

#### 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 human-managed 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.

#### 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.

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).

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

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).

L.135-136. According to Fig. 1, JN transect is an 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).

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

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

L.204. Please insert period after “parameter”.

L.218-220. There are two forested streams (one on the JN transect and one on the main transect, right?). To avoiding 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.

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.

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.

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?

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

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 Richey et al (1988) is somewhat outdated, please add Abril et al.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

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

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

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

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.

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?

L.385-402. In this paragraph, could you explain the spatial longitudinal pattern of δ<sup>13</sup>C-DOC?

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

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

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 δ<sup>13</sup>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 δ<sup>13</sup>C-CO<sub>2</sub> signature but will influence δ<sup>13</sup>C-HCO<sub>3</sub><sup>-</sup> and thus δ<sup>13</sup>C-DIC signature (e.g., Deirmendjian and Abril, 2018).

Second, you mentioned  $\delta^{13}\text{C-CO}_2$  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  $\delta^{13}\text{C-CO}_2$  value originating from riverine organic matter degradation with  $\delta^{13}\text{C-CO}_2$  value originating from lakes to highlight the fact that there are other processes than bacterial degradation to explain the variability  $\delta^{13}\text{C-CO}_2$  in your dataset. According to the  $\delta^{13}\text{C-CO}_2$  value of the lake, in this lake a high proportion of the  $\text{CO}_2$  originates from terrestrial degradation of DOC from C3 plants. So when you compared  $\delta^{13}\text{C-CO}_2$  originating from degradation of C3 plants with  $\delta^{13}\text{C-CO}_2$  originating from degradation of riverine phytoplankton, the difference you observed originates from a different  $\delta^{13}\text{C}$  signature of DOC. In addition, the lake you mentioned is boreal, so, you cannot compare boreal system with yours. Here, I supposed that you need to focus on your data to explain that there is another process than bacterial degradation involved in the shifting of  $\delta^{13}\text{C-CO}_2$  in your dataset. At the same transect, figure 7 shows  $\delta^{13}\text{C-DOC}$  values being very lower than the corresponding  $\delta^{13}\text{C-CO}_2$  values. As during degradation of DOC, the main source of  $\text{CO}_2$  in large river (Hotchkiss et al., 2015), fractionation do not occur (Amundson et al., 1998), the difference between  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-DOC}$  is due to another process than bacterial degradation of DOC.

The next sentence, you refer to study dealing with  $\delta^{13}\text{C-DIC}$ , but you did not measure this parameter. This brings misunderstanding, because you cannot compare the evolution of the  $\delta^{13}\text{C-CO}_2$  with  $\delta^{13}\text{C-DIC}$ . Indeed, I mentioned previously that dissolution of carbonates would increase  $\delta^{13}\text{C-DIC}$  but not  $\delta^{13}\text{C-CO}_2$ . In addition, we do not know where comes the carbonates could come from. Is there some carbonate precipitation in some part of the studied river, and then dissolution in other part? Did carbonates come from weathering of carbonates in land?

Last sentence remain also unclear to me. I am agree with the first statement that photosynthesis will increase  $\delta^{13}\text{C}$  signal of  $\text{CO}_2$  by a preferential using of lighter  $^{12}\text{CO}_2$ . In the second statement, you mentioned that dissolution of atmospheric  $\text{CO}_2$  with a heavier signature (approximately -8‰) will increase  $\delta^{13}\text{C}$  signal of  $\text{CO}_2$  in the water. This is true when riverine water is undersaturated in  $\text{CO}_2$  with respect to the atmosphere equilibrium, which enables atmospheric  $\text{CO}_2$  to enter the water. However, in oversaturated water, due to water-air  $\text{CO}_2$  gradient, no  $\text{CO}_2$  (light or heavy) enter the water but on the contrary,  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  are both degassed to the atmosphere. In addition,  $^{12}\text{CO}_2$  degassed to the atmosphere at a faster rate than  $^{13}\text{CO}_2$  because  $p^{12}\text{CO}_2$  gradient between air and water is larger than the  $p^{13}\text{CO}_2$  gradient, this process will increase  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-DIC}$  signature in the riverine water (e.g., Deirmendjian and Abril, 2018; Polsenare and Abril, 2012). What is the influence of degassing in the variability of  $\delta^{13}\text{C-CO}_2$  in

your transect? In the third statement, you mentioned the preferential used of  $^{12}\text{CO}_2$  by heterotrophic bacteria, but how heterotrophic bacteria can use  $\text{CO}_2$ ? Please, clarify.

L.417-418. I supposed that you refer at the isotopic fractionation due to the thermodynamic equilibrium between  $\text{CO}_2$  and  $\text{HCO}_3^-$ ? However, you cannot status only with this information that in your studied river  $\delta^{13}\text{C}$ -DIC signature will be 10‰ higher than  $\delta^{13}\text{C}$ - $\text{CO}_2$  signature. Indeed, Equation of  $\delta^{13}\text{C}$ -DIC is

$$\delta^{13}\text{C-DIC} = (\delta^{13}\text{C-CO}_2^* \times [\text{CO}_2^*] + [\text{HCO}_3^-] \times \delta^{13}\text{C-HCO}_3^- + [\text{CO}_3^{2-}] \times \delta^{13}\text{C-CO}_3^{2-}) / ([\text{CO}_2^*] + \text{TA})$$

The signature of  $\delta^{13}\text{C}$ -DIC depends thus on complex interplays between initial 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.

L.418.420. However, in the first part of the figure  $\delta^{13}\text{C}$ - $\text{CO}_2$  increased at the same rate as in the second part of the figure but without any increase in Chl a. Please, explain.

L.421.422. Can you explain the difference in  $\delta^{13}\text{C}$ - $\text{CO}_2$  between tributaries and main stem?

L.431.432. Does degassing of  $\text{CH}_4$  to the atmosphere could have an impact on the upstream-downstream decrease of  $\text{CH}_4$ ?

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?

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

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.

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

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

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