# Cover letter

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Effects of land use and water quality on greenhouse gas accumulation in an urban river system by Long Ho, Ruben Jerves-Cobo, Matti Barthel, Johan Six, Samuel Bode, Pascal Boeckx, and Peter Goethals.

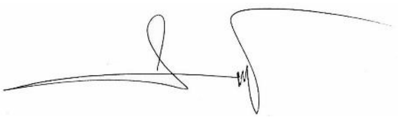
Dear Editors and Reviewers,

We would like to thank the reviewers for their relevant and constructive remarks. We have revised our manuscript accordingly. We acknowledge that the revision, including the removal of flux calculation and the estimation of annual greenhouse gas (GHG) emissions from the rivers, abridged the manuscript and clarified the story of our research. Moreover, by removing these calculations, we also eliminated their uncertainty in our study while still reaching the same conclusions based on the dissolved GHG concentrations that were measured in the sampling campaigns. Other comments were also taken into account to further improve the manuscript.

We hope that the changes and explanations are acceptable and satisfactory with the expectation of the editors and reviewers. Below are their details. Note that the line numbers indicated below aim to clarify where the modifications can be found in the revised manuscript that can be provided upon the request of the editors and reviewers.

Thank you very much for your time and consideration!

Yours sincerely,



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**Referee #1**

The manuscript entitled "Effects of land use and water quality on greenhouse gas emissions from an urban river system" provides data on GHG emissions from aquatic systems in a watershed located in Ecuador and investigates the link between water quality, adjacent land cover types and the magnitude of GHG emissions. The manuscript brings the importance of considering water quality on the estimates of the total GHG emissions from aquatic systems in addition to considering the total area only. This is a promising approach. However, there are many technical problems that need to be addressed.

***Major comments***

**1. The estimation of gas transfer velocity (k)** is largely discussed in the literature, and k estimates from empirical models should be used with caution. One major technical problem is that the gas fluxes were estimated using k600 parameterized as a function of wind speed, which is valid for open water systems, such as reservoirs, lakes and oceans, but not recommended for rivers and streams. A flow-velocity- or water-depth-based model to estimate k600 should be considered as an alternative, and the associated uncertainties should be addressed. I suggest the authors to consider a recent paper published in the Biogeosciences by Li et al. 2019 and the cited papers to better estimate k.

**Authors' responses:**

We agree that the estimates of k600 values from empirical models should be carefully implemented. As indicated in Raymond et al. (2012), direct measurement is needed for an accurate estimate of gas exchange. Moreover, we recalculated the k600 values as a function of stream velocity, slope, and water depth via different fitted equations in Raymond et al. (2012); however, the obtained result of the different equations varied significantly. From that viewpoint, we removed the flux calculations and used the dissolved gas concentrations that we directly collected and measured in our sampling campaign. By doing so, we removed the uncertainty of the flux calculation as the measurement of the dissolved GHG required no additional assumptions. Despite this replacement, the conclusions of the study remained unchanged regarding the effects of land use and water quality on the accumulation of greenhouse gases in Cuenca urban river system. The modification of the abstract and conclusions in the revised manuscript can be found as follows.

**Abstract** (line 10-25)

- Rivers act as a natural source of greenhouse gases (GHGs). However, anthropogenic activities can largely alter the chemical composition and microbial communities of rivers, consequently affecting their GHG production. To investigate these impacts, we assessed the accumulation of $CO_2$, $CH_4$, and $N_2O$ in an urban river system (Cuenca, Ecuador). High variation of the dissolved GHG concentrations was found among river tributaries that mainly depended on water quality and neighboring landscapes. By using Prati and Oregon Water Quality Indexes, a clear pattern was observed between water quality and the GHG accumulation in which the more polluted the sites were, the higher were their dissolved GHG concentrations. When river water quality deteriorated from acceptable to very heavily polluted, the mean value of $pCO_2$ and dissolved $CH_4$ increased by up to ten times while this value of dissolved $N_2O$ was boosted by 15 times.

Furthermore, surrounding land-use types, i.e. urban, roads, and agriculture, significantly affected the GHG production in the rivers. Particularly, the average $pCO_2$ and dissolved $N_2O$ of the sites close to urban areas were almost four times higher than these values of the natural sites while this ratio was 25 times in case of dissolved $CH_4$. Lastly, by applying random forests, we identified dissolved oxygen, ammonium, and flow characteristics as the main important factors to the GHG productivity. Conversely, low impact of organic matter and nitrate concentration suggested a higher role of nitrification than denitrification in producing $N_2O$. These results highlighted the impacts of land-use types on the river emissions via water contamination by sewage discharges and surface runoff. Hence, to estimate the emissions from global streams, both their quantity and water quality should be included.

**Conclusion** (line 341-367)

- Being the most polluted tributary running through the city of Cuenca (Ecuador), Tomebamba contained four times higher amount of $pCO_2$ and dissolved $N_2O$ compared to the two purest tributaries, Machangara and Yanuncay, in the Cuenca urban river systems while this proportion was ten times higher in case of dissolved $CH_4$. Similarly, much higher dissolved GHG concentrations were also found in Tarqui and Cuenca tributaries which could be attributed to their high influx of nutrients and organic matter as a result of agricultural runoffs and WWTP discharges.
- A clear pattern between water quality and dissolved GHG concentrations was observed, in which the more polluted the sampling sites were, the higher were their dissolved GHG concentrations. Specifically, according to Prati Index, when river water quality worsened from acceptable to very heavily polluted, the mean concentration of $pCO_2$ and dissolved $CH_4$ rose by around 10 times while in case of dissolved $N_2O$, it was by 15 times. A similar, yet less obvious, trend was also found in case of Oregon Index. These results suggest that to estimate of the global emissions from inland waters, both their quantity and water quality should be considered for which Prati Index is recommended over the other.
- Adjacent land-use types, i.e. urban, transportation systems, and agriculture, had significantly contributed to the increase in the GHG accumulation in the rivers in Cuenca. Specifically, the mean value of $pCO_2$ and dissolved $N_2O$ increased fourfold from natural sites to urban sites while this ratio was 25 times in case of $CH_4$. Similarly, the average dissolved concentration of $CH_4$ increased by 10 and 20 times when the sites were surrounded by agricultural areas and roads, respectively, instead of natural forests. These results highlighted the indirect impacts of land-use and land cover change on increasing GHG production from inland waters which are currently being omitted in land-use planning and resource management.
- The main important factors on dissolved GHG concentrations were identified by the application of random forests. Dissolved $O_2$ appeared to be the most important factor for the variation of the $pCO_2$ and dissolved $CH_4$ and the second most important factor for the variation of the dissolved $N_2O$. Ammonium, together with variables indicating flow characteristics, such as turbidity, average velocity, average depth, and water temperature, also affected the variation of the dissolved GHG concentrations. Conversely, a margin effect of organic matter concentration

was found, which is in contrast to their strong correlation obtained from the previous studies. This result implies a higher role of (partial) nitrification compared to denitrification in producing $N_2O$ in these river systems.

**2. The annual emissions were estimated using only data from 17/09/2018 to 21/09/2018 (5 days).** This does not seem acceptable to me. There is no information about the number of samples per sampling site or any other information that justifies such extrapolation

**Authors' responses:**

We agree that the data of our sampling campaign is insufficient for estimation of the annual emissions given the temporal effect of seasonal variation and whole diurnal cycle. Besides, as we removed the flux estimations as indicated in our response to the first major comment, we also removed the estimation of the annual emissions in the revised manuscript. This removal abridged the manuscript and condensed the research findings to the effects of land-use changes and water quality on the GHG accumulation in an urban river system.

**3. In the manuscript, the authors mistakenly seem to use the Global Warming Potential (GWP)** concept in the Results and Discussion section. Then, it is difficult to evaluate how authors estimated the emission of GHG in CO2-eq.

**Authors' responses:**

We had used the GWP to convert the $CH_4$ and $N_2O$ emissions to mg-$CO_2$ equivalent $m^{-2}$ $d^{-1}$. The values had been extracted from the Fifth Assessment Report by the Intergovernmental Panel on Climate Change (IPCC) 2015. This is the most recent report of IPCC. However, we realized that this conversion did not add to the story, we excluded this conversion in the revised manuscript to make the story of the research more concise and clear. Therefore, we used only the non-converted direct concentration data.

**4. In summary, the paper needs improvements on the method section**, on the k estimates and the described data does not support most of the interpretations and conclusions.

**Authors' responses:**

As mentioned in our response to the first major comment, the k600 estimate was removed in the revised manuscript. As such, no description of this estimation is needed. On the other hand, we agree on the addition of a description of land use and land cover in the Materials and Methods section as indicated in our response to the second and eighth specific comments.

***Specific comments***

**1. Ln 15 -** Specify here that these indexes are water quality indexes.

Added.

**2. Ln 23 -** What authors mean with "nature sites"? Do you mean "sites close to forested areas"?

The explanation of nature sites was included in the new section **2.5 Land use and land cover** in the Materials and Methods section as follows.

- To evaluate the effects of land use on the dissolved GHG concentrations of the tributaries, we considered five different types of land use, i.e. nature (close to the forests), industry (close to factories, and mining areas), agriculture (close to arable land, orchard, and farms), roads, and urban areas (close to residential and urban areas). (line 153-156)

**3. Ln 49-51 -** The estimation of k600 is also a large challenge to estimate GHG emissions from aquatic systems. You should discuss k in the manuscript.

The flux calculation was removed; hence the discussion of $k_{600}$ values is not necessary. This helped to keep the story of the research focused and concise.

**4. Ln 71 -** The authors mentioned that the study area is 223 km2 but this value is less them the sum of the area of the studied sub-basins added in Ln 79. Please, verify, clarify or specify the study area.

This info had been incorrect in the original manuscript and was adjusted in the revised manuscript as follows.

- The study area is 572.92 $km^2$, representing 25% of the Cuenca River basin (Figure S2.1). (line 70)

Moreover, a figure was added in the revised supplementary material to indicate the study area under the scope of the whole Cuenca river basin.

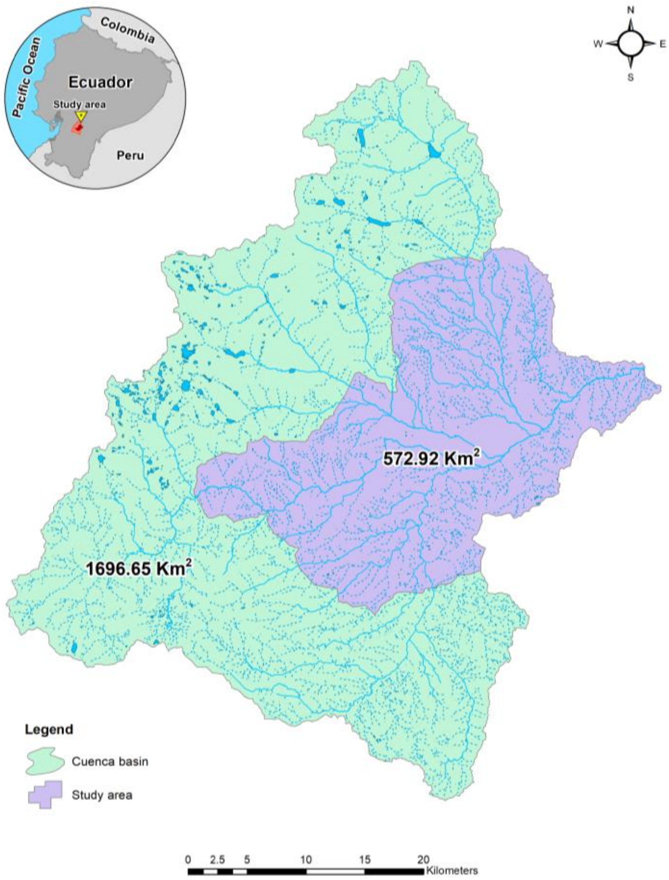


Figure S2.1. Study area in the scope of the whole Cuenca river basin.

**5. Ln 81 -** All data in the manuscript were collected in five days (from 17/09/2018 to 21/09/2018). Is it representative to discuss temporal variation? I agree that authors can evaluate temporal variation in a day scale approach. However, data from five consecutive days do not represent the annual variability and are not enough to estimate annual emissions of GHG.

As mentioned in our response to the second major comment, we agree that our data were insufficient to calculate the annual variability of the GHG concentrations in the Cuenca river basin. Hence, we removed this sentence in the revised manuscript.

**6. Ln 83 -** This sentence is not clear and there are many assumptions in the same sentence. Why do you assume that covering only daylight will ensure the investigation of temporal effects? Additionally, the connection between oxygen and GHG emission is not as simple as you stated in this sentence. Please, rephrase or remove this sentence.

We removed this sentence in the revised manuscript as mentioned in the previous comment.

**7. Ln 90 -** How many samples per sampling sites?? Were samples collected every day in each sampling site? Ln 95 - Please, change "Hack kit" to "Hach kit" in the Supplementary Material S1.

Changed.

**8. Ln 96 -** Land use is one of the main subjects of the manuscript and it is also in the paper tittle. I suggest adding a subsection in the methods (as you did with the water quality) specifying what types of land use you considered, how they were determined and the characteristics of each land use (types of forests, agricultures, urban areas etc). Additionally, I suggest using the term "land use and land cover".

We agree that details of the land use and land cover should be introduced, hence we added a new subsection 2.5 Land use and land cover in the Materials and Methods as follows.

- Due to the large sampling area, land-use types widely varied while other hydro-morphological variables remained relatively stable across the five tributaries. Particularly, urban and resident areas were dominant with around 55% of the total sampling areas, while forest and agriculture occupied 8-11% and 14-20%, respectively. Minor sampling area was surrounded by industrial factories and construction sites, with less than 5% each. Several riversides were next to the road, occupying 11-19% of the total sampling area. The distribution of the land-use types was not evenly among the rivers. Intensive urban activities can be found near the Cuenca and from the middle to the end of Tomebamba rivers. Conversely, Yanuncay and Machangara cross two natural reserves, i.e. Cajas National Park and the Machangara-Tomebamba protected forest, leading to their pristine water quality conditions. In addition, these two aforementioned rivers cross the city of Cuenca in the latest part of their path before the confluence with the Tomebamba River (Jerves-Cobo et al., 2018). In addition, these two aforementioned rivers cross the city of Cuenca in the latest part of their path before the confluence with the Tomebamba River. Tarqui river locates near agricultural irrigation and livestock production areas, causing their high nutrient and organic inputs (Jerves-Cobo et al., 2018). To evaluate the effects of land use on the dissolved GHG concentrations of the tributaries, we considered five different types of land use, i.e. nature (close to the forests), industry (close to factories, and mining areas), agriculture (close to arable land, orchard, and farms), roads, and urban areas (close to residential and urban areas). (line 145-156)

**9. Ln 150** – Authors I suggest use a different symbol for partial pressure of the gas in the adjacent air.

As mentioned in the previous comments, the flux calculation including this part was removed.

**10. Ln 157 -** This sentence is not clear. The total watershed area should not be used for this calculation, but the water surface area should be used.

As the calculation of the fluxes was removed, the calculation of the total annual emissions per tributary was also removed.

**11. Ln 158-161 -** There is a serious conceptual problem in this sentence. GWP is based on the capacity of a given gas to absorb heat compared to CO2. And here, the authors are assuming they are "determining" the GWP of the three gases. I assume that the authors are using GWP used on the Fifth Assessment Report to calculate emission in carbon dioxide equivalent (CO2-eq)

As mentioned in our response to the third major comment, we realized that this conversion did not add to the story, thus we excluded this conversion in the revised manuscript to make the story of the research more focused and concise. We used only the results obtained from our sampling campaign instead to avoid the confusion of the readers.

**12. Ln 165-170 -** The cited paper addressed lakes and pond, not streams and rivers. Additionally, this sentence is displaced in the text and should be removed from the method section. The following sentences showing some results should not be here in the method section. Please, remove.

Removed.

**13. Ln 174 -** Why calculate two different indexes? I suggest using only one index. Why are you using Prati and Oregon indexes? The author stated that the Oregon index was developed to express ambient water quality for general recreational use. Are the aquatic systems in the watershed for recreation purposes? If yes, I suggest the authors to describe the multiuse purpose in the Study Area section.

The justification of the two indexes was added in the revised manuscript as follows.

- By aggregating the measurements of multiple water quality parameters, WQI as a single number can be used to assess the quality of a water resource for serving different purposes (Lumb et al., 2011). However, as each WQI has its own demerits, no WQIs can be universally applicable (Tyagi et al., 2013). Among 30 WQIs listed in Sutadian et al. (2016), Prati and Oregon indexes were chosen in this study because of their successful establishment for river water quality assessment (Zotou et al., 2019) and their required parameters were measured during the sampling campaigns. Other WQIs, such as National Sanitation Foundation (NSF) WQI or Stoner's index, need parameters that were not measured in this study. Additionally, despite their suitable required parameters, Canadian Council of Ministers of Environment (CCME) index and Weighted Arithmetic WQI were not applied due to their common application in drinking water use (Sutadian et al., 2016) and their limitations listed in Tyagi et al. (2013). (line 126-134)

Similar to Prati Index, Oregon Index has been applied not only in Oregon but also in many places in the world. In fact, it is one of the most important water quality indices according to several review articles on water quality indexes, such as Lumb et al. (2011), Sutadian et al. (2016), and Zotou et al. (2019). We added the review article to illustrate the justification of the two indexes as follows.

- Prati index, developed by Prati et al. (1971), is often used to evaluate surface water quality with a consideration of numerous pollutants. Oregon Index was developed by Dunnette (1979) and then modified by Cude (2001) to initially express ambient water quality for general recreational use. After that, both indexes have widely been applied to assess river water quality for different purposes (Lumb et al., 2011;Sutadian et al., 2016;Zotou et al., 2019). (line 135-138)

**14. Ln 223 -** "total emissions of the three gases per year from the whole river basin". This statement is not supported by your data because you analyzed only five consecutive days of the year. Authors should consider use "during the sampling period" instead of "per year".

As mentioned in our response to the third major comment, we realized that this conversion did not add to the story, thus the estimation of total annual emission from the tributaries was removed.

**15. Ln 247-256 -** This entire paragraph does not add any useful information to the manuscript. I suggest removing this paragraph. Additionally, I suggest using only one index and focus on the relationship between the index and GHG emissions

This paragraph aimed to analyze and compare the obtained results of the two indexes. Particularly, the river water quality was categorized more consistently in case of Prati Index compared to Oregon Index which can be attributed to the heavy penalty for high concentrations of organic matter and nutrients in case of the latter. In fact, this led to only two sites of the Cuenca river basin were considered either good or fair water quality. The categorization based on Prati Index was more in line with the results of the previous sampling campaigns of Jerves-Cobo et al. (2018) and Jerves-Cobo et al. (2020). Because of these reasons, together with its simple calculation, Prati Index was recommended over Oregon Index in our case study. This was illustrated in the revised manuscript as follows.

- Prati and Oregon Indexes were applied to assess the effects of water quality on the dissolved GHG concentrations in the Cuenca river basin. According to the Prati Index, the rivers had higher water quality than the results obtained from the Oregon Index. Particularly, 18 sampling sites were categorized in either good quality or acceptable quality following the Prati Index while only two sites were considered either good or fair water quality according to the Oregon Index. The results obtained by using Prati Index appeared to be more in line with the results obtained from the previous sampling campaigns of Jerves-Cobo et al. (2018) and Jerves-Cobo et al. (2020). (line 233-238)

Regarding the justification of the two WQIs, since each WQI has its own demerits, no WQIs can be universally applicable (Tyagi et al., 2013). The two indexes were chosen among 30 WQIs listed in Sutadian et al. (2016) because of their successful establishment for river water quality assessment (Zotou et al., 2019) and their required parameters were measured during the sampling campaigns. The justification of the two WQIs was added in the revised manuscript as follows.

- By aggregating the measurements of multiple water quality parameters, WQI as a single number can be used to assess the quality of a water resource for serving different purposes (Lumb et al., 2011). However, as each WQI has its own demerits, no WQIs can be universally applicable (Tyagi et al., 2013). Among 30 WQIs listed in Sutadian et al. (2016), Prati and Oregon indexes were chosen in this study because of their successful establishment for river water quality assessment (Zotou et al., 2019) and their required parameters were measured during the sampling campaigns. Other WQIs, such as National Sanitation Foundation (NSF) WQI or Stoner's index, need parameters that were not measured in this study. Additionally, despite their suitable required parameters, Canadian Council of Ministers of Environment (CCME) index and Weighted Arithmetic WQI were not applied due to their common application in drinking water use (Sutadian et al., 2016) and their limitations listed in Tyagi et al. (2013). (line 126-134)

**16. Figure 3** – Please, add the number of samples (n) that compose each box. And, I cannot identify which class does not have any value in the Oregon Index graphs. I suggest insert the class names in the x axis of each panel.

The name of the WQ categories was added to the x-axis while the number of samples was put in Table S3.1 to avoid making this figure complicated.

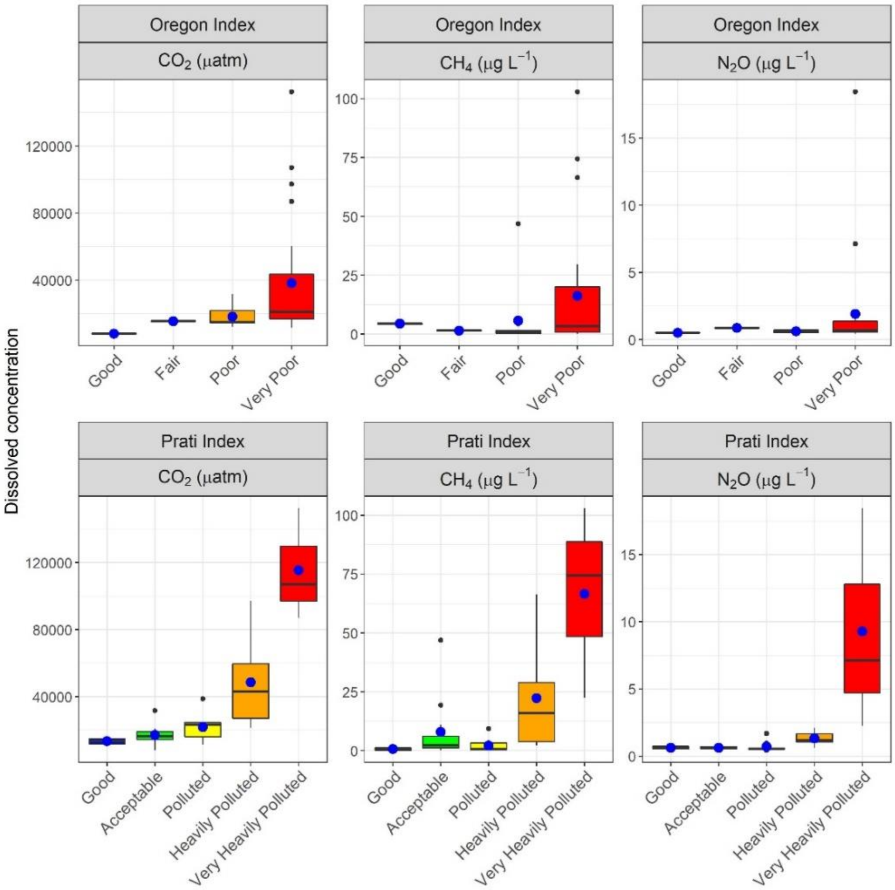


Figure 3. Dissolved concentrations of the three greenhouse gases from the Cuenca urban river system in different water quality categories using Oregon and Prati Indexes. Box plots display 10th, 25th, 50th, 75th and 90th percentiles, and individual data points outside the 10th and 90th percentiles. Blue dots represent the mean of the dissolved concentrations in the water quality categories.

Table S3.1 Number of sites in each water quality category in both indexes

| Water Quality Category (Prati/Oregon Index) | Number of sites Prati Index | Number of sites Oregon Index |
|---|---|---|
| Good/ Excellent | 6 | 0 |
| Acceptable/ Good | 12 | 1 |
| Polluted/ Fair | 9 | 1 |
| Heavily Polluted/ Poor | 6 | 10 |
| Very Heavily Polluted/ Very Poor | 3 | 24 |

**17. Ln 261-266 -** This is an important information and the authors do not need both indexes to have the same conclusion. As I suggested before, use only one index.

As mentioned in the previous responses, the justification of the two indexes was described in the revised manuscript.

**18. Ln 268 -** GWP should not be used here in this sentence. Please see the comments in the methods section.

As mentioned in the previous responses, GWP part was removed in the revised manuscript.

**19. Ln 271-274** – Holgerson and Raymond (2016) do not address emission from streams, as the authors stated in this sentence. They estimated emissions from non-running inland water. Please, verify

We removed this reference.

**20. Table 2 -** What is the difference between "Urban" and "Industry"? Are urban areas residential areas? Please, specify each land use and land cover in the method section.

We clarify this aspect in the new section ***2.5 Land use and land cover*** in the Materials and Methods as follows.

- To evaluate the effects of land use on the dissolved GHG concentrations of the tributaries, we considered five different types of land use, i.e. nature (close to the forests), industry (close to factories, and mining areas), agriculture (close to arable land, orchard, and farms), roads, and urban areas (close to residential and urban areas). (line 153-156)

**21. Figure 6 -** This figure is in both the main text and Supplement Material. Please, remove from the SM.

We removed this figure since the estimation of the total annual emissions from the tributaries was removed.

**References**


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