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Editor
Biogeosciences

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Dear Dr. Abril,

We appreciate your detailed and insightful comments on the revised manuscript.

To respond to your comments and suggestions, we have thoroughly revised our manuscript and included some new data such as alkalinity and calculated $\delta^{13}\text{C}$ -DIC values, as detailed in the enclosed list of detailed responses. Many additional changes made in this version have been marked by a weak blue color to distinguish them from [the blue-marked previous changes](#) in the first revision.

We would appreciate your kind consideration of our revised manuscript for publication in Biogeosciences.

Sincerely,

Ji-Hyung Park

Cc: Hyojin Jin, Tae Kyung Yoon, Most Shirina Begum, Eun-Ju Lee, Neung-Hwan Oh, Namgoo Kang



<Responses to Editor's comments on the first revision>

Because the first round of reviews of your paper was quiet detailed and comprehensive, I wanted to move forward its edition process based on my own reading. My conclusion is that your paper contains all the necessary data to reach your conclusions, that these conclusions are original and well within the scope of Biogeosciences, but that presentation and selection of the data must re-thought, and the text must be intensively re-worked in order to make your conclusion clear and understandable for all BG readers. Note that my evaluation is based only on text and figure and not sup. Material

One first big problem with your MS is your phrasing that often creates confusion. On many occasions, what should be a strong and precise message is diluted in very general statements using sophisticated expression likely of your own invention. In other occasions, the structures of sentences are very long and repetitive and something that could be clearly said in a few words is hardly expressed in a long and awkward sentence. The style of your text is really a major weakness of your paper because it dilutes the main messages in unnecessary superficial text, including the occurrence of some wrong or imprecise statements. Here an example: L500 "The observed reach-specific patterns of altered water quality and GHG dynamics provide an empirical evidence for ecosystem structural and functional responses to anthropogenic changes in hydrogeomorphic patches of the fluvial landscape, which have been emphasized in recent conceptual models integrating fluvial geomorphology and ecosystem processes at the valley to reach scales (Thorp et al., 2010)." This looks like a suite of savant words without real precise meaning and without referring to objective scientific facts to sustain the statements: what is a "reach-specific pattern"? What pattern? of increasing/decreasing what parameter? "water quality" and "dynamics" are very general terms that can be either positive or negative; "ecosystem structural and functional responses" ecosystem structure is a vast domain, be more precise : what ecological processes are you dealing with here? What responses? What is a "hydrogeomorphic patch"? sorry, I do not understand and I doubt this expression has been defined in the literature. What is a "reach scale"? how many km for the reach scale?... etc., etc. You use the term "reach" (upper reach, lower reach, river reach... etc.) throughout your MS without giving a clear definition for it. Other kind of problem with your style is illustrated by the following sentence from the abstract (there are many other cases in the MS) "The basin-wide surveys of three GHGs revealed distinct increases in the concentrations of three gases along the lower reach receiving urban tributaries enriched in GHGs and DOC". You are repeating 3 times "GHG" here and 2 times "three GHGs" although the meaning of the sentence is simply that urban tributaries are a source of GHG and DOC for the river. This kind of phrasing occurs all through your MS and makes it very hard to read and follow, because crucial new original findings are diluted in very general statements, without clearly hierarchizing what is new, what is specific from the study site, what can be generalized elsewhere, and, where and when a statement applies... You will find a list of problematic sentences below, because I am not English native, the list is probably not exhaustive, and I did not try to re-phrase all of them. Please consider seriously that your MS needs profound revision of the style, including detailed editing of language meaning, avoiding vague conceptual statements not based on precise scientific facts (eg "the parameter X increases downstream when the parameter Y decreases" and not "parameters X and Y evolve according to complex biogeochemical processes occurring from upper to lower reaches of river basin and tributaries..."). Simplifying and shortening sentences so it becomes easier for readers.

<Response> We agree that there were many long and general descriptions in the previous version. To avoid any unnecessary confusion, we have tried our best to rephrase all the long, general, or redundant descriptions. In the case of Thorp et al citation, we used the terms and descriptions as appeared in the paper to respond to a reviewer's suggestion. We understand your point, so the sentence has been removed from the text. The rewritten paragraph does not require this sentence any more. "Reach" is now used based on our definitions of the upper, middle, and lower reaches provided at their first use in the abstract and main text. Please note that we have revised the entire manuscript including the sentences you mentioned here and below.

Second general problem is the choice of data you are presenting in the MS. The MS deals preliminary with CO₂, CH₄ and N₂O (or GHGs); Ancillary parameters include, nutrients, oxygen, pH, CH_{1a}, alkalinity, DIC DOC concentration, ¹³C and ¹⁴C, UV absorbance, and fluorescence excitation. I found questionable the choice you made in showing these data in the figures and tables and in the supplementary material.



UV absorbance, and fluorescence excitation bring very little information to the paper, I wonder if these data are really necessary here (they could appear in a couple of sentences in the discussion as “unpublished data” avoiding long description in the Mat & Met.

<Response> Our manuscript is not just about longitudinal patterns of the three GHGs. We also need to provide explanations of the key controls. In this sense, DOM optical properties are invaluable to characterize anthropogenic DOM abundant in the lower Han River in relation to GHG dynamics. To make this point clear, we have added key findings on DOM properties and their implications for longitudinal patterns of both DOM and GHGs in the abstract and results/discussion.

To the contrary, because your data include pCO₂, and because pCO₂ was measured with a headspace technique, the information on the entire carbonate system is necessary: provide TA values and calculated DIC values (from TA and pCO₂). Values of these crucial parameters are not even mentioned in the text. WWTP generally release DIC in the form of TA, it should be the case here, a detailed analysis of TA might be important for the paper.

In addition, if TA values are high, the buffer capacity of the carbonate system should be taken into consideration in order to calculate in situ pCO₂ from pCO₂ measured in a headspace. The Henry's law is not sufficient in the case of carbonate rich waters, because equilibrium between CO₃⁼ and HCO₃⁻ and between CO₂ and HCO₃⁻ are displaced when creating the headspace (CO₂ decreases, CO₃⁼ increases and HCO₃⁻ may increase or decrease depending on the conditions). Thus for alkaline waters, calculation of in-situ (pre-headspace) pCO₂ must include the entire DIC and the changes in CO₃⁼, HCO₃⁻ and CO₂. In the headspace technique, the volume of water is finite; this is different from the equilibrator technique, where an infinite volume of water is equilibrated with a finite volume of air.

<Response> We have included TA data (Tables S1-S3, S5, S7). We also understand the importance of TA and DIC in addressing pCO₂ dynamics, but we could not include this topic for two reasons. First, another manuscript is now being prepared to compare measured pCO₂ and calculated DIC species. Second, the key goal of the current manuscript is to compare the three GHGs measured using the same headspace equilibration technique. Because we deal with the multiple gases and numerous ancillary data, we thought that the topic of DIC should be addressed in a devoted manuscript to maintain our focus on three-gas comparison. Please understand that our approach is not different from other papers addressing multiple gases. And that this manuscript is already overloaded with different sets of data and topics.

One of the reviewers pointed out the question of δ¹³C-CO₂ and I agree with her/him that stable isotopes studies must rely on data of δ¹³C-DIC and not δ¹³C-CO₂. You mention in your revised MS a difference of about 10 to 11 per mil between δ¹³C-DIC and δ¹³C-CO₂, referring to Mc Callister and del Giorgio. I haven't read this paper, but almost all the literature reports δ¹³C-DIC and not δ¹³C-CO₂. The problem is that the difference between δ¹³C-DIC and δ¹³C-CO₂ and the value δ¹³C-CO₂ are strongly dependent on water temperature, pH, and alkalinity, because the fractionation between CO₃⁼, HCO₃⁻ and CO₂ depend on these parameters. To the contrary, δ¹³C-DIC is a conservative notion that considers all the ¹²C and the ¹³C contained in the DIC of a sample, whatever the temperature and/or the pH and whatever the proportion of each chemical form.

<Response> We have cited more papers employing δ¹³C-CO₂ measurements (e.g., Campeau et al., 2017) and provided more detailed interpretations of our measurements in comparison with other papers. We also calculated δ¹³C-DIC according to your suggestion, and compared with more literature information on δ¹³C-DIC to describe implications of our findings. Please note that the entire section has been almost rewritten (L 460-563).

You put a lot of emphasis in your MS on the importance and interest of using the dual isotopes approach; however, you apply this approach only to DOC in a very limited amount of samples. And in fact the dual isotope approach brings little information because of the contamination of WWTP with old DOM such as gasoline. If the paper deals mainly with GHG, one would expect the dual isotopes techniques to be applied to DIC or CH₄... So be less ambitious when introducing the dual isotope approach because when applied to DOC here, it gives little information for the interpretation of the three gases

<Response> We agree that our dual isotope approach is limited in many aspects. First of all, the small number of samples has been indicated in the abstract. We also paid more attention to interpreting the dual isotope ratios of DOM and tried to restrict our data interpretation to source



tracking. For example, we focused more on wastewater-derived aged DOM and gases when we linked DOM isotope data to gas isotope ratios, as detailed in the thoroughly revised section 4.2.

Inversely, discussion on ^{13}C - CH_4 data is relatively superficial and could be strengthened and be more quantitative. These values are quite high and reveal strong oxidation, maybe up to 95% of the CH_4 is oxidized

<Response> We have provided more explanations for CH_4 oxidation based on additional references and observed values in the revised paragraph (L 540-563).

Alternative choices of data to be shown in figure and table in the main MS are necessary, reminding that the main topics is CO_2 , CH_4 and N_2O

<Response> Explained.

Below the detailed comments on the MS

Repeating “GHG” >8 times in the abstract is awkward. Instead, specify at least the ranges of concentrations of each individual dissolved gas. Some key numerical values are missing in the abstract.
<Response> The entire abstract has been rewritten to reduce redundant terms and expressions and provide key values.

L35 not sure “body of research” is appropriate here

<Response> The whole sentence has been changed to “A growing number of studies have provided a wide range of estimates for the global greenhouse gas (GHG) emissions from inland waters”

L40 specify that wetland are source of dissolved CO_2 FOR RIVERS (not source of CO_2 for the atmosphere as it suggests here)

<Response> The sentences now reads “Recent studies in large river systems such as the Amazon and Congo have identified wetlands as previously unrecognized sources of CO_2 and organic matter for rivers”.

L45 I guess you mean Abril et al. 2015 and not 2014

<Response> Corrected.

L49 change “natural” to “pristine”

<Response> Changed.

L53 what’s the meaning of “concurrent” here? Please rephrase

<Response> The sentence has been changed to “While global river systems are now subject to multiple environmental stresses, including water pollution, impoundments, and climate change, most research efforts have addressed these multiple stresses separately.”.

L55 insert measured “simultaneously” CO_2 , CH_4 and N_2O and remove “together”

<Response> Done.

L56 what’s the meaning of “interrelated”? Please rephrase

<Response> The phrase has been changed (some common longitudinal patterns of gas concentrations determined by major sources and production mechanisms).

L60 “comparison of three GHGs” do you mean “these three GHGs” or could be any other GHG?

<Response> The word “these” has been added.

L70 “measurements of multiple GHGs...” you are repeating what you already stated before

<Response> The sentence has been rephrased (Several recent studies conducted in highly human-impacted river systems have found unique longitudinal and seasonal patterns of CO_2 and other GHGs that might be explained by different factors and mechanisms from those relevant to large pristine rivers).



L83 “shifting balance between autotrophy and heterotrophy at diel to decadal scale” please be precise: shifting in favour of what? Favouring autotrophy or heterotrophy? All through the MS avoid the numerous sentence with such incomplete information.

<Response> The sentence has been rewritten (GHG dynamics in impounded waters and sediments may be explained by temporal changes in a suite of concomitant metabolic processes including primary production, methanogenesis, methane oxidation, nitrification, and denitrification).

L85 what is a “reach” ? I understand it is a portion of a river, but what is its typical length? Few meters, hundred meters, kilometres? The continuous use of this term all through the MS is really perturbing.

<Response> The term in L85 has been changed to “impounded waters and sediments”. When we use the term “reach” to indicate the three compared river sections (upper, middle, and lower), it is based on the definitions provided at its first use in the abstract (L 16-) and main text (L 108-). Otherwise, it is used to indicate a river section with similar structure and function, as commonly used in the literature. It should be noted that there is no agreed length definition. For example, hydrogeomorphologists often deal with short reaches < km (e.g., Poole, 2002), but some river biogeochemists use very long reaches > 1000 km (e.g., Richey et al., 1988).

Although you repeated several times the necessity of measuring the three GHGs, nothing on the interests of measuring isotopes in the abstract.

<Response> As described earlier, we have restricted the interpretations of isotope data, as described in L 31-36.

L110 “we expected that the comparison of reach-specific spatial pattern of three GHGs and C isotopic composition in DOM, CO₂ and CH₄ ... emerging concepts of anthropogenically created discontinuities in riverine metabolic processes and GHG emissions”. Long, awkward sentence. What is a “reach-specific spatial pattern”? Do you simply mean that the longitudinal (or spatial) distributions of dissolved gases are probably impacted by dams and urban areas? “metabolic processes” do you mean primary production and/or respiration? Or other food-web metabolic processes?

If later in the MS you refer to the river continuum concept, it would be interesting to mention it in the intro.

<Response> The sentence has been rephrased to be more specific, though it is still long (The comparison of the three GHGs, DOC, and other ancillary water quality measurements across the three reaches affected by different anthropogenic perturbations would provide empirical data that can be incorporated into the emerging concept of anthropogenic discontinuities in riverine metabolic processes involved in primary production, organic matter degradation, and GHG emissions.). **The river continuum concept has been introduced in a preceding paragraph (L 72-76).**

L150 change “reported” by “described”

<Response> Changed.

L151 “in each SAMPLING, water SAMPLE...” rephrase

<Response> “In each sampling” has been removed.

L153: we don’t care about the brand of the peristaltic pump

<Response> The brand name has been removed, though some people cared in other review processes.

L157 we don’t care about the brand of the syringe, exetainer (L160), temperature and pressure sensor (L164)

<Response> All those brand names have been removed.

L178 Your analysis of d¹³C in CO₂ in a headspace without acidification is problematic. Instead, measurements of ¹³C-DIC should have been made.

<Response> We are also aware of the usefulness of d¹³C analysis, but had a different objective, namely to track downstream changes in d¹³C-CO₂/CH₄, as a growing number of studies have used CRDS measurements. We hope that the rewritten section 4.2 would shed some insight on gas isotopic ratios.



L183-184 “The concentration of total suspended solid (TSS) was measured as the difference in the filter weight before and after drying at 60°C for 48 hours.” this procedure will give you the water content in the filter and filtered material, not the TSS.

Did co-authors did not revise the MS?

<Response> Rephrased (The concentration of total suspended solid (TSS) was determined by filtering a known volume of water sample through a pre-weighed GF/F filter and then weighing the filter again after drying at 60°C for 48 hours).

L204: “subsamples of filtered water samples” please reword

<Response> Rephrased (Some filtered water samples).

You do not explain how d13C-CO₂ and d13C-CH₄ were measured: GC/C/IRMS?

<Response> Already described in a preceding paragraph (...analysed for stable C isotope ratios of CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) and CH₄ ($\delta^{13}\text{C}_{\text{CH}_4}$) by a GasBench-IRMS (ThermoScientific, Bremen, Germany) at the UC Davis Stable Isotope Facility.).

L234 “tended to be lowest” please reword

<Response> The entire sentence has been rewritten, beginning now with “The pCO₂ values at the four dam sites, ranging from 51–761 μatm , averaged 304 μatm , lower than the level expected for atmospheric equilibrium (~ 435 μatm).”

L234 “particularly low: provide value”

<Response> The ranges of pCO₂ values have been provided in L 242-247.

L243 “of two gases” > of these two gases

<Response> The word “these” has been added.

L251 “points to” check English language

<Response> The whole sentence has been reformulated (Given the relatively small proportion of tributary discharge in the mainstem flow ranging from ~5% in the monsoon period to 12% in dry seasons, [the comparison of monthly water quality measurements between the six sites and the urban tributary \(HR12\)](#) illustrates [the disproportionate influence.](#))

L252 “fraction” is a more usual word than “moieties”

<Response> The term “moieties” has been changed to a common term used in the literature (protein-like DOM “components”).

L254 “three nutrients” which ones?

<Response> Specified (three major nutrients (NH₄⁺, NO₃⁻, and PO₄³⁻)).

Nomenclature HR11... HR14... etc. are difficult to follow, indicating the characteristics of the river sections would help

<Response> Site characteristics have been added to the site names (from HR11 downstream of the last cascade dam to HR14 in the middle of the lower reach).

L260... you mention correlations with parameters such as DO, pH, TA but the numerical values of these important parameters only appear in the supplementary material. Maybe an additional table could help

<Response> Please note that Fig. 5 can provide an overview of very complex correlations between GHGs and ancillary measurements. We still hope that readers can refer to more detailed numerical information provided in supplementary table (Table S4).

L279 “pointed to WWTP effluents driving the concentrations of...” revise English language

<Response> Rephrased (revealed the dominant influence of WWTP effluents).

L280-283 you are repeating twice “GHGs” and “WWTP” in the same sentence, awkward sentence



<Response> **The sentence has been reformulated** (All the three GHGs exhibited similar levels and variations in the WWTP effluents and the tributary outlet, indicating a strong contribution of treated wastewater to the tributary gas export to the lower Han River.).

L283 “increase abruptly along the most downstream reach after passing the WWTP located within a few km upstream” do you mean they “ rapidly increase immediately downstream of the WWTP”?

<Response> **Changed** (Both $p\text{CO}_2$ and N_2O concentrations in the tributary abruptly increased along the terminal section downstream of the WWTP).

L284 what does “ending-up” mean here? End of what?

<Response> **The whole sentence has been rewritten** (In contrast, CH_4 concentrations were very low at the three upstream sites, exhibited large fluctuations along the middle reach, and decreased slightly in the terminal section downstream of the WWTP.).

L285 “Corresponding to the large scatter of the box plots representing three GHG concentrations measured at the WWTP effluents and outlet site, two locations exhibited similar patterns of temporal variations in GHG concentrations” awkward and confusing sentence, please rephrase.

<Response> **Rephrased** (The levels of the three gases displayed large, similar temporal variations at the WWTP effluents and the tributary outlet site (Fig. 6e, 6f, 6g)).

L290-298 specify if “high” and low” $\delta^{14}\text{C}$ values correspond to “old” or “young” DOC

<Response> **Specific $\delta^{14}\text{C}$ values and corresponding ages have been added in L 319-.**

L296 unit is missing after -100

<Response> **Added.**

L300 “Concentrations of three GHGs (Fig. 8; Table S7) combined with $\delta^{13}\text{C}$ in CO_2 and CH_4 (Fig. 8; Table S8) collected along the lower Han River during a cruise expedition revealed clear tributary effects on the C isotopic composition of two GHGs sampled at the mainstem site” very awkward sentence. In addition it says almost nothing in terms of “results”

<Response> **The revised sentence reads** “The concentrations of the three GHGs and the values of $\delta^{13}\text{C}$ in CO_2 and CH_4 (Fig. 8; Tables S7, S8) measured along a cruise transect exhibited large increases in gas concentrations and either gradual increases in $\delta^{13}\text{C}_{\text{CO}_2}$ or abrupt decreases in $\delta^{13}\text{C}_{\text{CH}_4}$ along the confluence of the urban tributary (HR12).”.

L303 “ $\delta^{13}\text{C}_{\text{CO}_2}$ continued to increase toward the river mouth, with its values bracketed by those measured for the two upstream tributaries and a downstream tributary” to what figure does this refer to? Is “values bracketed by” correct English?

We would need $\delta^{13}\text{C}$ -DIC and DIC concentrations here

<Response> **The new sentence now reads** “The gradual downstream increases in $\delta^{13}\text{C}_{\text{CO}_2}$ along the mainstem transect reflected the tributary contributions to the mainstem isotopic composition, because the values found in the two upstream tributaries (-18.2% , -18.3%) and a downstream tributary (-14.7%) were higher than the upstream mainstem values (Table S8).”. **Regarding $\delta^{13}\text{C}$ -DIC, please refer to our response to a major comment on the same issue.**

L308 remove “three”

<Response> **To be consistent, we use “the three GHGs”.**

L328 “lack of these natural source” do you mean the absence of floodplain? Not sure Richey 1988 considered wetlands as the “primary factor”.

<Response> **The sentence has been rewritten** (Those natural sources are rarely found in the Han River basin, where the middle and lower reaches have been modified substantially by man-made structures. This lack of natural sources, combined with the differential patterns of the three GHGs attributed to dams and urban wastewater, suggests that increased water retention time and nutrient enrichment may play crucial roles in the production and consumption of the three GHGs in this highly regulated river system (Crawford et al., 2016)).



L332 and at many other places: not sure “of three GHGs” is correct (it could be other gases), I would say either “the three GHGs” or “these three GHGs”

<Response> Corrected throughout the manuscript.

L335. “Spatial variations in three GHGs observed along the middle reach (Figs. 2 □ 4) suggest that complex interacting metabolic processes in water column and sediment influence the levels of three GHGs to varying degrees depending on gas and reservoir”

Avoid this type of sentences that says basically nothing. What “metabolic processes” ? be precise.

“depending on gas and reservoir” Awkward wording. Again the use of “three GHGs” is confusing

<Response> Rewritten (The highly variable concentrations of CH₄ and N₂O along the middle reach in contrast to the consistently low levels of pCO₂ at the dam sites (Figs. 2 – 4) suggest that the rates of concomitant metabolic processes involved in the production and consumption of these gases in reservoir water and sediments may vary with predominant dam conditions such as water depth and sediment accumulation.).

“Lower values of pCO₂ measured at all impoundment-affected sites including site HR11 downstream of the last dam (HR10) indicate an enhanced planktonic CO₂ uptake, in agreement with enhanced photosynthesis and lowered pCO₂ levels observed in some eutrophic impounded reaches of the Mississippi (Crawford et al., 2016), the Yangtze (Liu et al., 2016), and a Yellow River tributary (Ran et al., 2017)”

You repeat twice the “lower pCO₂ here, rephrase, something like “in impoundments phytoplanktonic primary production is favoured (REF...) and pCO₂ is lowered”

<Response> Rephrased (the lowered pCO₂ levels as a consequence of increased primary productivity).

L343 what does “taper” mean?

<Response> Changed (gradually decrease).

L348 “which may be associated with terrestrial DOM components and their microbial transformation products”. Is it “may be associated” or does it reveal a degradation of terrestrial DOM to CO₂?

<Response> To specify each indicator’s meaning, the sentence has been reformulated (While HIX and C1/DOC indicate the degree of humification and the proportion of terrestrial DOM components, respectively, C2/DOC represents the proportion of “microbial humic components” in the bulk DOM (Fellman et al., 2010; Parr et al., 2015).).

L348 “However, the concurrence in the relatively high levels of pCO₂ and DOC moieties of terrestrial origin at some middle reach sites that are less affected by impoundments (e.g., HR 7 and HR8) might have resulted in the observed significant correlations.” Confusing sentence. Please rephrase

<Response> Rephrased (In contrast, the relatively high levels of pCO₂ concurred with strong optical intensities of terrestrial DOM components at some middle reach sites that are less affected by impoundments (e.g., HR 7 and HR8), resulting in the significant correlations between the relatively wide ranges of pCO₂ and DOM optical properties.).

L358 what is a “low head dam”?

<Response> More detail has been provided (low dams constructed for river navigation).

L361 “depth-dependent gradient” > vertical gradient?

<Response> Yes, and changed.

L363-367 what does d13C-CH₄ say about CH₄ oxidation?

Conversion of DOC to CH₄ is extremely speculative, (in fact here the correlation is indirect, as they both come from urban areas) because methanogenesis is marginal in the water column, and methanogenesis occurs in sediments using sediment OM and not water column DOC.

“based on the coupling between anaerobic organic matter degradation and methanogenesis” what coupling? This is meaningless. In fact, methanogenesis IS anaerobic organic matter degradation.

<Response> The sentences have been revised to provide a more coherent explanations (CH₄ concentrations in the middle reach exhibited a weak, but significant correlation with DOC concentrations (Fig. 5, Table S4). This correlation may indicate an active methanogenesis in anaerobic reservoir



sediments that is often accompanied by increases in surface water DOC concentrations (Chen et al., 2009; Wang et al., 2017b). It is also possible that some local sources of organic wastes surrounding the reservoirs may have directly discharged wastewater rich in DOC and CH₄ (Bergier et al., 2014; Wang et al., 2017b).

L374 “might be explained by the complex interactions between microbial N transformations in the oxygen-rich epilimnion and oxygen-poor hypolimnion” be precise, what processes?, nitrification, denitrification, DRNA, anamox? In addition the fact that N₂O does not peak in reservoirs does not mean it is a result of “complex” processes, it might be very simple: no production of N₂O...

<Response> The new sentence reads “The lack of clear impoundment effects on N₂O concentrations except for one reservoir (HR6; Fig. 2) can be explained by little N₂O production in the other reservoirs or the complex interplay between N₂O production from nitrification and denitrification and N₂O consumption under changing availability of O₂”.

L375 “a suite of related processes” related to what? “in stream metabolism” ok, but heterotrophic or autotrophic, respiration or primary production? Please be more precise.

<Response> The phrase has been changed to make clear the point of the sentence (Large increases in GHG concentrations along the lower reach may be a combined result of the net in-stream production and direct inputs from WWTPs.).

L378 and later in the MS: the term “pulse” refer to temporal changes not spatial changes. It is not appropriate for describing local inputs due to urban areas

<Response> We have replaced the term “pulse” by “pulse-like” or “pulsatile” or “peak concentrations” to indicate some strong localized concentration increases, as often found in the literature.

L379 “benthic sediment” is a truism

<Response> Changed to “bottom sediment”.

L384-388 how was this budget calculated? “was estimated to be consumed by phyto...” how? “same reach” do you mean the same river section?

<Response> More details on the mass balance approach have been provided in the preceding sentences (Previously we used a mass balance approach based on three cruise underway measurements of *p*CO₂ and DOC and the estimated rates of CO₂ outgassing from the same reach of the lower Han River, and additional measurements of *p*CO₂ and DOC at two urban tributaries (TC and JN) to show that the two tributaries JN and TC delivering WWTP effluents accounted for up to 72% of the CO₂ concentration measured at a downstream location of the lower reach (Yoon et al., 2017). **When the rates of CO₂ production, consumption, and outgassing were estimated** using the mass balance approach for a section upstream and two sections downstream of the two tributaries lower reach **in June 2016** (Yoon et al., 2017),.... **The last sentence has been changed to indicate the mass balance-based estimation (...the mass balance suggested that the bulk of CO₂ delivered by the tributaries might have been consumed by phytoplankton photosynthesis in the downstream section of the lower reach (Yoon et al., 2017)).**

L390 “By directly measuring d13C in CO₂ respired by bacterioplankton across a gradient of streams and lakes in Canada, McCallister and del Giorgio (2008) showed that the production of CO₂ through bacterial degradation of terrigenous DOM decreased in sharp contrast to the increasing proportion of algal-derived DOC and CO₂ with increasing levels of Chl a” It is hard to find the relevance of this observation on boreal lakes with that here in Korean rivers. If the question here is whether algae release (exudate DOC) that is further mineralized to CO₂ by heterotrophic microbes, or does the algae directly respire in the dark, I think you will never answer this question. Out of the scope of the paper.

<Response> Yes, we agree, but we just wanted to emphasize the relative importance of these two processes by citing this rare finding. We have added a caveat that we need to consider different mechanisms in different climate zones (... although it would require further research to verify the findings in the boreal freshwaters in temperate and other biomes).

L398 “ranges of two gases” please specify which gases

<Response> Specified.



L401 “point to” is not correct English

<Response> Changed to “indicate”.

L405 “In contrast to the lacking or weak correlations indicative of anaerobic CH₄ production in the impounded middle reach” I wonder what is a “correlation indicative of anaerobic CH₄ production”? please rephrase.

What is a “correlation related to anaerobic metabolism”? please rephrase

<Response> To avoid any confusion of data interpretation, the sentence has been rephrased to describe the different correlations found in the middle and lower reaches (In contrast to the nonsignificant correlation between CH₄ and DO in the impounded middle reach, CH₄ measurements in the lower reach exhibited either a significant negative (DO) or positive correlation (water temperature, C1/DOC, and C2/DOC).).

L408 “eutrophication (indicated by significant positive correlation with PO₄)” correlation of what parameter with PO₄? Please rephrase

<Response> Two related sentences have been rephrased:

In contrast to the nonsignificant correlation between CH₄ and DO in the impounded middle reach, CH₄ concentrations in the lower reach exhibited a significant negative correlation with (DO) as well as positive correlations with PO₄³⁻, water temperature, C1/DOC, and C2/DOC. As observed in other urbanized river systems (Beaulieu et al., 2015; Smith et al., 2015; Wang et al., 2018), CH₄ correlated positively with PO₄³⁻, but negatively with DO, implying that the nutrient enrichment often leading to severe phytoplankton blooms during warm summer months may create favourable conditions for anaerobic methanogenesis in the lower reach that is almost impounded by the two submerged weirs.

In general the ideas contained in this 4.1 section are ok and make sense, but the phrasing in English is hazardous which makes the message confusing

<Response> In addition to correcting the commented sentences, the entire section has been double checked to enhance clarity.

L419: 14CDOC in a wide range of global river systems” Please rephrase

<Response> Changed to “rivers around the world”.

L423: “large fluctuations in d13CDOC along the upper to middle reaches from HR2 to HR11 do not present any consistent longitudinal trend of the stable C isotopic composition” Awkward sentence, please rephrase

L425 you use here the term “autochthonous”, do you mean phytoplankton in majority? d13C-DIC of phytoplankton varies a lot depending of the 13C signature of the DIC it has been using.

L426 “which deviated substantially from those of the headwater DOM dominated by allochthonous components”. Please be precise, mentioning what isotope and what are the respective values. What’s the meaning of “allochthonous component” here?

<Response> In response to these three comments, the sentence has been split and rephrased (While $\delta^{13}\text{C}_{\text{DOC}}$ was highly variable along the upper to middle reaches from HR2 to HR11, the values of $\delta^{13}\text{C}_{\text{DOC}}$ at the most downstream site HR14 (-20.6‰ and -23.2‰) were distinctively higher than those measured at the forested headwater stream (-28.2‰ on both sampling dates) (Table S6). The DOM optical properties measured at HR14 were also significantly different from the high HIX and low FI values indicating the predominance of soil-derived DOM in the headwater stream (Fig. 3; Table S1). Taken together, the isotopic composition and optical properties of DOM in the lower reach may reflect the downstream addition of DOM components derived from anthropogenic sources such as WWTP effluents ($\delta^{13}\text{C}_{\text{DOC}}$ around -26‰ ; Table S6) or plankton biomass (note the wide range of the plankton $\delta^{13}\text{C}_{\text{DOC}}$ in Fig. 7).).

L428 “In addition, the distinct seasonal differences in isotopic signatures suggest that the age of DOM is generally younger at five mainstem sites across the river basin during the monsoon period (July 2014; modern -590 years B.P.) than in the dry season (May 2015; 180 - 675 years B.P.)” Do the isotopic values



suggest they vary or do they simply show variation? Please rephrase. Provide the values of ^{14}C together with the age.

<Response> ^{14}C values have been provided in the relevant result section and the rephrased sentence now reads “...the distinct seasonal differences in $\Delta^{14}\text{C}_{\text{DOC}}$ across the five mainstem sites illustrate that the age of DOM is...”.

L433: why “latitudinal” here? Are values plotted versus latitude?

<Response> Corrected to “longitudinal”.

L434 is WWTP DOC older or younger? Could the downstream trend in ^{14}C originate from selective degradation of young C?

<Response> The rephrased sentence reads “The longitudinal increase in DOM age from a modern age to 180 years B.P. at the forested headwater stream to 590–675 years B.P. at the most downstream site may reflect a preferential degradation of young, labile components during riverine DOM transport (Raymond and Bauer, 2001), but also indicates a significant contribution of aged DOM derived from downstream anthropogenic sources; for example, the age of DOM measured at the outlet and WWTP effluents of the urban tributary JN ranged from 765 to 1050 years B.P. (Table S6).”.

L438 “As suggested by Griffith and Raymond (2011), aged DOM moieties in WWTP effluents (765 - 905 years B.P.; Table S6) may not only leave clear isotopic signatures on DOM in downstream reaches, but also fuel the riverine heterotrophy by providing labile sources for biodegradation” Is it younger or older DOC being degraded? Please reword “may not leave clear”

<Response> Griffith and Raymond (2011) suggested that even aged DOM from wastewater can provide labile sources. The rephrased sentence reads “...aged DOM derived from the WWTP effluents (765–905 years B.P.; Table S6) may contain labile materials, which, mixed with other labile components from in-stream sources such as phytoplankton, can fuel the riverine heterotrophy along the lower reach.”.

L440 “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_2 , bicarbonate, and carbonate “ this is too general and confusing. Gas exchange fractionated because ^{12}C CO_2 degases faster than ^{13}C CO_2 , uptake by phytoplankton fractionate because algae preferentially use ^{12}C , leaving more ^{13}C -DIC, and respiration releases DIC with a signature close to that of the OM source (not fractionation but mixing with ^{13}C depleted DIC). It looks you only refer to Mc Callister and del Giorgio regarding ^{13}C -DIC (or ^{13}C CO_2), but their study site is very different from yours

<Response> As mentioned before, we have rewritten the entire section including the commented sentences and cited more papers on d^{13}C - CO_2 (e.g., Campeau et al., 2017) in L 500-515. Briefly summarized, we now compare the observed d^{13}C - CO_2 values with d^{13}C -DOC values measured at the forest stream and d^{13}C - CO_2 values in Swedish forest streams reported by Campeau et al. to emphasize that downstream riverine processes (outgassing and photosynthesis) constrain the downstream enrichment of ^{13}C in CO_2 along the lower reach. In the following paragraph, we compare our estimated d^{13}C -DIC values with literature information to explain further processes involved in downstream changes in DIC sources.

L447 “When the observed values of ^{13}C CO_2 .. it follows then that other riverine processes than bacterial degradation of plant (predominantly C_3 in the studied basin) and algal biomass might be involved in the upward shift of ^{13}C CO_2 .” The interpretation is wrong here: algal biomass must be considered as a fractionating process during primary production rather than an input of DIC from degradation of algae. The production of algal biomass will increase d^{13}C - CO_2 and ^{13}C -DIC and is probably responsible for the observed trend, maybe with water-air isotopic equilibration.

“assuming an enrichment of 10‰...” this enrichment may vary between what and what values? (I guess between 5 and 15‰). In fact because you have alkalinity, you should be able to calculate the DIC and the concentration of all DIC species as well as the isotopic composition of each species and the total DIC. See Zhang J., Quay P. D. and Wilbour D. O. (1995) Carbon isotope fractionation during gas–water exchange and dissolution of CO_2 . *Geochim. Cosmochim. Acta* 59, 107–114.

<Response> The estimated d^{13}C -DIC values based on Zhang et al. are now provided in L 522-525.



L463 what does “flanked” mean here?

<Response> Changed to “separated”.

L467 Weir will enhance CO₂ degassing and increase d¹³C-DIC

What is a “tributary-specific process”?

DOM from WWTP have old ¹⁴C signal because of a small contribution of fossil OM such as fuel and gasoline. However, these compounds represent a very marginal contribution to the total DOC. Thus the ¹⁴C signal as a tracer of source is hampered by this contamination. See Marwick et al. 2015

<Response> As mentioned, we have restricted the use of d¹⁴C-DOM to evaluate the wastewater effect on the lower reach DOM.

L473 why referring to “latitudinal” here? No latitude in figure 8

<Response> Corrected to “longitudinal”.

L478 “pulsating” or “pulse” refer to temporal dimension. Maybe you mean “hotspots” or “point source” here?

<Response> As explained before, we have used the term “pulse-like” or “pulsatile” to emphasize very strong, localized peaks, as used in the literature.

L483 “Down-river concentration decreases and ¹³C enrichment in CH₄ are consistent with the underway measurements conducted using a cavity ring-down spectroscopy(CRDS) along a 15 km reach of the North Creek estuary in Australia, which displayed CH₄ concentrations.... respectively (Maher et al., 2013).” Comparing river with an estuary is not necessarily appropriated because in estuaries, mixing with seawater occurs.

<Response> We cited this paper to compare the opposing patterns of CH₄ and its d¹³C, both of which have rarely been measured simultaneously in rivers. That’s why we had to keep the estuarine study. To make the point (CH₄ oxidation enriching ¹³C) clearer, another river study has been added and the related sentences have been rephrased, as follows:

The contrasting down-river trends of decreasing CH₄ concentrations and ¹³C enrichment are consistent with the longitudinal patterns of CH₄ concentration and its stable C isotope ratios measured simultaneously in large rivers such as the Amazon River (Sawakuchi et al., 2016) and estuaries (Maher et al., 2013). Sawakuchi et al. (2016) found the increases in δ¹³C_{CH₄} and the abundance of a genetic marker for methane-oxidizing bacteria (*pmoA*) in waters with lower CH₄ concentrations across the mainstem and tributaries of the Amazon. They used stable isotopic mass balances of CH₄ in the water column and estimated that 17–100% of CH₄ produced in the riverbed sediment may be oxidized during transport through water column to the atmosphere. During cruise expeditions employing a cavity ring-down spectroscope (CRDS) along a 15 km reach of the North Creek estuary in Australia, Maher et al. (2013) observed increasing δ¹³C values from –61.07 to –48.62‰ in contrast to large decreases in CH₄ concentrations from 74 to 2 nmol in the downstream direction. CH₄ oxidation was suggested as the primary driver of downstream increases in δ¹³C in the studied estuary with relatively low levels of anthropogenic pollution (Maher et al., 2013). The down-river patterns of CH₄ concentration and isotopic composition observed in this study also suggest that CH₄ oxidation in the well-mixed, shallow water, in combination with physical evasion to the atmosphere, may efficiently remove CH₄ derived from multiple sources including the urban tributaries enriched in CH₄ and riverbed sediments affected by the eutrophic water and frequent phytoplankton blooms.

L489. You did not measure d¹⁵N-N₂O so no need for this last sentence

<Response> The sentence has been removed.

Section 4.2 needs profound revision making clearer the question of ¹³C CO₂ versus ¹³C DIC and the story of old/young DOM

<Response> The entire section has been revised thoroughly. Regarding ¹³DIC, please refer to our earlier responses to the major comment on the same issue.

L493: “5. implications” of what? strange title for a last section



Mentioning the river continuum concept here is too late. In addition, one may say that your study does not show a “limited validity” of the concept, to the contrary, it suggest that anthropogenic actions might alter it, but the concept continues being valid if we consider these impact as artificial.

<Response> A more specific title (Implications for integrative concepts and future research) is used for this final discussion section emphasizing the necessity of novel concepts reflecting anthropogenic perturbations. The river continuum concept is described in Introduction. Please note that we have revised the text so that we emphasize, not “limited validity”, but “anthropogenic alterations”.

498 “Borges and Abril 2011” is for estuaries, not adapted here

<Response> Removed.

L499 “eutrophic reaches receiving wastewater” do you simply mean river sections receiving WW?

<Response> Rephrased (eutrophic waters polluted by wastewater)

L500 awkward sentence, please rephrase

<Response> As explained earlier, we have removed the sentence and instead reformulated the following sentences to focus more on the implications of our findings.

L506 “Reach-specific significance levels observed for the correlations between GHGs and DOC or its optical properties (Fig. 5; Table S4) imply that...” awkward sentence, please rephrase
the relative contributions of autochthonous production and external supplies of GHGs derived from WWTP effluents

L510, “pulse” refers to time, not to space

<Response> Now “peak” used.

L511 replace biodegradation by respiration

<Response> Replaced

L514 “gas-specific sets of significant correlations between gas concentrations and related water quality measurements shown for the lower reach” such sentence says basically nothing. What parameters, what gas?

<Response> Rephrased (The different significance levels established between the three GHGs and measured nutrients implied some different roles that those nutrients may play in the production of each gas in the eutrophic lower reach).

L517 algal productivity will NOT favour CO₂ production, to the contrary, it favours consumption

<Response> The sentence has been rephrased to describe the net effect of excess algal growth and subsequent development of anaerobic conditions (...enhanced phytoplankton growth and anaerobic metabolic activity in the eutrophic reach often plagued by phytoplankton blooms may result in the net positive effect on the production of both CO₂ and CH₄ despite the immediate negative effect of algal uptake on the surface water level of dissolved CO₂).

L522 “Urban tributary effects on metabolic processes in the eutrophic lower reach were also reflected in the lower-rech values of d13C in CO₂ and CH₄ resembling those measured in the tributaries”. This sentence is almost impossible to understand. What metabolic processes are you referring to?

<Response> This secondary information has been removed not to cause any unnecessary confusion.

L525 what “metabolic processes”?

Strange the term “hotspot” only appears here

<Response> New words have been selected to compare two different sources (the relative contributions of autochthonous production and external supplies of GHGs derived from WWTP effluents).

Figures: why are time courses of monthly monitoring shown only in Fig6 and not before in the MS?

<Response> Monthly data are presented in the beginning section (Tables 1 and S1 and Fig. S2). Because there is no clear temporal pattern (Fig. S2) and it is simply too complex to show the three gas measurements at six sites in a single figure, we opted for the tables and the summary figure.



Fig2 I could not see the “Dashed horizontal lines”. What is the yellow area?

<Response> An updated version has been included. Dashed lines indicating atmospheric equilibrium have been added and the yellow shade has been described in the figure caption.