Anonymous Referee #2

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The manuscript submitted by Marescaux et al. presents a technical upgrade of the pyNuts-Riverstrahler model and its application to simulate the organic and inorganic C balance of the Seine River for the period 2010-2013. The work is original and could be suitable for a journal like HESS. At its present state however, the manuscript is rather weak, in particular because of quite poor writing. I have also some concerns regarding model description and the evaluation and discussion of model results. Substantial revisions are required before I can recommend publication of this manuscript. Please,find my comments below.

A1. We thank the reviewer for his/her comments and advice on how to improve the manuscript. We have taken into account all of his advice. The manuscript has been already revised by a professional English native person. However another complete proofreading of the article has been done again after our own revision to make the paper stronger and in order to improve the English writing.

Major comments:

#1: Writing

The manuscript is poorly written. In particular the introduction and abstract are very weak, mainly because of bad English, but also with regard to structuring of the text and content-wise. It reads like someone wrote this in a great hurry with no time to read through the text again. I suggest that the authors put much effort into rewriting the manuscript. Results and discussion sections read fortunately better. Moreover, I would like to suggest that the authors try to get professional help for proofreading.

A2. We restructured the text and following your advice we sent the manuscript for professional proofreading.

#2: Alkalinity

I am a bit confused by your use of total alkalinity (TA). To my understanding, TA is the sum of carbonate alkalinity (sum of charges of carbonate and bicarbonate ions) and non-carbonate alkalinity (incl. charges of ammonium, phosphate, silicate, borate and organic ions).

You state that you would need only two parameters to implicitly define all elements of the carbonate system, which is basically correct. But you say you would use DIC and TA for that. You could use DIC and carbonate alkalinity to calculate CO2 concentrations, for instance. But using TA instead would lead to erroneous result because of the non-carbonate contributions to TA. I see that you are representing ammonium and phosphate in your model, and it seems like they are included in TA in the model. But It is not clear to me whether you subtract ammonium and phosphate from TA to calculate carbonate alkalinity, and use that to calculate CO2. Here, I would like to see a much more detailed description of how you actually calculate CO2 concentrations and pH, including equations. Also I would like to see an equation that defines TA in yourmodel, to see which ions are actually taken into account. Last but not least, I find it very strange that you report TA inµmol L-1, and not inµeq L-1 like it is normally done.

A3. We agree with the reviewer that total alkalinity TA is could be defined as:

$$TA \equiv 2[CO_3^{2-}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] + [organic/inorganic\ H^+ acceptors] - [H^+]$$

In our approach TA is defined by terrestrial boundary conditions (point and diffuse sources, see TA inputs Eq. 9). TA concentrations were measured in ground waters and in headwater streams. TA is then affected along the simulations by heterotrophic planktonic respiration of bacteria, zooplankton and benthic bacteria, nitrification, denitrification and photosynthesis (see Eq. 10) according to the stoichiometry defined in table 2.

TA and DIC are used to calculate the pH as proposed by Culberson (1980). The equations of Culberson were derived with the assumption that only bicarbonates, carbonates and borates contribute to TA. The author specifies that phosphate concentration < 3.10^{-6} mol/l and silicate at concentrations < 50.10^{-6} mol/l have negligible effect on the calculation of the pH (< ~0.001 pH). In addition, total dissolved boron concentration can generally be ignored in freshwaters (Emiroglu et al., 2010).

So in the carbonated freshwaters of the Seine River we make the assumption that for the pH calculation TA can be used as an approximation of CA. We added this remark in the supplementary material section S3.

Regarding the detailed equations for pH calculation, there are provided in the supplementary information “3.4”

Nevertheless, in this later section, we wrongly refer to carbonate alkalinity (CA) instead of Total Alkalinity (TA). This error probably misled the reviewer, making him/her think that we were recalculating the carbonate alkalinity based on the total alkalinity and ammonium + phosphate ions (which is not the case, we only use TA in our approach, as simplified for freshwater, see above).

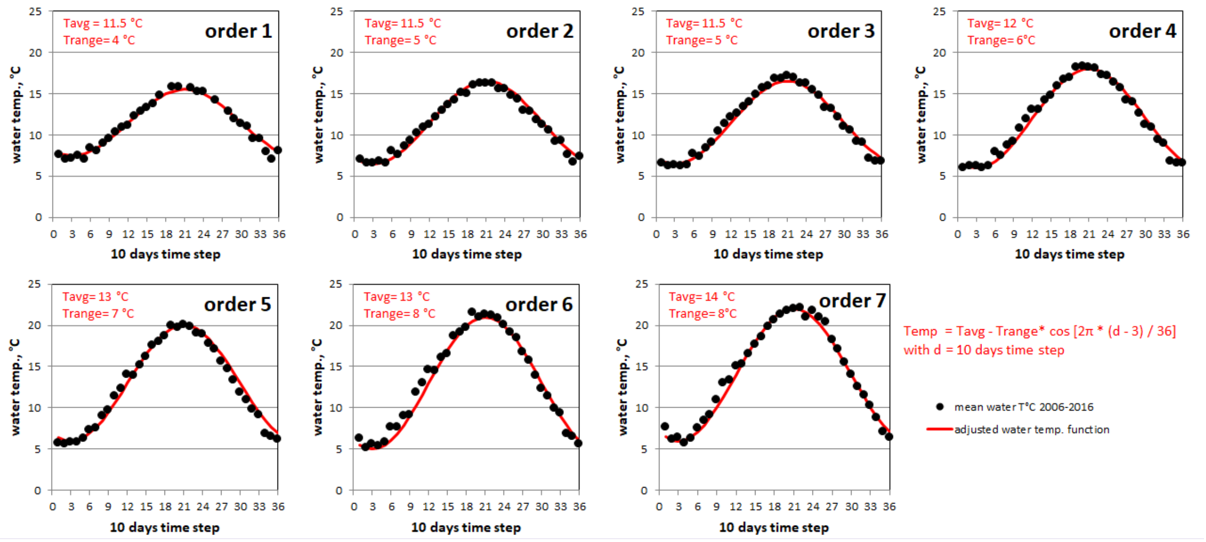
Regarding the reviewer remark about units used for alkalinity. In biogeochemistry modeling, total alkalinity used to be described in meq/L however more and more manuscripts described it now in µmol/L since chemical formula enable to make the conversion (among others: Borges, A. V. and Abril, G.: Carbon Dioxide and Methane Dynamics in Estuaries., 2011.; Regnier, P., Arndt, S., Goossens, N., Volta, C., Laruelle, G. G., Lauerwald, R. and Hartmann, J.: Modelling Estuarine Biogeochemical Dynamics: From the Local to the Global Scale, Aquat. Geochemistry, doi:10.1007/s10498-013-9218-3, 2013).

We decided to keep this unit.

#3: Water temperature

It is not clear to me in how far the effects of water temperature on water viscosity (impact on k) and solubility of CO2 (impact on pCO2 and emission flux) are taken into account by the model. The seasonality in water temperature could have an effect on the seasonality of CO2 concentrations, with a tendency for higher concentrations at lower temperatures. Here, I would like to see some clearer description in the method section, and maybe also some discussion in how far water temperatures could affect the weak performance of the model to reproduce the seasonality in CO2 concentrations, in particular in the higher stream orders (Fig. 6).

A4. At this stage the Riverstrahler model does not include a proper thermic model. A mean temperature function (reproducing seasonal variations) is provided for each stream order as boundary condition, as described in Billen et al 1994. We adjusted the parameters of this empirical temperature function for each Strahler order according to measurement available for the recent period. Results of this calibration for observed water temperature averaged by 10 decade over time period 2006-2016 is provided here after:



We can observe that the equations used enable a good representation of averaged water temperature variation for each Strahler order. Then, the weak performance of the model to reproduce the seasonality in CO_2 concentrations cannot be explained by the water temperature.

We added a sentence in the methodology :

“Water temperature was calculated according to an empirical relationship, adjusted on inter-annual averaged observations (2006—2016), and describes seasonal variation of water temperature in each Strahler order with a 10-days time step (see S2).” [L200-202]

The section 3.5 in SM3 describes in detail how temperature is taken into account to calculate *k*-value (Eq. 26 and 27).

Solubility is calculated according to Weiss (1974) and the reference is provided in section S3.6 table 1. We added a reference to this table in the manuscript:*”The different values of constants and parameters used in the inorganic carbon module are introduced in Table 1 of S3.6. The full inorganic carbon module is described in S3 (3.1 to 3.5).” [L262-264]*

We also modified the discussion section to better explain the possible factor limiting the performance of our model in the representation of CO_2 seasonality (temperature, hydrology, phytoplanktonic biomass etc.):
“The model showed a weak performance in representing CO_2 seasonality. Referring to a previous study (Marescaux et al., 2018b), pCO_2 seasonality in the Seine River resulted from a combination of water temperature and hydrology leading to an increase in pCO_2 and CO_2 evasion fluxes from winter to summer/autumn. The pyNuts-Riverstrahler model however has an accurate representation of these constraints and would not account for these discrepancies. Also, despite the fact that the biomass level of phytoplankton was consistent with the observations, the seasonal pattern was not satisfactory reproduced by the model. ” [L606-612]

#4 Uncertainty sources in the model vs. observation based estimates

When comparing simulations with observation based estimates, you should take into account more carefully that the uncertainties related to *k* or total river surface area can have a very different impacts.

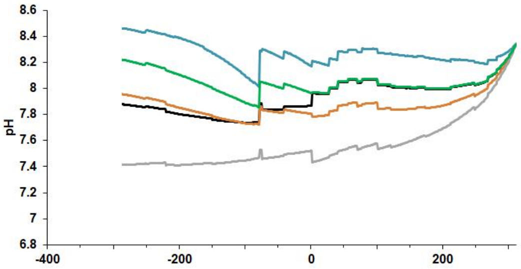
When you use observed (or calculated) CO2 concentrations (or better partial pressures) to estimate the total CO2 evasion flux, you will first calculate the water-air CO2 gradient and multiply that by the estimates of k and the total stream surface area. That Means that uncertainties related to the estimates of k and the total stream surface area will have a direct and proportional impact on the uncertainties related to the estimated total CO2 evasion flux. If you calculate the CO2 evasion rate per water surface area,only the uncertainty related to k matters, but not that of the total stream surface area.

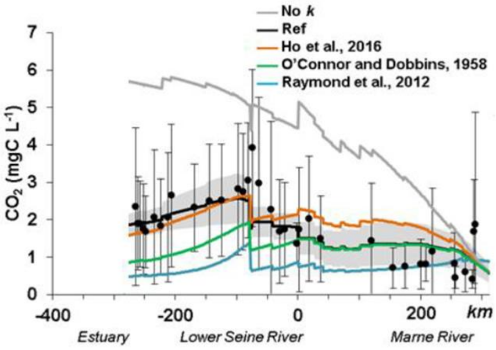
When you use a process based model that represents the different sources of CO2 to the stream network, the choice of gas exchange velocity will have a substantial impact on simulated CO2 concentrations (as you have shown in Figure 7), but not on the CO2 emission flux (when talking about annual fluxes). For instance, Lauerwald et al. 2017 GMD found for their model on the Amazon River that increasing or decreasing k by 50% does not lead to a significant change in simulated aquatic CO2 emissions.This is because over a large river network, aquatic CO2 emissions will be close to the total of CO2 inputs (external inputs plus instream net-heterotrophy). If a too small k is chosen, CO2 will concentrate in the water column until a higher water-atmosphere CO2 gradient is reached that allows for a total river CO2 emission that is close to the sum of the CO2 inputs minus instream production (i.e. too high simulated CO2 concentration in the water column). Similarly, when a too high k is chosen, the total CO2 emissions cannot exceed total CO2 inputs, and the too high k will be compensated by a too low water-atmosphere CO2 gradient (i.e. too low simulated CO2 concentration in the water column). In Figure 7, you have shown the impact of the choice of k on the simulated CO2 concentrations. I suggest that you also report the different CO2 emission fluxes that you simulated based on the different k-values. Based on that, you can maybe show that the choice of k does not have a too big impact on your IC balance calculation. But That leaves the impact of k on the CO2 concentration and pH. Could you maybe also show if and how the choice of k impacts the simulated pH?

A5. It seems important to us to repeat here that the *k*-values modification tests only concern the downstream parts of the network (order 6 or 7 greater than 100), i.e. a total of 367 km out of the 24,306 km of the Seine network.

We understand the reviewer's suggestion on the impact of different single *k*- values applied to an entire hydrosystem on IC balances. However, this work does not primarily aims at working on the sensitivity of *k*- values. We have chosen the formulation of Alin (2011) applicable to the great majority of the Seine network, and we only propose a second formulation for the last hundred kilometres to better take into account a specific feature of the basin Seine (the huge Seine Aval wastewater treatment plant).

The presence of a large wastewater treatment discharge (6 million Inahb. Eq) makes CO_2 concentrations very sensitive to formulation of *k*- value in this downstream sector (as shown in the figure 7). Such an impact on CO_2 concentrations, directly affects pH, showing abrupt decrease when CO_2 concentrations increase right after the WWTP release, and then an increase concomitant with the decreasing of CO_2 concentrations.





Nevertheless, we followed the reviewer's remarks and estimated the impact of these *k*-values variations in the most downstream parts (width >100m) on the total emission of the Seine network. For the 4 formulations tested (wide > 100m; formulations tested only on 1.5% of the total length of the drainage network), the variations in the IC balance is up to 6.18%.
Consequently, we have modified the manuscript in the following way:

- We better explain the test performed on the k formulation (restricted to order 6 and 7): *“Different values of k were explored specifically in the downstream part of the Seine river network (SO6 and SO7 where river width exceeds 100m) (Figure 7)”*[L464-466]

- better discuss the impact of changes in k with respect to the IC balance with reference to the work of Lauerwald et al. 2017

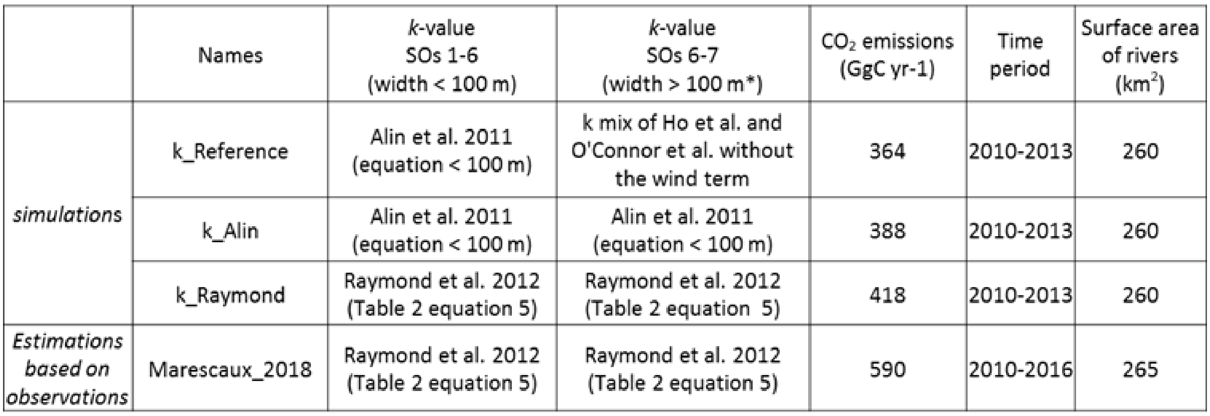
Thanks to the suggestion of the reviewer, we were interested in comparing our work with that of Lauerwald et al. (2017). As described by the reviewer, Lauerwald et al. (2017) found for their Amazon River model that a 50% increase or decrease in *k*-value does not result in a significant change in simulated aquatic CO$_2$ emissions.

New simulations were performed in order to compare the CO$_2$ emission estimates using different *k*-formulations. In addition to the simulation selected in our manuscript (here call k_Reference), we calculate emissions when the *k*-values were formulated as:

- Alin et al. (2011) (equation <100 m) (k_Alin) all along the drainage network

- Raymond et al. (2012) (Table 5 Eq. 2) (k_Raymond) all along the drainage network.

The results are presented in the table below. We also add CO_2 emissions estimated by Marescaux et al (2018a) based on observations.



	Names	*k*-value SOs 1-6 (width < 100 m)	*k*-value SOs 6-7 (width > 100 m*)	CO_2 emissions (GgC yr-1)	Time period	Surface area of rivers (km^2)
simulations	k_Reference	Alin et al. 2011 (equation < 100 m)	k mix of Ho et al. and O'Connor et al. without the wind term	364	2010-2013	260
	k_Alin	Alin et al. 2011 (equation < 100 m)	Alin et al. 2011 (equation < 100 m)	388	2010-2013	260
	k_Raymond	Raymond et al. 2012 (Table 2 equation 5)	Raymond et al. 2012 (Table 2 equation 5)	418	2010-2013	260
Estimations based on observations	Marescaux_2018	Raymond et al. 2012 (Table 2 equation 5)	Raymond et al. 2012 (Table 2 equation 5)	590	2010-2016	265

* SOs 6-7 > 100m represent 367 km out of the 24,306 km of the river network until its outlet at Poses (either 1.5 % only)

Comparison of the k_Reference and k_Alin simulations: A change in the k-value on rivers with a width > 100m (representing only 1.5% of the total length of the Seine River) led to a difference in CO_2 emissions of 28 GgC yr-1 (6.18%). Alin et al. (2011) (<100m) equation cannot be used on wide rivers and the formulation using Ho et al. (2016) and O'Connor and Dobbins (1958) allows a better description of the longitudinal profile of CO_2 concentrations along the Seine.

Comparison of the k_Reference, k_Alin and k_Raymond simulations: Our estimates of CO_2 emissions do not confirm the statement of Lauerwald et al. (2017) that large variations of k (+/- 50%) lead to a marginal change in simulated aquatic CO_2 emissions (around 4%). Indeed, compared with the k_Reference, the simulations according to k_Alin increase CO_2 emissions from the river system by 5.6% and the simulations according to k_Raymond et al. 2012 increase CO_2 emissions by 15%.

A main difference with the work of Lauerwald et al. (2017) is that we used a more accurate *k* calculated at each time step (10 days) and at every kilometer of the river network (according to water temp., velocity, depth). In addition, Lauerwald et al. (2017) carried out simulations on a natural network without the huge organic carbon load brought by wastewater treatment plants in an urbanized system that disrupts carbon dynamics, like the SAV-WWTP (10 million Inhab. Eq) in the downstream part of the Seine river.

Comparison of the simulations vs. Marescaux et al (2018)

Our estimates of simulated CO2 outgassing are lower than our previous estimate based on observation (Marescaux et al. 2018a). This difference is explained below:

- Marescaux et al (2018a) use k formulates according to Raymond et al. (2012) all along the seine drainage network (not adapted for large river section) and CO_2 emission value is most likely overestimated

- Comparison between the k_Reference, k_Alin and k_Raymond simulations demonstrated that CO_2 emissions from the Seine are sensitive to k-formulation (until 15% difference).

- Among the 3 simulations we have compared (k_Reference, k_Alin and k_Raymond), only the k_Reference simulation takes into account a k formulation adapted for large river sections.

For these reasons, we believe that our estimate of 364 ± 99 GgC/yr, using a process based model, is a more accurate value of CO_2 emission from the Seine River. We also acknowledge that this value might be slightly underestimated with respect to Figure 4 (of the present paper) which shows that our simulated CO_2 concentrations were overestimated for SO1 but underestimated for SO2 to SO7.

We reformulated the following section in “4.1. Evaluation of the model” :

“Future work with direct k measurements and/or a new representation of k-values in the model could help improve outgassing simulations with pyNuts-Riverstrahler. A test of different k formulations on high stream orders (width > 100 m) representing only 1.5% of the length of the river system showed an increase of the total CO_2 outgassing estimates by up to 6.2%. Our model is k sensitive and our estimates differs from the results of Lauerwald et al (2017), who observed that a large variation in k does not lead to a significant change in simulated aquatic CO_2 emissions. For the Seine River here, we indeed used a more accurate k-value calculated at each time step (10 days) and at every kilometers of the river network (according to water temperature, velocity, depth). In addition, a huge organic carbon load is brought by WWTPs in this Seine urbanized hydrosystem that disrupts carbon dynamics (e.g., WWTPs treating 12 million inhab. eq in the Parisian conurbation) in the downstream part of the Seine River, in contrast to simulations on a natural network (Lauerwald et al., 2017).” [L579-590]

General comments

Abstract

L16-38: The abstract needs better structuring. At the beginning in particular, after the first sentence, you should quickly explain the reasons of developing and applying a process-based model like you did. What are the specific research questions a model like this could help you with?

A7. We have reformulated the abstract

L20: Remove the commas around pyNuts-Riverstrahler

A8. Commas have been removed.

L21: Replace "implemented on" by "applied to" .

A9. We replaced implemented by “developed” as this version take into account a new CO_2 module.

L23: By “diffuse constraints”, do you mean “diffuse sources”? Please, clarify.

A10. Thanks we replaced diffuse constraints by diffuse sources

L24: Replace “characterised” by something like “assessed”.

A11. Done

L25: Remove “In average,”.

A12. Done

L26: WWTP has not been defined.

A13. Done

L18-27: Please, state over which period you have applied the model.

A14. The period is clearly stated in the right paragraph as:

“During the period studied (2010–2013) ...” [L28]

L33-38: The comparison to the 1990’s comes out of nowhere. It’s not clear why this comparison is made, what it implies, and where the data come from (are they also modelled in this study, or are they taken from another study?).

A15. We removed the mention to the 1990’s, which is not necessary here. This refers to previous studies, mentioned in the discussion.

introduction

L61-64: “as plant detritus, soil leaching or soil erosion and groundwater supply” This Doesn't make sense. You are mixing characteristics of the carbon and sources of carbon in the same list. Better write something like “as plant detritus, organic carbon bound to eroded soil particles and organic acids which are brought in by runoff and drainage from soils”.

A16. Thank you for this remark. We used your own sentence.

“*Organic carbon entering rivers can originate from terrestrial ecosystems as plant detritus, soil leaching or soil erosion and groundwater supply, but it can also be produced instream by photosynthesis or brought by dust particles (Prairie and Cole, 2009; Drake et al., 2017)*” [L61-64]

L64: Delete “sources”!

A17. We suppressed “sources”

L67-69: That doesn’t make any sense.

A18. We changed the sentence as:

“Beside air-water exchanges, carbon exchanges occur at the water–sediment interface, through biomineralization and/or burial (Regnier et al., 2013b).”[L67-68]

L106-108: That should go to conclusion and outlook.

A19. Indeed, the sentence has been removed from the introduction.

Materials and methods

L111: Degree signs needed.

A20. We changed decimal coordinates by unit in degree, minute, second.

L114-115: replace “annual water flow” by simply “water flow” because you report any-way the average flow over a longer period, and moreover, you report that flow in volume of water per second, and not per year.

A21. Indeed! We changed as recommended

L195-197: Please shortly list the characteristics which are represented.

A22. The sentence is now as follows :

“*Here, the Seine drainage network starts from headwater until it fluvial outlet (Poses) and was divided into 69 modeling units, including six axes (axis-object) and 63 upstream basins (basin-object). A map and a table introducing the main characteristics of the modeling units are provided in S2*” [L187-190]

We have also done a new map and a table describing the characteristics of the different modeling units. This description includes: type of modeling units (axis or basin); min and max Strahler orders; drained area; number of river stretches; cumulated length.

L216-219: You state that you could use two variables, DIC and TA, to calculate all other components of the carbonate system. Here I have to disagree. You could be doing this with DIC and carbonate alkalinity, but not with TA which is the sum of carbonate alkalinity and other sources of alkalinity including phosphate, silicate, ammonia and organic ions. But as you represent at least phosphate, ammonia and silicate, you can derive carbonate alkalinity from TA. Is that maybe what the model is doing? If yes, please clarify. But it would mean that you use more variables than just DIC and TA to calculate for instance CO2 concentrations.

A23. See our response A3, above in the #2 Alkalinity section :

In the section 3.4 concerning “pH calculation”, we wrongly refer to carbonate alkalinity (CA) instead of Total Alkalinity (TA). This error probably misled the reviewer, making him think that we were recalculating the carbonate alkalinity based on the total alkalinity and ammonium + phosphate ions (which is not the case, we only use TA in our approach, as simplified for freshwater, see above).

L229: “CO2 gradient concentrations” should be “CO2 concentration gradients”
A24. We changed the formulation accordingly.

L265-269: How have these studies refined that approach? Did they simply re-calibrate the annual average concentration? Are these average concentrations adapted for different land use types, soil types, etc.? Or do you use only one average concentration per nutrient species which you apply everywhere? Please, clarify.

A25. These studies helped refining the approach through new determination of parameters of the kinetics equations, but also using more detailed spatially explicit databases describing for example: lithology, land use, N surplus and the fraction leached according to agricultural statistics.
An average concentration is calculated for each nutrient species at the scale of each modeling unit, taking into account land use, lithology etc. Methodology for calculating these nutrient diffuse sources is specific for each nutrient and described in the literature quoted. We here only detailed the methodology for OC and IC species.

We modify the paragraph to make it clearer:

“Diffuse sources are calculated at the scale of each modeling units, based on several spatially explicit databases describing natural and anthropogenic constraints on the Seine River basin. Diffuse sources are taken into account by assigning a yearly mean concentration of carbon and nutrients to subsurface and groundwater flow components, respectively.” [L267-270]

L278-281: Are these degradability classes defined somewhere? What is the basic turn-over time or decomposition rate for each class under some sort of standard condition (which needs to be defined)?

A26. These degradability classes are described in degradability classes in the book chapter by Billen & Servais (1989). Modélisation des processus de dégradation bactérienne de la matière organique en milieu aquatiques. In : Micro-organismes dans les écosystèmes océaniques (M. Bianchi, Ed), Masson, Paris, page (219-245), and other following papers (e.g. Servais P., Barillier A. & Garnier J. (1995). Determination of the biodegradable fraction of dissolved and particulate organic carbon. Annls Limnol. 31: 75-80).

Here, the fraction of biodegradability were further determined for WWTP effluents, due to the change in treatments, and in new compartments of the hydrosystem (groundwater and small upstream stream).

Reference to Billen & Servais (1989) was added to the text.

For the decomposition rater (turn-over), see our answer just after.

L291-292: Here you should clarify if these degradability classes have the same turnover rates as those for DOC, or if they are defined differently. Otherwise, this statement might be confusing.

A27. The fractions of degradability are taken the same for POC and DOC, but the representation of their degradation is different, and parameter of the RIVE model could be found in *(Garnier et al., 2002).*

This precision has been brought:

"The kinetics for POC and DOC hydrolysis and parameters however are different (Billen and Servais, 1989; Garnier et al., 2002)." [L299-300]

L293-297: Do you really mean TA here? Or maybe carbonate alkalinity? Note that phosphate, ammonia, silicate and organic ions count into TA.

A28. Please refer to our detailed answer about the use of TA in our modeling approach (see **A3**).

L299: You should write mg CO2-C L-1 instead of mg C-CO2 L-1. Figure 3: How can alkalinity be reported in µmol L-1? Do you meanµeq L-1? Also, you should report DIC inµmol L-1 to be consistent, even if you report alkalinity inµeq L-1 (which you definitely should!).
A29. As suggested, we modified the 'mg C-CO_2-C L^{-1}' in 'mg C L^{-1}'.

Alkalinity can be report in µmol L^{-1} by dividing the atomic weights of elements by their charges. It is becoming more and more common in to work in µmol L^{-1} (see **A2**).

All our biogeochemical processes are in mgC L^{-1}, so we decided to keep CO_2 and DIC in mgC L^{-1} to compare them more easily.

L339-340: Could you please give the implied average concentration of free dissolved CO2 for these effluents?

A30. The implied average concentration of free dissolved CO_2 is 12 mgC L^{-1}.

Alshboul et al. (2016) measured CO2 concentrations in WWTP effluents up to 8.5 mgC L^{-1} however these measurements were in German rivers (mean DIC of 20 mgC L^{-1}) less carbonated than the Seine River.

L368-370: Did you have additional hydrochemical data available to correct for at least phosphate and ammonia contributions to TA?

A31. We do have hydrochemical data for phosphates and ammonia, but according to our use of TA in our modeling approach (see **A3**), we do not use them for correcting TA.

Results

L420: What do you mean by "good levels"?

A32. "Good level" means right order of magnitude, which is not trivial, as the model is not calibrated, the value of the parameters being determined independently. However, the wording had been changed as follows:

"*Upstream, within Paris, and downstream of Paris, the model provides simulations in the right order of magnitude of the observed CO_2, DIC, TA and pH values, despite the fact that TA was underestimated in the two upstream stations selected for all seasons (Figure 6). DIC and TA simulations followed the observed seasonal patterns with a depletion of concentrations occurring in summer/autumn related to low-flow support by the reservoirs. Indeed, reservoirs showed lower TA and DIC concentrations than rivers (Table 3). In addition to the intra-/inter-stream order variabilities of CO_2 (Figure 4), CO_2 concentrations showed a wide spread in values over the year (Figure 6). Although simulated CO_2 concentrations fitted rather well with the level of the observations (NRMSE = 15%), the model tended to overestimate the winter values upstream and within Paris (Figure 6, left).*" [L428-437]

Figure 6: For the river network within and upstream of Paris, the model shows a very weak performance with regard to seasonality in CO2 concentrations and pH. There appears to be a systematic underestimation of TA throughout time and space. That Would have to be discussed. Moreover, I wonder if a simple recalibration could help to simply solve this problem.

A33. The performance of the model has been better described (see the paragraph **A32**).

Recalibration is not the philosophy of the approach. Indeed the principle of the modelling approach is to formalise mathematically the major processes (kinetics equations) from experiments (our own or those from literature) and to determine their parameters independently from the model simulations. Once kinetics and parameters have been a priori fixed on the basis of the current knowledge, the simulations are compared with the observations. A disagreement between simulations and observations may question either the processes/parameters as represented in the model or/and the quality of the data (in terms of limit conditions and/or observations for validation). Perspectives for improvement are provided in the discussion at several places.

L459-462: Raymond et al. 2012 trained their empirical model for k on relatively small rivers (defined by discharge). As you have discussed before, the equations by Alin et al. may only be valid for a stream width up to 100 m. Also Raymond et al.'s equation is only valid up to a certain discharge. Following that same logic, you cannot apply their equations here. These issues should be discussed here.
A34. Indeed, the Raymond et al. equation is not pertinent in high orders; however we decided to keep the formulation for comparison because such *k* formulation has been widely used in previous research works. Especially, IC budget for the Seine budget provided by Marescaux et al. (2018a) are based on Raymond et al. equation. Keeping a test-simulation (on order 6 and 7) using this equation, allows us to better discuss the differences obtained between this work and previous research work.

But, we totally agree that except for such a comparison, this *k*-value should not be used for high stream orders.

L463-466: As discussed in Alin et al., in wider rivers, wind stress might become the dominant control of k. It seems to be potentially problematic to just omit the term related to wind speed in the equation by Ho et al.. I would expect that the underestimation of k might arise from that. You should quantify that potential bias for a realistic range of wind speed, and discuss why you think that this bias would be negligible. Wouldn't it be better to simply assume an average wind speed? Or you could simply use average monthly wind speed values per stream order from e.g. http://worldclim.org/version2.

A35. Indeed, the wind may have a big influence on *k*-value. We only state again that the equation by Ho et al. and O'Connor et al. are only used for SO6 and SO7 and where width > 100m (i.e., less than 400 km of river). Averaging wind by order does not appear relevant here. Also, calculating a mean wind along the main stem of the Seine River seems difficult to use because some sections of the Seine River are highly urbanized and some others are very open. So according to our expertise, implementation of the wind will be considered in our future work, which implies new development in the model. But we thank the reviewer for the database reference that should be useful in the future.

Our previous answer **A5** clearly explains that changing k formulation in these sectors (less than 1.5% of the cumulative length of the Seine network) will lead to a maximum of 5% of change in CO_2 emissions from the Seine River.

Consequently, we agree that in these downstream sectors, omitting wind leads to an underestimation of the k, but we also add that this underestimation has very limited impact on our CO_2 emissions balance.

L469: Here section 4.1 follows after section 3.1.4.. I have the strong feeling that some sections have gone missing here. But I hope it's just some stupid mistake with numbering. I will simply assume that this is still the results section, and discussion section starts in L550.
A36. Sorry, this is indeed a stupid mistake in numbering. Section 4.1 and 4.2 have become 3.2 and 3.3

L492-493: I assume that "ventilation" means CO2 emissions from water surface. Anyway, you should use a more consistent terminology to not confuse the reader.
A37. Thank you. We changed ventilation by CO_2 emissions, in Table 4 included.

Discussion

L554-555: Öquist et al. found that for which river? In how far is that river comparable with the Seine river?

A38. We think that this pattern can be applied to the Seine, because a previous experiment was done for N_2O and showed a similar result (see Garnier et al. 2099, AEE, Fig 5)
We have added this sentence:
"*Such a CO_2 emission pattern can be applied to the Seine, as a similar result was found for N_2O (Garnier et al., 2009)*" [L564-566]

L562-569: You could still calculate the average wind speed per stream order and simply use that in your equation. Also, you could simply adapt k empirically in a way that optimizes the fit between observed and modelled CO2 concentrations.
A39. See the above comment on the wind (**A35**).

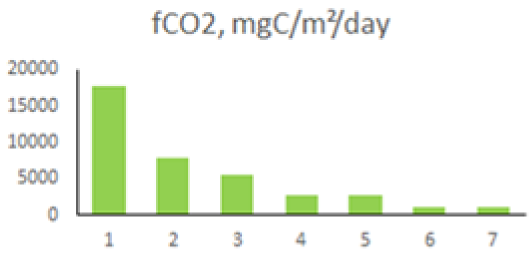
We slightly modify the sentence to clarify that taking wind speed into account in Ho et al. equation could potentially improve the validation of CO_2 concentrations (decrease NRMSE) in these downstream sectors (only).

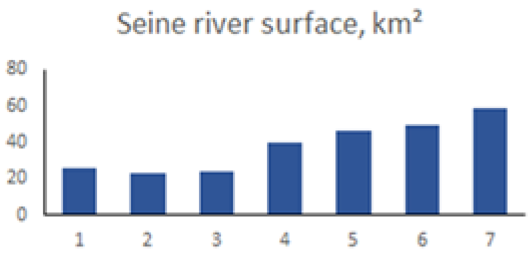
"Regarding gas transfer velocity values, an equation for large rivers with no tidal influence using wind speed could be more appropriate (Alin et al., 2011) and could decrease NRMSE in these downstream sections of the river." [L572-574]

L589-594: Temporal dynamics in CO2 are likely the strongest control on the temporal dynamics of pH. As long as you don't get those right, you won't be able to reproduce pH, no matter what formulation you will use.
A40. We agree with your comments and have deleted the sentence.

L610-618: Here you should mention how much SO1 contributes to the total CO2 emission and to the total stream surface area of the Seine river network. Then you could give the average CO2 emission rate per stream surface area for SO2-SO7 only. Like This, you could support your statement with numbers.

A41. Thanks for the suggestion. SO1 represents 9.6% of the Seine River surface area and contributes to 40% of the total CO_2 emissions.





We have Add the following sentence:

"The mapping of CO_2 outgassing in the Seine basin clearly showed these spatial trends, with smaller streams releasing more CO_2 than median and larger rivers (see Figure 8). Indeed, first-order streams of the Seine River represents 9.6% of the Seine surface area and contributed to 40% of the total CO_2 emissions by the river network." [L651-655]

L684-686: Your results do not support this conclusion. In particular the performance with regard to reproducing observed CO2 concentrations is quite bad, and a decent discussion on why that is missing so far.

A42. We understand your remark and we rephrased the conclusions.

However, taking into account that the same biogeochemical model is used from headwaters to the outlet of the river, without tuning the parameters at the scale of the whole basin, it is satisfying to obtain simulation in the correct range of the observed values. We agree that our results call for more work, both in refining the diffuse and point sources, improving the processes taken into account in the model, etc.