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Interactive comment on "Optical and molecular-level characterization of fluvial organic matter biodegradation in a highly urbanized river system" *by* Most Shirina Begum et al.

Anonymous Referee #2

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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.

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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.

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.

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.

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

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chemical equilibrium of DIC. Do the authors have additional data to take this into account? The comparison between optical measurements and FT-ICR-MS is very interesting but remains speculative, so the conclusion lines 475 492 should be moderated.

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?

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.

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