measured DOC concentrations, all absorbance and fluorescence data, absolute component-specific fluorescence intensities from PARAFAC, and the results from size-exclusion chromatography. Different colours indicate differences in DOM composition. Site codes are given in Table S1. Sites marked by asterisks () were restricted to three seasons and were hence excluded from the PCA.*

Supplemental Information – I am not certain why the SI is needed given the large set of appendices. Why not move table S1 to the appendix and incorporate

the DOM analysis information into the main methods. At least for, FT-ICR-MS the SI methods are very similar to the main methods.

We will move this information in the supplement to the main text or the appendix.

Table A4 - Should the FIX for rivers be 1.68 rather than 0.68? 0.68 is well outside the normal range for FIX and could indicate an issue with how EEMs were processed, contamination or scanning error, or a coding error for the calculations

Thank you for spotting this mistake. We checked the value and found that it must indeed read 1.68. We will correct the number.