

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 #1

Received and published: 14 April 2017

General Comments: This manuscript describes optical and FT-CRR MS characterization of dissolved organic matter, results of DOM bioavailability bottle experiments, and dissolved CO₂ for water samples collected at range of sites throughout the Han River watershed. Samples were collected under base flow conditions at locations spread longitudinally along the river system and from both forested and urban headwater locations. Changes in DOM characteristics following bioavailability incubations and results of bioavailability experiments where water from upstream and downstream sites was mixed are described. Correlations among measured parameters are utilised to suggest potential implications of DOM quality differences between sites on CO₂ emissions. This study does provide interesting insights into how microbial processing is likely to

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shape DOM character and how changes in DOM quality with landscape alteration and along the stream continuum might influence DOC metabolism. I do have some concern that alternative explanations for the observed correlations have not been fully evaluated and suggest that the assumption causal links between DOM characteristics, BDOC, and CO₂ emissions should not occur without acknowledging and preferably, testing some of the alternative explanations that might be suggested. I'm not sure that the objective of testing whether "priming effects of labile OM can enhance biodegradation of riverine OM and hence CO₂ emissions" can be addressed using bottle experiments and without controlling (statistically or through experimental manipulation) nutrient concentrations and starting CO₂ in samples. Outlined in more detail with the specific comments below are those alternative explanations that I'd suggest are most important to address:

Specific Comments:

1) Water samples were collected from forested, urban, and a variety of in-channel locations upstream and downstream of dams. I would anticipate that concentrations of non-organic forms of nitrogen and phosphorus differed significantly between samples. The abundance of these nutrients may correlate with DOM characteristics, particularly if production of autochthonous DOM occurs in association with algal productivity. The abundance of these nutrients may also act to limit rates of microbial metabolism and assimilation of DOM. Potential differences between sites and samples in the availability of nutrients should be noted in the text and preferably potential relationships with concentration should be explored. Concentrations are noted in supplementary information so this should be possible.

2) If Chlorophyll a in samples was measured this would also be extremely valuable in discussing mechanisms and alternative explanations for those patterns observed. In particular, where unfiltered samples were used in incubation experiments I would expect that death and release of labile DOM from phytoplankton could fuel the disproportionate increase in BDOC that was observed at productive sites when filtered and

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unfiltered samples were compared. This is somewhat problematic in that this would be an artifact of the design used since under light exposed conditions productivity of phytoplankton would continue.

3) How did concentrations of inorganic carbon and alkalinity compare between samples? Can DIC be ruled out as a potentially significant source of CO₂ and did pH differ significantly between sites or change over the course of experiments? It looks like BDOC is only about 30% of CO₂ produced in the incubation experiments. Where is the other CO₂ originating? If that is all POM, the POM wasn't really the focus of characterization, so I wonder about speculating too much into mechanistic links between DOM and CO₂ until the other potential sources have been noted in more detail.

4) The only significant correlation between BDOC and DOM character is with the FI, which relates to source and I anticipate correlates with concentration of DOC (Figure 4). All other metrics are more or less reflection higher or lower DOC concentration. Absorbance and fluorescence of each component will increase with concentration. To make a link with DOM character the relationship with indices or relative abundances of fluorescent components to total fluorescence needs to be explored. For HIX and SUVA which are not a function of DOC, no relationship was observed. I suggest examining the relationships in figure 4 using relative abundances of fluorophores, specific absorptivity, and % BDOC to gain insight about alternative explanations and to differentiate between the effect of differing concentration (overall abundance of DOC) and differing characteristics / structure of DOM. Is there a relationship between %BDOC and nutrients, or overall C:N or C:P. . . if so this is also very interesting.

Other Comments:

Line 116 – How long were samples stored after collection before BDOC incubations were started?

Conclusions – Much of the conclusion is quite speculative and would be better addressed in the general discussion. (471-474, 482-486)

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Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2017-93, 2017.

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