Biogeosciences Discussions

Biogeosciences Discuss., author comment AC1
https://doi.org/10.5194/bg-2021-340-AC1, 2022

Reply on RC1

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-AC1, 2022

Overall, this is an interesting dataset and questions.

Thank you

The results and discussion are somewhat challenging. The discussion and results lack a clear organizing structure.

We will improve the links between the Methods, Results and Discussion sections to better structure the manuscript. We realized that information about some sites was first mentioned in the Discussion only, which made it difficult to follow. Therefore, we will describe the sites with greater detail in Methods. This concerns particularly information on WWTP effluents and other specific features of various sites. We will also introduce the idea of DOM monitoring in the Introduction and return to it in the Discussion.

Some of the relationships claimed in the analysis have no clear/singular interpretation. For example, the authors say that C2 and C8 are associated with wastewater because authors have said they were associated with wastewater in other study in other regions of the world and because they are associated with TrOCs. A similar statement is made about nutrients. The problem, however, is that all of the components ordinate in the same direction. So all of the components are correlated with wastewater and all of the components are correlated with nutrients (at least on RDA 1). What then makes you focus on a few components over others?

The similar behavior of the various PARAFAC components was caused by using raw absolute fluorescence values without any normalization. Prompted by another reviewer comment, we will normalize PARAFAC components by DOC concentration. As a result, compositional changes of DOM will emerge more clearly, which also alleviates the problem of non-singular interpretation. In particular, the humic components C3, C4 and C5 point in a different direction than the other PARAFAC components. Furthermore, a new correlation analysis shows that C3, C4 and C5 were not or negatively correlated with the TrOCs, whereas the other PARAFAC components were positively correlated with the TrOCs. Note that apart from their relation to the TrOCs, C2 and C8 have been previously found in WWTP effluents.

Some more methodological details are needed on the PARAFAC process. Which

software and how did you handle validation.

Details of the PARAFAC process were provided in the supplement of the manuscript (see lines 1-20 there). This includes information on the software we used and how we handled validation. In the revised manuscript, we will further expand this description in the appendix. Please also see the response further below.

An overlay of the split halves would be nice to see on the plot of the PARAFAC model. It helps the reader evaluate the quality of the model.

We will add a graph showing results of the split-half validation of the final PARAFAC model to the appendix as suggested.

A number of times DOM diversity is equated with functional diversity 'in the aquatic system' and I don't seem much evidence of this or a framework built for it. Connection DOM composition to ecosystem functioning is still pretty speculative (to be clear it is speculation I support, just still feel it has a long way to go). In particular the authors point to the diversity of DOM as an indicator of diversity or functional diversity in the aquatic system, but provide little evidence why it should be so. Clearly, DOM diversity is an indicator of the diversity of watershed processes both natural and anthropogenic – source diversity if you will. Is that function 'in the aquatic system' or function in the watershed? I would argue that it is the latter.

There appears to be agreement with the reviewer about the idea that DOM can encapsulate information about ongoing or past processes. However, it is less clear how such information may best be exploited. We investigated a set of diverse urban ecosystems to assess whether expectedly strong environmental gradients arising naturally across sites affect DOM diversity, which can refer to the diversity of DOM compounds at a given site (alpha diversity), or to the compositional turnover of DOM across sites (beta diversity). In both cases, the rationale behind the linkage of DOM diversity and functional diversity is the idea that individual processes leave an imprint on DOM composition, for instance by generating specific compounds. We will clarify these aspects in the revised manuscript.

However, with respect to the watershed you only ever look at a 50 M buffer (see detailed comments on this below).

Please see our response below.

In several places hydrology and runoff are presented as the cause of an observed relationship, but there is no mention of any aspect of the study design that evaluates hydrology. E.g. "…for example, was formerly connected to a sewage farm and appeared to be influenced by previously unrecognized storm water runoff that likely delivered inputs during heavy rain. " No storm sampling was ever discussed, no pre-post sampling that would disambiguate this. There are just a lot of instances of statements and conclusions that are not or are not unambiguously supported by collected data.

Our objective was to characterize DOM composition in diverse water bodies within an urban setting and relate it to site characteristics. We could not directly study runoff effects during precipitation events. Nevertheless, we can relate DOM composition to specific site characteristics such as imperviousness in the surroundings or upstream WWTP that make some sites more vulnerable to stormwater runoff than others. Importantly, DOM composition has potential to provide integrative information, which could inform about runoff legacies even though we did not specifically sample before and after storm events.

To clarify these points, we will provide more site-specific information in the revised manuscript. Specifically, we will provide information why some sites are more susceptible to surface runoff than others (as inferred from large proportions of impervious surface area within the 50-m strips adjacent to our sampling sites) as well as wastewater inputs (downstream sites in receiving streams) during storm events. To do so, we will add information on WWTP outlets potentially affecting our sampling sites both in Figure 1, the main text (first in Methods) and the table that was formerly in the Supplement and will be moved to the appendix. This will also help clarify the linkage between all the measurements taken and the Discussion, and make it easier to follow. We will further provide precipitation data showing that our own sampling did not occur during or shortly after heavy precipitation events. We will show this in a new figure in the appendix. We will also refer to the idea of storm sampling in the context of (potentially continuous, real-time) DOM monitoring.

All that said. This is an interesting dataset and general question, I do encourage the authors to develop it further and focus on the clear and well-supported interpretations of the data.

Thank you very much.

Specific comments

39 'failure of citizens' … inappropriate and subjective statement. You blame the public, but have scientists properly communicated the issue to the public? Rather adversarial language that will only function to pit the general public against science. Why make an enemy?

Thank you for drawing our attention to the fact that this statement could be perceived as being offensive, which was of course not our intention. We will rephrase the sentence to "This and the limited recognition of urban freshwaters as…"

47-48 Subjective. What is the purpose of monitoring? What is the endpoint. Often it is something much larger like ensuring healthy available habitat for human or animal use. If a primary driver of healthy habitat for animals is the availability of oxygen in the water, is that really a 'narrow focus' or is it the focus that is appropriate for monitoring given the monitoring goals. I think you would be better arguing that high resolution approaches can expand the suite of bigger picture ecosystems states that can be monitored with DOM.

We will rephrase the sentence to "These approaches do not take advantage of the extreme diversity of DOM observed in freshwaters, which potentially can provide insights into water quality status and the factors driving it, complementing established procedures".

78-80 More info on this. What about these sites, what type of pollution do they represent. All the same type/intensity, different types?

We will add information about these sites in the table in the supplement (appendix in the revised manuscript): nature of the sites (i.e. natural vs artificial), channelization, receiving streams of WWTP effluents. As stated above, we will also add information on potential WWTP inputs in Figure 1a.

84-86 Why only a 50 buffer? Why not a series of buffers to determine what the spatial scale is that is most relevant. The water interconnections in an urban ecosystem are complex, I doubt 50m captures the reality of the source areas. See Kaushal and Belt 2012.

The 50-m strips we chose were supposed to capture influences in the vicinity of the sites, i.e. influences of the riparian zone and somewhat farther away but not from the whole watershed, which is difficult to define in urban areas. This choice enabled us particularly to distinguish between urban sites adjacent to paved surfaces and others in green spaces. Note also that Tufekcioglu (2020) and Johnson (2005) used buffer zones of similar size and a study on ponds by Declerck (2006) used a range of widths (ranging from 50-3200 m) and found 50 and 100 m to be most appropriate to assess land-cover effects.

105-110 Did you collect and process any blanks?

We used ultra-pure water as blank. This information is given in the former supplement (appendix in the revised manuscript) where method details are described.

105-110 Was iron measured in any of these samples? This can have significant effects on optical DOM determination and is often elevated as it runs through urban infrastructure.

We did not measure iron in our water samples, but a recent study on the River Spree in Berlin indicates that total iron concentrations are <0.3 mg/l (Friedland et al., 2021). Concentrations in the other water bodies we sampled are likely to be lower. Nevertheless, since we cannot rule out Fe-DOM associations in our samples, we will add a short discussion on the potential interference of Fe with our optical DOM signatures. We will also provide a rough assessment of the potential importance of iron for water colour and absorption-based data by calculating abs_{420}*/DOC and compare these data with (i) literature values and (ii) available from the Senate database iron concentrations in Berlin´s surface waters*.

123 A few things here. This is almost universally abbreviated FI and not FIX. You are using the wavelengths for you calculations for samples corrected for instrumental bias. This is appropriate. However, the citation you reference here was based on FI values calculated from a the old wavelengths that were not corrected for instrumental bias. McKnight updated this in Corey et al. 2010 and it makes a significant difference in the reference values of allochthonous and autochthonous endpoints. Lastly in heavily impacted urban systems, the classical interpretation of FI as developed by McKnight may simply not be applicable. You may be getting a 1.2 or a 1.9, but it may not mean the same thing as it would in a more natural system.

Thank you for sharing these insights. We will replace FIX by FI, use Cory et al. (2010) as the reference, and revise the discussion to point to the limited applicability of McKnight's framework to urban waters.

126-127 Would like to see the split half validation overlaid on this PARAFAC model (Figure A1). Overall more details on the PARAFAC modelling process used would be nice.

We will add the split-half validation as suggested in the appendix. The PARAFAC modelling was described in the supplement (now moved to the appendix), but it will be expanded particularly to provide information on cross-validation. See also the response above.

286-288 Does it reflect high functional diversity across the 'aquatic network'? So far it would seem to suggest a variety of inputs or a diversity of input. I don't know if it says anything about what is going on in terms of fucntional/metabolic processes in the aquatic network. Also consider what 'functional diversity' means and what is 'desirable' vs. 'undesirable.' High functional diversity might be due to the wide range of degradation states that stream in an urban

landscape may be experiencing.

We agree with the reviewer that the processes we think of as leaving an imprint on DOM composition include internal processes (such as intense primary productivity) as well as watershed processes (such as terrestrial-aquatic coupling through allochthonous inputs). Both types of processes shape functioning of the various ecosystems, specifically as our study encompasses small as well as large lentic and lotic ecosystems. Our point here is simply that high diversity of DOM translates to potentially high information content about these various processes. We agree that the phrase "across the aquatic network" may be misleading and we will replace it by "across the urban landscape". We note that a value judgment ('desirable' vs 'undesirable') is not needed, indeed degraded ecosystems to some extent add to the ecosystem-level diversity of urban environments.

306-308 Could be, but you have provided no information on the hydrologic conditions at the time of sampling. Also within a season you haven't sampled during runoff conditions and during 'base flow' conditions to determine if there is a difference.

All samples were taken during base flow conditions, which we will clarify by including a graph on precipitation overlain on our sampling periods. We will also clarify that we do not refer to immediate effects of high flow, WWTP overflow etc. but to legacy effects that we expect to differ among sites depending on impervious surface area in the surroundings of the sites and other factors. See also the response above.

313-315 weak inference. All of your components ordinate in the same direction of TrOCs. Also how did you establish the link to WWTPs. Is it just based on what other people said who found similar looking components?

We will strengthen the discussion based on two changes in the expression of our data that we will make. First, we will replace the PCA based on TrOC data by an aggregate measure of TrOC abundance, which we interpret as an indicator of the influence of WWTP effluents. Secondly, we will normalize the PARAFAC data by expressing them as a proportion of total DOC, which will enhance the information value of the PARAFAC components as indicators by emphasizing qualitative differences in DOM composition (see also above).

316-317 I would think that the greater abundance of light might be as big or a bigger factor than nutrients.

High nutrient levels would be expected to correlate with a DOM signature reflecting autochthonous primary production as the source. That, however, was not the case in our study, where high nutrient levels were rather related to WWTP effluents. We will revise the paragraph to clarify this point.

320-321 Again, not sure I see where that statement comes from. All of your DOM components ordinate in the same direction not just C2 and C8. C1,2,4,5,7,6,8 (what happened to C3?) are all pretty well correlated with elevated nutrients on the primary RDA axis. It just seems like increased fluorescence is associated with increased nutrients.

The C3 label was inadvertently omitted in the graph. We will include it in the revised manuscript. The problem of the lack of differentiation will be alleviated by normalizing the PARAFAC data, as explained above.

340-341 why would you propose green space as a proxy for paved surfaces when you said you measured paved surfaces earlier?

While paved surfaces and green space are to some extent (negatively) correlated and may thus be hard to separate as controls, it was the variable green space that was identified as significant in the RDA. In the revised manuscript, we will directly discuss the meaning of green space in a more straightforward way and bring up important mechanisms such as facilitated soil infiltration and input of allochthonous organic matter.

353 I don't know if your map is showing urban heterogeneity or not. I mean, none of this is clearly linked to urban influences (clearly some of it has to be). I just don't think the data and analyses you have presented lead to strong support for this statement.

Different colours in the Figures 1b and 1c translate to different DOM compositions. That these colours do not cluster indicates that the maps illustrate the spatial turnover of DOM composition across the urban area. We will include this rationale in the legend of Figure 1 or the main text.

374-375 what do you mean by that? This study is based on single grab samples and average data? Most monitoring is part of a broader survey. This needs to be clarified.

We will revise the paragraph to clarify that we refer to changes in DOM composition over time (or compositional turnover) and the potential of using analyses of DOM composition as a complementary integrative measure for urban freshwater monitoring.

384 How are you coming to this conclusion? You have presented no information that you ever sampled storm runoff?

This conclusion is based on very high levels of various variables we measured, especially NH_4^+ concentrations, and historical information that the site used to receive stormwater runoff in the past. We will provide more information about this site in the Methods section.

385 This is the first time it is mentioned. You should talk about this up in the sites section of the methods. Overall, a map showing the location of WWTPs would be very helpful. The WWTPs are being treated as a bit of an afterthought in the analysis when I feel like you should be framing your study and analysis around them.

As suggested, we will add information on potential WWTP influences to Figure 1a and the table in the Appendix describing the sites.

388-389 how do you know it "actually" received the inputs anything you have showing the hydrologic connectivity to a WWTP would be appreciated.

As stated just above, we will add information about which sites could have received WWTP effluents upstream.

404-405 What was actually detected? Which optical properties? Fluorescence? All the components ordinate in the same direction. TrOCs seem to be more a function of increasing DOC fluorescence overall. In this particular case for Berlin, I would then argue that the simplest thing to do is to measure FDOM fluorescence as an aggregate value as opposed to the finer resolution.

We will clarify that we refer here to the PARAFAC components indicative of WWTP effluents. As explained above, with the new PCA, using normalized components, all the components do not ordinate in the same direction.

References

Cory, R. M., Miller, M. P., McKnight, D. M., Guerard, J. J., and Miller, P. L.: Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra, Limnology and Oceanography: Methods, 8, 67-78, https://doi.org/10.4319/lom.2010.8.67, 2010.

Declerck, S., De Bie, T., Ercken, D., Hampel, H., Schrijvers, S., Van Wichelen, J., Gillard, V., Mandiki, R., Losson, B., Bauwens, D., Keijers, S., Vyverman, W., Goddeeris, B., De meester, L., Brendonck, L., and Martens, K.: Ecological characteristics of small farmland ponds: Associations with land use practices at multiple spatial scales, Biological Conservation, 131, 523-532, https://doi.org/10.1016/j.biocon.2006.02.024, 2006.

Friedland, G., Grüneberg, B., and Hupfer, M.: Geochemical signatures of lignite mining products in sediments downstream a fluvial-lacustrine system, Science of The Total Environment, 760, 143942, https://doi.org/10.1016/j.scitotenv.2020.143942, 2021.

Johnson, M.R., and Zelt, R.B., Protocols for Mapping and Characterizing Land Use/Land Cover in RiparianZones: U.S. Geological Survey Open-File Report 2005-1302, 22 p. 2005

Tufekcioglu, M., Schultz, R. C., Isenhart, T. M., Kovar, J. L., and Russell, J. R.: Riparian Land-Use, Stream Morphology and Streambank Erosion within Grazed Pastures in Southern Iowa, USA: A Catchment-Wide Perspective, Sustainability, 12, 6461, 2020.