Review #2

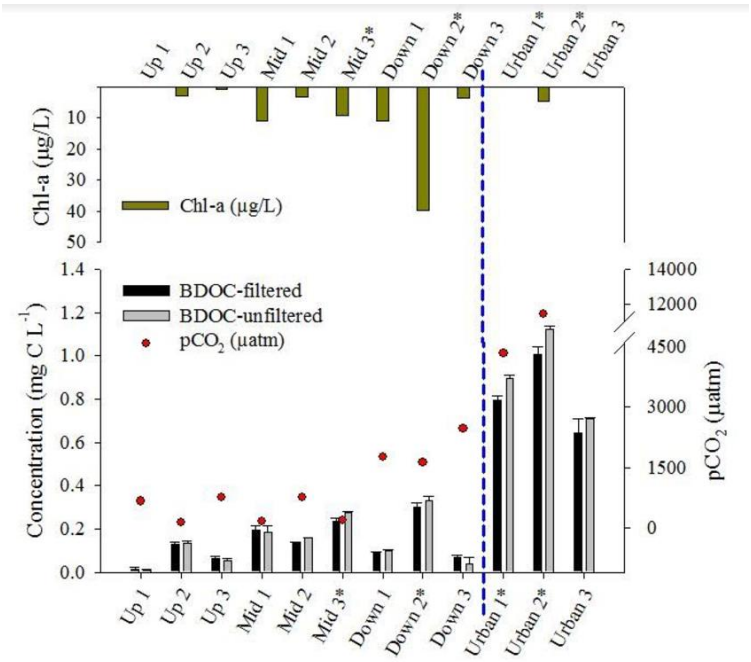
RC#2: *This manuscript presents optical and FT-ICR-MS characterization of dissolved organic matter (DOM) before and after bioassays for samples collected during base flow in the Hans River basin, an urbanized river system. Samples have been collected at different location along the river in a longitudinal axe and also in three additional urban tributaries, and then incubated during 7 days with both filtered and unfiltered treatments. An additional incubation experiment is also presented where a mixed sample (Hans River at a downstream location + an urban tributary) has been incubated for 5 days and compared to unmixed samples. Biodegradable dissolved organic carbon (BDOC) has been determined along with changes in DOM composition and dissolved CO2 for each bioassay.*

Overall the data presented here are interesting but I found that the manuscript does not fulfil the objectives presented in the introduction. Sampling and incubations designs don't provide direct and unquestionable evidences for priming effect and interaction between DOM and POM, and consequently most of the conclusions remain speculative.

Response: Thank you for your comments and suggestions. Yes, we could not provide direct evidence supporting the priming effect and the role of POM as a source of labile OM. We will provide a more balanced discussion of the implications and limitations of these findings in the revised manuscript.

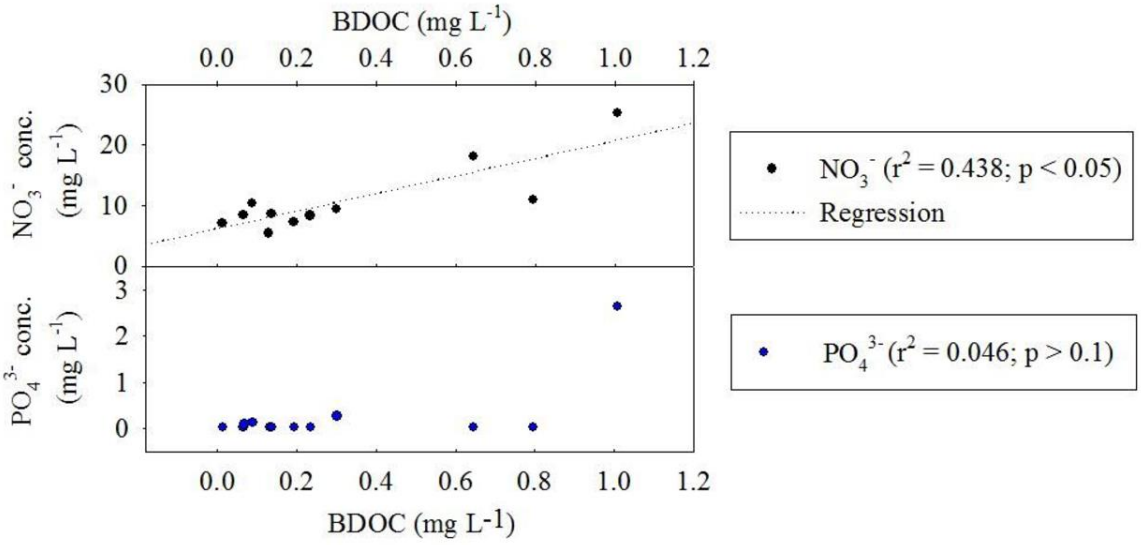
Thus, there is no direct evidence that the spatial variability of BDOC results from water impoundments and water pollution (466-467). Some additional information such as water residence time, and indicator of primary production such as Chlorophyll-a concentrations would be benefit in order to better constrain the spatial pattern observed in BDOC.

Response: As mentioned in our response to another reviewer, Chlorophyll-a concentrations will be included in Figure 2 to provide more information on the effect of impoundments on the primary production and BDOC. We will also provide additional information including water residence time to better constrain the observed spatial variations in BDOC.



RC#2: *The authors should also consider the role of changing land use in the basin and the impact of nutrients released in stream waters on BDOC. Also, the fact that bioassay results are presented as BDOC concentrations (Fig. 2) is confusing as initial DOC concentrations is highly variable between sampling location. Thus, urban tributaries that have the greatest BDOC concentrations are also characterized by the highest initial DOC concentrations. It would be more relevant to present the results as %BDOC to investigate the spatial variability of BDOM in the basin and to incorporate these data in the discussion. Finally, the different relationships presented in the figure 4 should be considered with caution. Indeed, we can speculate that waters with more DOC contain also more potential BDOC due to greater molecular diversity (Kellerman et al., 2014, Nature Communication, DOI: 10.1038/ncomms4804; see also Lapierre & del Giorgio, 2014, Biogeosciences, doi:10.5194/bg-11-5969-2014). As also noted by the reviewer #1, absorbance and fluorescence are also very dependent of DOC concentrations in a sample. I also suggest to use %BDOC instead of BDOC concentrations and to investigate other relationships with nutrients and landscape properties such as land use or, if available, water residence time at different location along the river.*

Response: As mentioned in our response to the other reviewer, we focused on the relationships between BDOC concentrations and the reported optical measurements and indices because of (1) the importance of BDOC as an important factor correlating with pCO_2; and (2) the insignificant relationships of % BDOC. We will further explore the relationships between %BDOC/BDOC and other variables including nutrients and their ratios and discuss the implications of significant or insignificant relationships in the revised manuscript. The relationship between BDOC and two nutrients (NO_3^- and PO_4^{3-}) is provided below as an example.



RC#2: *In the mixing experiment, the authors suggest that all CO2 produced results from the biodegradation of DOM, but some fraction of the CO2 could come from changes of the chemical equilibrium of DIC. Do the authors have additional data to take this into account?*

Response: We are aware of the possibility of CO_2 coming from the DIC pool. As mentioned earlier in response to RC1, based on previous studies and our laboratory tests, we assumed that CO_2 would originate mostly from OM biodegradation with a minor contribution from DIC. We will provide a more detailed explanation of this assumption in Methods and also discuss the possibility of chemical conversion from DIC to CO_2.

The comparison between optical measurements and FT-ICR-MS is very interesting but remains speculative, so the conclusion lines 475 492 should be moderated.

Response: Yes, the comparison between EEMs and FT-ICR-MS may look speculative. We will provide a more balanced discussion of the possibility and limitation of the visual inspection of two analyses.

RC#2: *Do the authors have envisaged to apply PARAFAC modeling om EEMs in order to get more information on the different fractions of the DOM pool?*

Response: We are now testing and comparing PARAFAC runs with the reported values and therefore we may be able to report the PARAFAC results if the modeling results can conform to PARAFAC validation criteria.

RC#2: *Table S3a and S3b: DOC and BDOC data in table for filtered (S3a) and unfiltered (S3b) samples are identical, I guess it is a mistake. Also, I don't understand why the optical indices differ between tables S3a and S3b and why all the optical proxies have not been calculated for both filtered and unfiltered incubations.*

Response: Yes, there were some mistake in presenting data in Table S3B. We will show all correct data in the revised table.