

bg-2018-278

## Author response to RC2

General comments.

The manuscript bg-2018-78: “Longitudinal discontinuities in riverine greenhouse gas dynamics generated by dams and urban wastewater” by Hyojin Jin et al provides an interesting study about the basin-scale patterns of the three major greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) in a highly urbanized watershed. The study outlines the importance of dams and wastewater treatment plant with regards to the river continuum concept (Vannote et al., 1980) and could be significant in the field of biogeochemistry of highly humanmanaged watersheds. The study show that dams creates discontinuities in the hydrological continuum, which favored aquatic autotrophy and then the release of CH<sub>4</sub> and N<sub>2</sub>O from the sediments. Wastewater treatment plants release high concentration of the three GHGs and replenished labile riverine pool of DOM, fueling the river heterotrophy. The dataset is very large in both spatial and temporal scales, methods and sampling design are appropriate, figures are of high quality and the study is well documented. Statistical analysis are also appropriate but are only bivariate analysis and thus I think that it would be interesting to explore the dataset further by doing multivariate analysis (see my comments below). Overall, I support publication of this manuscript and below are some more detailed comments.

**<Response> We thank you for your positive evaluation of our manuscript. According to your suggestion, a multivariate analysis was carried out. Please refer to our detailed responses to your specific comments below.**

Specific comments.

L.40-43. Definitely, there is a lack of direct pCO<sub>2</sub> measurements in Asia and Africa, but this is also true in Europe and America since the GLORICH database used in global CO<sub>2</sub> synthesis originates from pH/TA/temperature calculations (Hartmann et al., 2014). pCO<sub>2</sub> calculated from pH/TA/temperature is strongly overestimated notably in low, buffered and high DOC waters such as boreal and tropical rivers, which strongly contribute to the global CO<sub>2</sub> degassing (Abril et al., 2015). In addition, taking into account that wetlands and flooded land are now recognized as significant to the regional and global carbon budget (Abril et al., 2014; Abril and Borges, 2018), we are still far to obtain a precise carbon budget at the global scale. Therefore, if authors want to introduce global CO<sub>2</sub> synthesis, I would suggest specifying the above information.

**<Response> Some issues on potential overestimation of calculated pCO<sub>2</sub> values, together with a growing recognition of the contribution of wetlands, have been cited as follows:**

**Lines 39-40 (recent recognition of wetlands as CO<sub>2</sub> sources):** [Recent studies in large river systems such as the Amazon and Congo have identified wetlands as previously unrecognized sources of CO<sub>2</sub> and organic matter \(Abril et al., 2014; Borges et al., 2015\).](#)

**L 42-46 (overestimation of pCO<sub>2</sub>):** [While pCO<sub>2</sub> calculated from available water quality data such as pH and alkalinity has been used widely to estimate CO<sub>2</sub> emissions from a wide range of inland water systems \(Lauerwald et al., 2013; Raymond et al., 2013\), substantial overestimation of pCO<sub>2</sub> can occur in acidic, organic-rich inland waters due to the contribution of organic acids to alkalinity and the limited carbonate buffering \(Abril et al., 2014\).](#)

L.43-45. I would suggest to add this reference where CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O have been measured simultaneously in the Zambezi River (Teodoru et al., 2015).

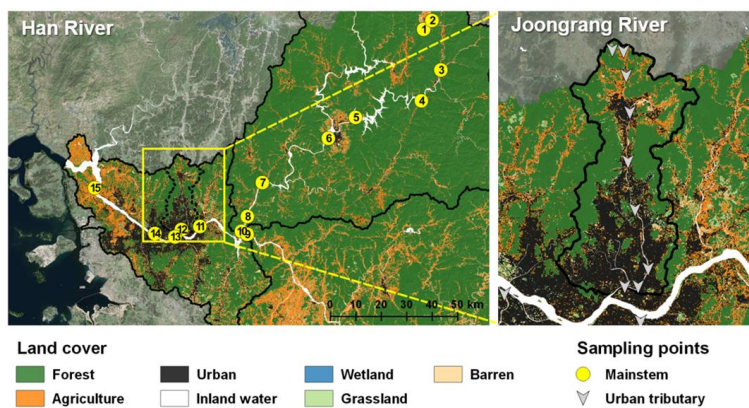
**<Response> The suggest reference has been cited in L 49, together with another recent paper reporting simultaneous measurements of three GHGs in a highly impacted river system (Borges et al., 2018).**

L.90-97. In my opinion, those sentences belong to the study site section.

<Response> Yes, the sentences might fit into the study section. But we wanted to provide an overview of previous studies on anthropogenic perturbations to various reaches of the studied basin. Since this brief overview is different from detailed site descriptions in the following method section, we had to keep the overview section in the introduction.

L.115-118. I would suggest to show land use on the map of the figure 1 (see my comments below for the figure 1).

<Response> We could not show dominant land use types together on Fig., 1 because there are already too many symbols to show on Fig. 1. Therefore, we included an additional map showing 7 major land cover types as a supplementary figure (Fig. S1).



L.135-136. According to Fig. 1, JN transect is a highly urbanized tributary but authors wrote that in this transect there is a forested headwater. This seems paradoxical to me (cf my comments of the Fig. 1).

<Response> In addition to the additional site map (Fig. S1), more information about the land use of the urbanized tributary has been provided in L 131 (~45% of which urban land use accounted for in 2014 (Seoul Metropolitan Government, 2017)), along with an explanation of site selection based on land use in L 145-146 (The 8 sites were selected to cover the spatial pattern of land use, ranging from the forested upper reach to the increasingly urbanized downstream reaches (Fig. S1)).

L.189. Please refer to Gran (1952).

<Response> Cited.

L.189. Usually, electro-titration of TA with the Gran method used 0.1N HCl as titrant.

<Response> That's right. We have indicated 0.1 N HCl as the usual concentration used for the Gran method (L 199).

L.204. Please insert period after "parameter".

<Response> Inserted.

L.218-220. There are two forested streams (one on the JN transect and one on the main transect, right?). To avoid any confusion, I would suggest to specify between brackets the station name. Otherwise, the reader always needs to search this information in other figures or tables. I would suggest doing the same for the remainder of the text.

<Response> Site names of two forested streams have been indicated throughout the manuscript.

L.225-227. Visualizing the Fig.S1, I am not totally agree with author's comment. At the HR14 sampling station, N<sub>2</sub>O and CH<sub>4</sub> seemed affected by season (notably spring and summer), as well at the HR2 and HR4 sampling stations where CH<sub>4</sub> seemed affected by summer/winter seasons. In order to determine if seasons significantly affects GHG concentrations at a given station, I would suggest performing a Kruskal-Wallis test accompanied with a Dunn's test in order to accounting for the multiple comparison.

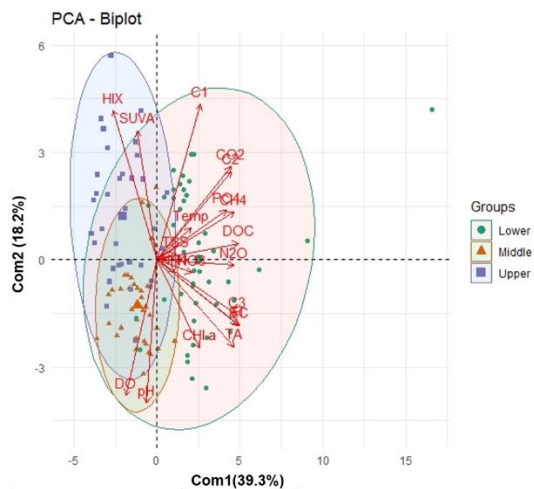
<Response> The results of the suggested tests are indicated on Fig. S2. The sentence has been split and rephrased in L 239-242 (*p*CO<sub>2</sub> tended to be higher in summer than in other seasons at all monthly monitoring sites except HR8 and HR 11, which are subject to direct or indirect influences of the cascade dams along the middle reach. There was no clear seasonality in CH<sub>4</sub> and N<sub>2</sub>O across the sites, but at the lower-reach site HR14 the concentrations of two gases tended to be higher in spring and summer than in fall and winter (Fig. S2).

L.228-237. I think that it would be interesting to know if decrease/increase described in this paragraph with the Figure 3 are statistically significant. For that, I would recommend performing a Mann-Whitney test between stations that are following each other's (testing HR1-HR2, then HR2-HR4...etc). In addition, I would suggest adding Mann-Whitney test results in the Figure 3.

<Response> The results of Mann-Whitney U test have been added in Fig. 3, with their descriptions added in L 244-247 (When Mann-Whitney *U* tests were conducted to detect downstream changes between two successive sites, both DOC and FI were significantly different between two mainstem sites (HR11, HR14) and the urban tributary JN (HR 12). HIX generally decreased downstream along the river, with significant changes occurring during transitions from HR1 to HR2 and from HR4 to HR8 (Fig. 3).).

L.241-252. To understand basin-scale controls on CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O concentrations, authors explore their dataset by doing bivariate analysis (e.g., Kendall rank correlation) between either CO<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>O and each water quality parameter for the lower/middle/upper reach. This statistical test is appropriate but I think that a multivariate analysis (as PCA, may be associated with a cluster analysis of variable) with all parameter for each lower/middle/upper reach would be also very interesting. Another possible PCA would be a PCA biplot (graph of individuals and variables together), with all the dataset, in order to see where the lower/middle/upper reach points are situated with regards to the variability of the dataset. I supposed that a multivariate analysis will learn the authors more about the variability of the dataset, and how control patterns of CO<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>O evolved from upstream (upper reach) to downstream (lower reach). In addition, it will give information about which variables are important to describe the variability of the dataset. What do you think?

<Response> In addition to the Kendall rank correlation, a PCA scatter plot has been included as a supplementary figure (Fig. S3). This plot supplements the cluster analysis suggested by the first reviewer (Fig. 4) and the Kendall analysis results (Fig. 5). Descriptions of this additional analysis have been provided in L 261-264 (Reach-specific clustering of data was also found on a PCA scatter plot with two primary components accounting for 57.5% of variations (Fig. S3). While the upper and middle reach data were overlapped considerably on the PCA scatter plot (the upper reach with a wider scatter), the majority of the lower reach data were separated from the overlap of the upper and middle reaches.).



**Fig. S3.** Reach-based grouping of all measurements in the upper, middle, and lower reaches of the Han River along two components identified by principal component analysis (PCA).

L.276-278. Please add per mil symbols.

**<Response> Added.**

L.301. Richey et al (1988) is somewhat outdated, please add Abril et al. (2014).

**<Response> Added.**

L.304. "...regulated river system". May the authors add references?

**<Response> A relevant reference (Crawford et al., 2016) has been cited.**

L.304-308. This is a 6 lines sentence, quite difficult to follow, please consider revising the sentence.

**<Response>The sentence has been split and reformulated in L 329-334** (It would be very challenging to tease out multiple, interrelated factors as shown by previous studies of GHG dynamics in urbanized river systems (Smith et al., 2017; Wang et al., 2017b). However, the observed longitudinal patterns of three GHGs (Figs. 2–4), along with their correlations with specific sets of water quality components (Fig. 5), make one thing clear: the primary factors and mechanisms for the production and consumption of three GHGs may change in response to longitudinal variations in dominant anthropogenic perturbations, often abruptly as shown by the localized pulses of GHGs downstream of urban tributary inflows (Figs. 2, 8)).

L.336. Please add references about methanotrophy in water column of lake (e.g., Morana et al., 2015; Roland et al., 2017).

**<Response> A relevant paper, together with descriptions of aerobic and anaerobic CH<sub>4</sub> oxidation, has been included in L 361-362** (aerobic and anaerobic CH<sub>4</sub> oxidation in water column with a depth-dependent gradient

of O<sub>2</sub> availability as a driving force for the observed spatial variations (Roland et al., 2017)).

L.343-346. In dam water column, you mentioned previously that the enrichment in CH<sub>4</sub> originates from anaerobic conditions in organic-rich sediments. Usually, in strictly anaerobic conditions as occur for the methanogenesis, denitrification in the sediment is 'complete' producing N<sub>2</sub> gas and not N<sub>2</sub>O. However, water column is oversaturated in N<sub>2</sub>O. How do you explain this? Did you measure GHG, O<sub>2</sub> or NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> in the profile of the water column?

**<Response> No, we did not measure the depth profiles. The limited production of N<sub>2</sub>O under anaerobic conditions has been mentioned in L 371-372 (although strictly anaerobic conditions might result in a more complete denitrification to N<sub>2</sub>, contributing little to N<sub>2</sub>O production).**

L.355-359. This is a 5 lines sentence, quite difficult to follow, please consider revising the sentence. In addition, it is not clear to me, all the data presented in this sentence originates from Yoon et al (2016)? Please, specify.

**<Response> The sentence has been split and reformulated (L 383-387: When the estimated rates of CO<sub>2</sub> production, consumption, and outgassing along the downstream reach were compared in June 2016, the amount of CO<sub>2</sub> produced from organic matter biodegradation was much greater than the amount of CO<sub>2</sub> consumed by phytoplankton and similar to the CO<sub>2</sub> efflux to the atmosphere. In May 2015, when Chl *a* concentrations were much higher than in June 2016, the bulk of CO<sub>2</sub> delivered by the tributaries was estimated to be consumed by phytoplankton photosynthesis along the same reach.).**

L.369.370. Authors mentioned that the amount of CH<sub>4</sub> and N<sub>2</sub>O discharged from the WWTP appeared to drive the magnitude and temporal variability of the tributary inputs to the lower reach. When I observed the figure 6, this is necessary true for N<sub>2</sub>O, but not necessary true for CH<sub>4</sub>. Indeed, CH<sub>4</sub> increased way before the appearance of the WWTP, and the two points of Nov 2015 and May 2016 that are very different suggest a high temporal variability that could explain CH<sub>4</sub> concentrations measured at HR12. Do not you think that there is another source of CH<sub>4</sub> than WWTP for this tributary?

**<Response> We agree that other upstream sources might also have influenced the observed large spatial and temporal variations of the tributary CH<sub>4</sub>. A sentence has been added in L 400-403 (In the case of CH<sub>4</sub>, however, the large spatial and temporal variations observed along the tributary upstream of the WWTP also point to the potential role of the benthic sediment as an upstream source of CH<sub>4</sub> (Stanley et al., 2016), although further research is needed to elucidate all important sources of the tributary CH<sub>4</sub>).**

L.385.402. In this paragraph, could you explain the spatial longitudinal pattern of δ<sup>13</sup>C-DOC?

**<Response> An existing sentence has been split and added by two new sentences in L 422-427 (In particular, large fluctuations in δ<sup>13</sup>C<sub>DOC</sub> along the upper to middle reaches from HR2 to HR11 do not present any consistent longitudinal trend of the stable C isotopic composition. However, distinct increases in δ<sup>13</sup>C<sub>DOC</sub> at the most downstream site (HR14) compared to the δ<sup>13</sup>C<sub>DOC</sub> at the forested headwater stream (HR1) indicate a potential contribution of autochthonous DOM components to the isotopic signature of the bulk riverine DOM, which deviated substantially from those of the headwater DOM dominated by allochthonous components (Fig. 7)).**

L.388. Did you mean 72 among 695 or did you mean 72%? Please, specify.

**<Response> It has been clarified by adding % (72%).**

L.403. What does RKM term means? Please, specify?

<Response> RKM has been replaced by “km from the river mouth” (L 439).

L.403-416. All the statements you mentioned in this paragraph are maybe true but remain unclear to me. To improve this paragraph, I think that you need to better identify inputs and processes playing a role in the variability of  $\delta^{13}\text{C}$ -CO<sub>2</sub> signature in the studied river. First, I am partially agree with the first sentence because dissolution of carbonates is  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+}$ . Thus, dissolution of carbonates will not influence  $\delta^{13}\text{C}$ -CO<sub>2</sub> signature but will influence  $\delta^{13}\text{C}$ -HCO<sub>3</sub><sup>-</sup> and thus  $\delta^{13}\text{C}$ -DIC signature (e.g., Deirmendjian and Abril, 2018). Second, you mentioned  $\delta^{13}\text{C}$ -CO<sub>2</sub> originating from riverine organic matter degradation. So, did you mean riverine organic matter coming from aquatic autotrophy? or riverine organic matter coming from soil and groundwaters leaching that is degraded in river? Because both sources have a distinct  $\delta^{13}\text{C}$ -DOC signature. Thereafter you compared  $\delta^{13}\text{C}$ -CO<sub>2</sub> value originating from riverine organic matter degradation with  $\delta^{13}\text{C}$ -CO<sub>2</sub> value originating from lakes to highlight the fact that there are other processes than bacterial degradation to explain the variability  $\delta^{13}\text{C}$ -CO<sub>2</sub> in your dataset. According to the  $\delta^{13}\text{C}$ -CO<sub>2</sub> value of the lake, in this lake a high proportion of the CO<sub>2</sub> originates from terrestrial degradation of DOC from C3 plants. So when you com your transect? In the third statement, you mentioned the preferential used of <sup>12</sup>CO<sub>2</sub> by heterotopic bacteria, but how heterotrophic bacteria can used CO<sub>2</sub>? Please, clarify.

<Response> We agree that there were some uncertainties in describing sources and processes related to the isotopic composition of riverine CO<sub>2</sub>. This is due to the fact that most studies have reported  $\delta^{13}\text{C}$  in DIC, not in CO<sub>2</sub>. To respond to reviewer comments, we have clarified some unclear descriptions of DIC vs CO<sub>2</sub> processes, as shown in the following revised paragraph (L 439-456):

The longitudinal increase in  $\delta^{13}\text{C}_{\text{CO}_2}$  from  $-20.9\text{‰}$  at 76 km from the river mouth to  $-16.7\text{‰}$  at 50 km from the river mouth in Fig. 8 might be related to a complex array of interacting processes such as organic matter degradation, photosynthesis by phytoplankton, and atmospheric gas exchange, which have usually been investigated as determinants of the isotopic composition of riverine DIC consisting of dissolved CO<sub>2</sub>, bicarbonate, and carbonate (Barth et al., 2003; Schulte et al., 2011; Zeng et al., 2011; Deirmendjian and Abril, 2018). The observed values of  $\delta^{13}\text{C}_{\text{CO}_2}$  fall within the reported ranges of  $\delta^{13}\text{C}$  measured for CO<sub>2</sub> dissolved in riverine and estuarine waters ( $-25$  –  $-15\text{‰}$ ) (Longinelli and Edmond, 1983; Maher et al., 2013). However, the values reported here are less negative than the ranges of  $\delta^{13}\text{C}$  measured directly for CO<sub>2</sub> respired by bacteria consuming organic matter of terrestrial and algal origin in two streams and eight lakes in Canada ( $-32.5$  –  $-28.4\text{‰}$ ) (McCallister and del Giorgio, 2008). When the observed values of  $\delta^{13}\text{C}_{\text{CO}_2}$  are compared with the low range of  $\delta^{13}\text{C}_{\text{CO}_2}$  reported by McCallister and del Giorgio (2008) and the usual ranges of  $\delta^{13}\text{C}$  in plant and algal biomass as two primary biological sources of riverine CO<sub>2</sub> (Fig. 7), it follows then that other riverine processes than bacterial degradation of plant and algal biomass might be involved in the upward shift of  $\delta^{13}\text{C}_{\text{CO}_2}$ . It has been reported that  $\delta^{13}\text{C}$  in riverine DIC derived from carbonate dissolution and bacterial respiration ranges from  $-15$  –  $-5\text{‰}$ , reflecting the balance between the concurrent processes that can either enrich or deplete DIC in <sup>13</sup>C (Telmer and Veizer et al., 1999; Barth et al., 2003; Schulte et al., 2011; Zeng et al., 2011). In contrast to the preferential use of the lighter organic C by heterotrophic bacteria depleting <sup>13</sup>C in the respired CO<sub>2</sub>, photosynthesis and atmospheric gas exchange can result in an enrichment of <sup>13</sup>C in remaining riverine CO<sub>2</sub> through preferential phytoplankton uptake of the lighter <sup>12</sup>CO<sub>2</sub> and dissolution of atmospheric CO<sub>2</sub> enriched in <sup>13</sup>C, respectively (Schulte et al., 2011).

L.417-418. I supposed that you refer at the isotopic fractionation due to the thermodynamic equilibrium between CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>? However, you cannot status only with this information that in your studied river  $\delta^{13}\text{C}$ -DIC signature will be 10‰ higher than  $\delta^{13}\text{C}$ -CO<sub>2</sub> signature. Indeed, Equation of  $\delta^{13}\text{C}$ -DIC is  $\delta^{13}\text{C}\text{-DIC} = (\delta^{13}\text{C}\text{-CO}_2^* \times [\text{CO}_2^*] + [\text{HCO}_3^-] \times \delta^{13}\text{C}\text{-HCO}_3^- + [\text{CO}_3^{2-}] \times \delta^{13}\text{C}\text{-CO}_3^{2-}) / ([\text{CO}_2^*] + \text{TA})$ . The signature of  $\delta^{13}\text{C}$ -DIC depends thus on complex interplays between initials concentration of each dissolved inorganic parameter as well as their signature, then processes producing or consuming DIC (primarily photosynthesis, degassing, respiration, weathering), and the isotopic thermodynamic equilibrium between each compounds.

<Response> To reflect your concern, a caveat has been added in L 457-459 (with a caution in mind that the actual  $\delta^{13}\text{C}$  in DIC might be determined by various factors including initial concentrations and isotopic ratios of each DIC species and complex processes producing or consuming those DIC species (Deirmendjian and Abril,



2018)).

L.418.420. However, in the first part of the figure  $\delta^{13}\text{C}$ -CO<sub>2</sub> increased at the same rate as in the second part of the figure but without any increase in Chl a. Please, explain.

**<Response> We have specified the reach where the general increasing pattern was observed in L 461-462 (general increases in Chl a along the lower reach flanked by two submerged weirs (69 – 50 km from the river mouth) (Fig. 8)).**

L.421.422. Can you explain the difference in  $\delta^{13}\text{C}$ -CO<sub>2</sub> between tributaries and main stem?

**<Response> Explanations for distinctive  $\delta^{13}\text{C}$ -CO<sub>2</sub> in tributaries have been provided in L 465-469 (The distinctively higher values of  $\delta^{13}\text{C}$  observed for the tributary CO<sub>2</sub> might have resulted from a combination of processes, including the same photosynthesis and atmospheric gas exchange as occurring in the mainstem and tributary-specific processes such as the transport and transformations of anthropogenic organic matter in urban wastewater. WWTP effluents have been shown to contain old organic matter with characteristic C isotopic composition (Griffith et al., 2009; Griffith and Raymond, 2011; Butman et al., 2015).**

L.431.432. Does degassing of CH<sub>4</sub> to the atmosphere could have an impact on the upstream-downstream decrease of CH<sub>4</sub>?

**<Response> Loss of CH<sub>4</sub> through evasion has been mentioned in L 480 (and/or evasion of CH<sub>4</sub> to the atmosphere).**

L.445. To conclude, do you have any recommendations for politician, river managers and stakeholders to improve water quality and reducing GHG concentrations in highly urbanized watershed?

**<Response> A concluding remark on integrated river basin management has been added in L 532-535 (Identifying hot spots of water pollution and GHG emissions in highly human-impacted river systems would contribute to establishing novel river basin management options integrating the traditional water quality control and an emerging challenge of climate change mitigation by helping watershed managers set priority areas of policy responses to multiple concurrent environmental stresses.).**

Tab. 1. I would suggest adding a left column to specify upper/middle/lower reach.

**<Response> A column has been included in Table 1.**

Fig. 1: I am not aware if a land use database exists for South Korea, but if such a database exists, I would recommend adding the land use in the map of the Figure 1, particularly to visualize where croplands, forest and cities are located. In addition, to visualize the proportion of croplands, forest and cities in the studied catchment. I would also suggest adding the forested headwater from the JN transect in another color than the other points of the JN transect. Indeed, JN transect is considered by the authors as an urban transect, and thus, this is strange to associate an urbanized river with a forested headwater. Perhaps, authors could also apply a different typology for the sampling points, with for example, one color for forested streams, one for agricultural streams...It would be easier to visualize sampling points in the map of the Figure 1. Please, also add metric scale on the map.

**<Response> As explained before, we have prepared an additional map showing land use (Fig. S1).**

Fig. 2. I would suggest specifying upper/middle/lower reach in the figure, perhaps at the top of the figure.

**<Response> Three reaches have been specified at the top of the figure.**

Fig. 3. I would suggest specifying upper/middle/lower reach in the figure, perhaps at the top of the figure.

**<Response> Three reaches have been specified at the top of the figure.**

Fig.4. I would suggest to specify which tributaries belong to the red points (JN? TC? AN? or this is just HR12?)

**<Response> Tributaries have been specified in the caption of a new figure made following the first reviewer's suggestion.**

Fig.8. I would suggest to specify sampling stations names on the graphs.

**<Response> Three mainstem sites have been marked on the graphs.**