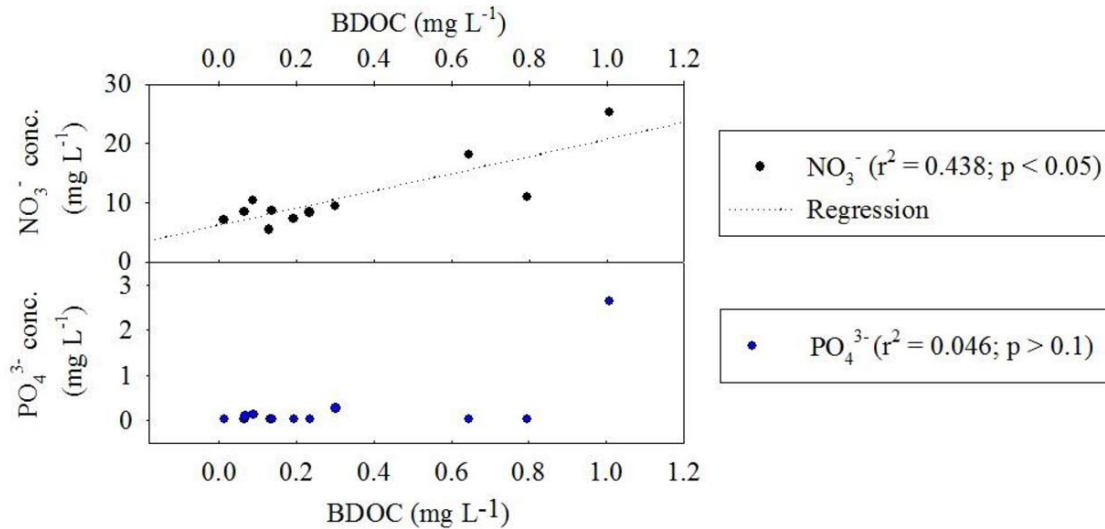
# Review # 1

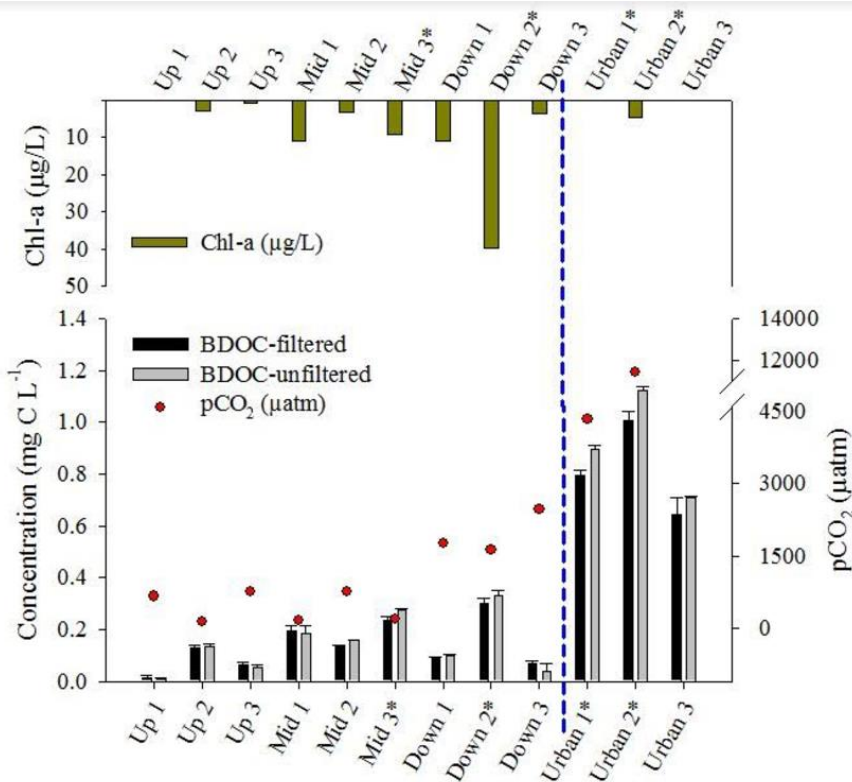
**General Comments:** *This manuscript describes optical and FT-CRR MS characterization of dissolved organic matter, results of DOM bioavailability bottle experiments, and dissolved CO2 for water samples collected at range of sites throughout the Han River watershed. Samples were collected under base 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 utilized 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 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:*

> **Response:** Thank you for your thoughtful suggestions and detailed comments! Alternative interpretations of the presented and new data including correlations with nutrient concentration, Chl-a concentration and initial DIC will be further explored and included in the revised version. Although laboratory incubation experiments might be limited in providing direct evidence of priming effects, the presented incubation results can at least suggest the potential role of priming effect in the highly urbanized river system. We will discuss in more detail both the significance and limitations of our experiments in the revised version.

**Specific Comments:**

*RC1: 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.*

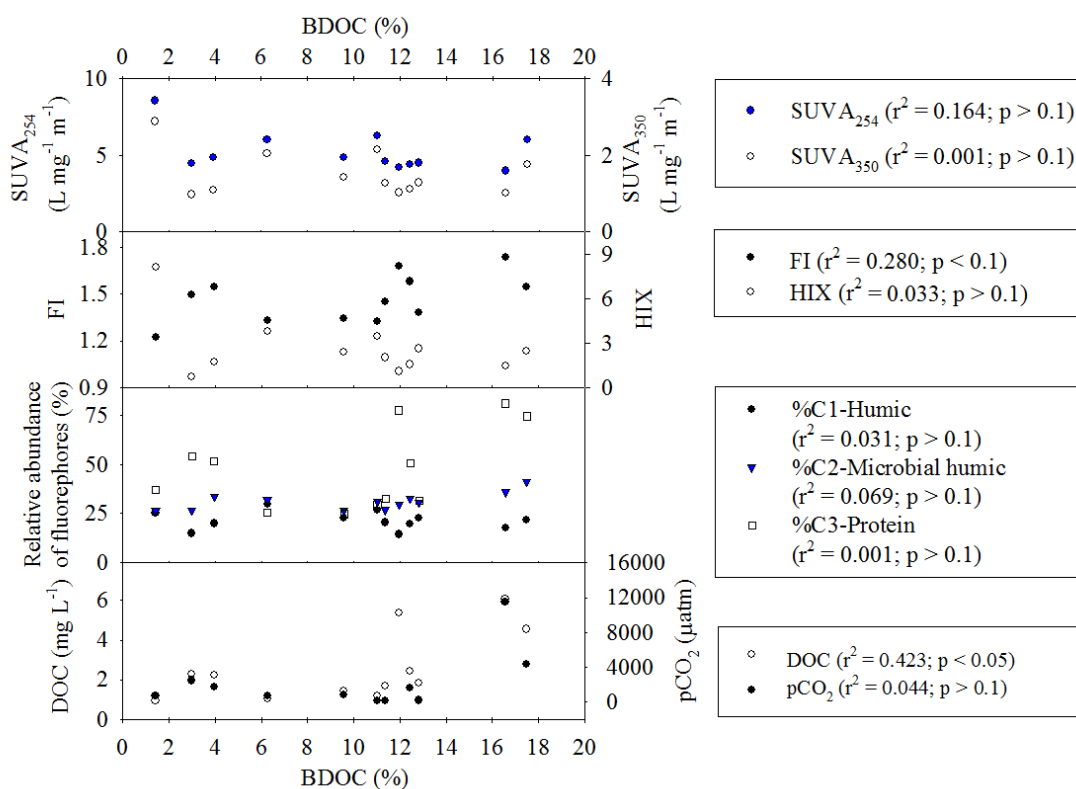
**Response:** The variability of N and P concentration among the sites will be noted in the text and relationships with the BDOC concentrations (as shown in the figure below) will be included in Figure 4.

*RC1: 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 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.*

**Response:** Thanks for the helpful suggestion! We will include Chl a data in Fig. 2 (as shown below) and discuss the implications of autochthonous DOM for BDOC and CO2 uptake at the productive sites.

***RC1:*** *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.*

**Response:** We assumed that $CO_2$ increases during incubation would reflect the biodegradation of DOM and POM, because previous studies such as Wickland et al. (2012) that measured both BDOC and $CO_2$ have revealed that $CO_2$ originates primarily from the biodegradation of DOM. Change in alkalinity and pH of the samples were not measured for the incubation experiment. Therefore, it is difficult to provide any direct evidence supporting our assumption that $CO_2$ produced in the incubation bottle primarily originated from OM degradation, with minor contribution from DIC. This will be discussed in further detail.

***RC1:*** *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.*

**Response:** Although we had analyzed correlations between %BDOC and optical measurements and indices, 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 (results shown below). We will further explore the relationships between %BDOC and other variables including nutrients and their ratios and discuss the implications of significant or insignificant relationships in the revised manuscript.

**Other Comments:**

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

**Response:** This detail will be added in the revised manuscript as "were stored at 4°C for a week".

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

> **Response:** The conclusion will be revised based on the additional analysis of the results suggested by the reviewers.