# Modeling inorganic carbon dynamics in the Seine River continuum in France

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- Answers to the reviewers
- List of all relevant changes
- Revised manuscript with track changes

## 1. Response to Referee #1

Received and published: 13 January 2020

This paper described a biogeochemical model incorporating inorganic carbon cycle and applied the model to the Seine River system. The model was built based on an existing biogeochemical model and the model structure and setup have been sufficiently described. The results from current study help to fill up the gaps in understanding the contribution of inland waters to the global carbon cycle. However, the model performance is not very convincing. There had been a few other models able to simulate inorganic carbon in rivers and have not been discussed. In summary, the manuscript has potential to be improved and I would like to suggest the authors to consider:

1. improving the model performance presentation (see specific comments below);

2. the discussion of current findings is too site-specific; I would suggest to expand the discussion to a more general sense, e.g. how the inorganic carbon system in Seine compared to other inland water systems? What are the meaning of current findings to estimating the roles of rivers in local and global carbon cycle? etc.

3. Also, the text writing in the introduction and discussion need to be polished. I list a few issues in the specific comments below but encourage the authors to go through the text and improve the writing in general.

We thank the reviewer for his comments and advice on how to improve the manuscript, especially the model performance presentation, where the text has significantly evolved.

We now discuss more generally the merits of a modelling approach in comparison with other measurement based CO2 emission estimates. Also, we have tried to replace our finding for the Seine River system to a broader context of aquatic CO2 evasion from temperate and/or human impacted river systems, providing comparative values.

We submitted the revised manuscript for a complete proofreading in order to improve the English writing.

Specific comments:

Line 37-38: some words are missing from this sentence. ‘Outgassing was the most important {carbon sink/inorganic carbon process}?

**A1.** We modify the sentence as: “*The most significant outgassing was in lower order streams while peaks were simulated downstream of the major WWTP effluent.*” [L31-32]

’Line 69-71: This statement seems controversial to some other findings that eutrophic system usually contains richer organic matters and pCO2 (e.g. Borges and Abril, carbon dioxide and methane dynamics in estuaries, DOI: 10.1016/B978-0-12-374711-2.00504-0). Can you please explain more about this statement?

**A2.** Thank you for your comment. Indeed, we wanted to highlight that some ecosystems can be a source and other a sink of $CO_2$. We now modify and precise that the statement is for lentic eutrophic systems and we change ‘can be’ by ‘may be’.

*“As a whole, oligo- and mesotrophic lotic hydrosystems generally act as a source of carbon while surface water of lentic eutrophic systems may be undersaturated with respect to atmospheric $pCO_2$ (Prairie and Cole, 2009; Xu et al., 2019; Yang at al., 2019).” [L68-71]*

Line 69-71: The Xu et al. 2019 reference is missing;

**A3.** Thanks, we added the references:

- Xu, Y. J., Xu, Z. and Yang, R.: Rapid daily change in surface water $pCO_2$ and $CO_2$ evasion: A case study in a subtropical eutrophic lake in Southern USA, J. Hydrol., doi:10.1016/j.jhydrol.2019.01.016, 2019. https://www.sciencedirect.com/science/article/pii/S0022169419300599?via%3Dihub
- Yang, R., Xu, Z., Liu, S. and Xu, Y. J.: Daily pCO2 and CO2 flux variations in a subtropical mesotrophic shallow lake, Water Res., doi:10.1016/j.watres.2019.01.012, 2019. https://www.sciencedirect.com/science/article/abs/pii/S0043135419300466?via%3Dihub

Line 72-76: This statement needs to be treated carefully. Other methods, such isotope surveys, can also be used to investigate the fate of carbon in aquatic systems.

**A4.** Thanks, we agree with your comment and modify the sentence as:

*“Direct measurements of $pCO_2$ or isotopic surveys (as realized by Dubois et al. 2010 in the Mississippi River) along the drainage network are still too scarce to accurately support temporal and spatial analyses of $CO_2$ variability. While calculations from pH, temperature and alkalinity may help reconstruct spatiotemporal patterns of $CO_2$ dynamics (Marescaux et al., 2018b), modeling tools can predict the fate of carbon in whole aquatic systems.” [L72-76]*

Line 85-90: A few early papers had reported models including the inorganic carbon cycle and pCO2 exchange but have not been mentioned here. Such as the CONTRASTE model (Vanderborght et al 2002, Application of a transport-reaction model to the estimation of biogas fluxes in the Scheldt estuary, Biogeochemistry 59: 207-237), RTM model (Regnier et al 2013, modelling estuarine biogeochemical dynamics: from the local to the global scale, Aquat Geochem 19: 591-626); How is the current model compared to these models?

**A5.** The CONTRASTE and the RTM models are estuarine models and we initially refer only to river models, but we added now these two references .
However, the main differences between the formalisms of pyNuts-Riverstrahler (a river model) and these estuarine models lie in the description of the phytoplankton groups, organic carbon matter and benthic activities which are more detailed in pyNuts-Riverstrahler, while these estuarine models described the shape of the estuary and take into account the tides, the salinity and the wind.

Estuaries are highly reactive systems from a biogeochemical point of view, also with proportionally greater gas exchanges at the water-atmosphere interface because of the river section enlargement in these area. In the case of the Seine, it is worth to mention to the reviewer that we recently carried out an integrated modelling approaches, by coupling the Riverstrahler model to the C-GEM estuarine model (developed by the same team of the RTM and CONTRASTE models), which made it possible to specify the respective ecological functioning and contributions of the fluvial and estuarine parts in the organic and inorganic carbon budgets.

Laruelle, G. G., Marescaux, A., Gendre, R. Le, Garnier, J., Rabouille, C. and Thieu, V., Carbon dynamics along the Seine River network: Insight from a coupled estuarine/river modeling approach, Front. Mar. Sci., doi:10.3389/fmars.2019.00216, 2019

Line 91-92: This individual sentence as one paragraph is not reading well. Can be merged with next paragraphs.

**A6.** Thanks, we merged the two sentences as:

*"The Seine River (northwestern France) has long been studied using the biogeochemical riverine Riverstrahler model (Billen et al., 1994; Garnier et al., 1995), a generic model of water quality and biogeochemical functioning of large river systems." [L92-94]*

Line 111: unit of the north and east coordinates?
**A7.** Thanks we added the coordinates:

Situated in northwestern France within (decimal degrees) 46.95° –50.01° north and 0.11° – 4.00° east.

Line 228-230: the gas transfer velocity only affect the exchange rate, not the change direction of $pCO_2$ (and therefore DIC).

**A8.** We changed the sentence to make things clearer:

*“The exchange of $CO_2$ between the water surface and the atmosphere depends, respectively, on the gas transfer velocity (k-value) and on the sign of the $CO_2$ concentration gradient at the water surface–atmosphere interface (S3.5). Change in $pCO_2$ will in turn affect DIC concentrations (see Table 2, Eq. 1).”* [L231-234]”

Line 383-384: why only 4 years simulated but NRMSE were performed on inter-annual variations per decade, instead of 2010-2013? Also, normalized against mean observational data instead of inter-annual variations is more representative.

**A9.** We performed NRMSE analysis on inter-annual variations per decade because the aim was to also evaluate the ability of the model to represent the seasonal trends. Because of the small amount of observations available for each year and for each 10-days period (especially for DIC concentrations), we preferred to average the available inter-annual values per 10-days period (which is actually the resolution of the RIVERSTRAHLER model). We choose to normalize the RMSE by the inter-annual variation because the mean of observations are not representative of the observations that can take extreme values.

Line 402-404: as CO2 concentrations are related to DIC and TA, it would be better if you show the comparisons of observed and modelled DIC/TA along with the CO2 concentrations.

**A10.** We fully agree. We do not have enough observation data especially in the upstream part of the Seine drainage network to propose similar analysis for DIC and TA by stream order. However, at the section “1.3.Seasonal variations”, we selected 4 stations with enough data available in an upstream-downstream gradient to jointly analyze the variations of observed CO2, TA and DIC and compare them to the model.

Line 517-518: can’t find CO2 outgassing in figure 9?

**A11.** We corrected the typo : ‘figure 8’

Figure 6: why there are two dark lines in the water flow of the outlet of the basin? Also, as the model timeframe includes dry and wet years, it is better to show the results year to year but not averaged from 4 simulated years;

**A12.** there is an error in the plot. One of the two black lines is in fact the link between the average observation points and should not have to be drawn.

Because of the lack of observation data (especially for DIC and CO2), we decided to provide average values and to assess the model performance using simulation averaged on this 4-years timeframe.

Also, looking at the standard deviations of observed discharge values, it could be seen that hydrological regimes were not so different over the 2010-2013 timeframe (e.g. drier in summer 2011). This is mostly explained by the water regulation by reservoirs occurring in the upstream part of the river basin. Impact of this flow regulation is evident upstream of Paris, then fades downstream and this is clearly visible when looking at the increase of observed discharges standard deviations from upstream Paris to Poses

Line 583-589: this sentence needs to be re-organized.

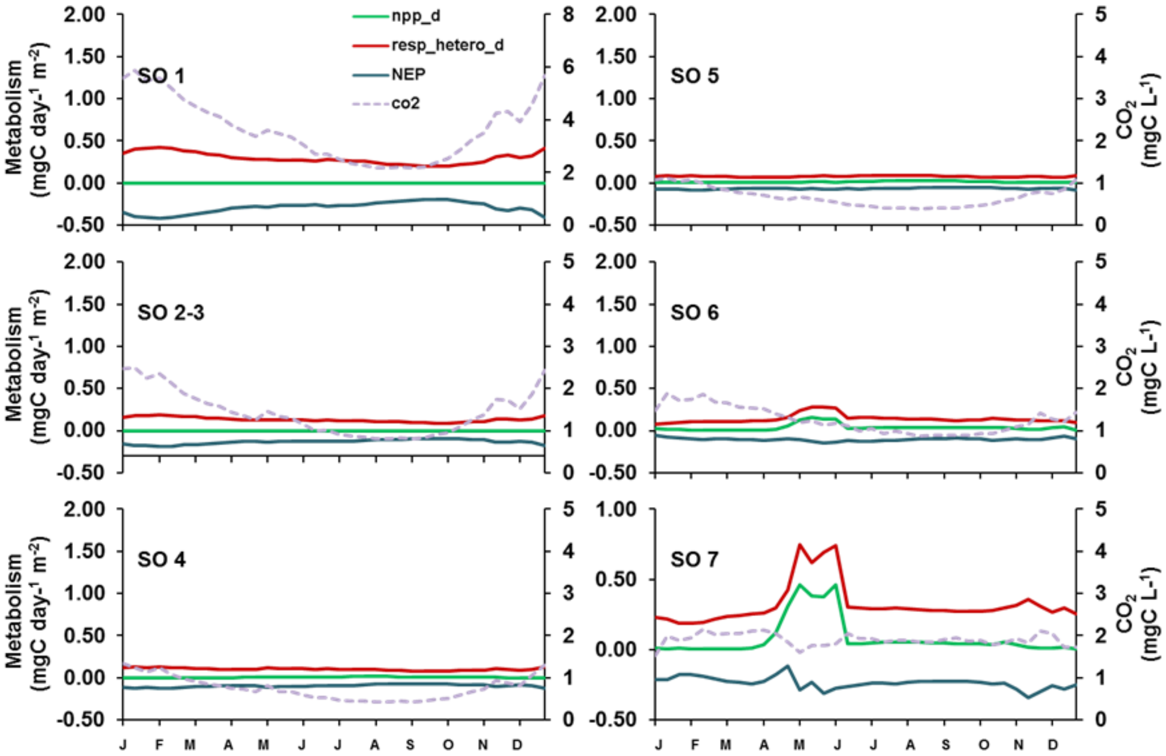
**A13.** The whole paragraph has been reorganised:

*"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. However, it is worth mentioning that phytoplankton parameters in RIVE were determined through laboratory experiments at a time when the amplitude of algal blooms was much higher than at present (up to 4.5-6 mgC $L^{-1}$ i.e., chlorophyll a reaching 150 µgChla $L^{-1}$, Garnier et al., 1995). Indeed, the implementation of the European Water Framework Directive in the 2000s with enhancement of treatments in WWTPs greatly improved water quality (Romero et al., 2016). New laboratory experiments for possibly taking into account additional phytoplankton groups or species in these new trophic conditions and/or mixing stochastic and mechanistic modeling are required to better represent phytoplankton temporal dynamics in the model. In addition, the observed incident light, instead of the empirical relationship used, would improve the early winter bloom, newly occurring in a changing environment" [L611-622].*

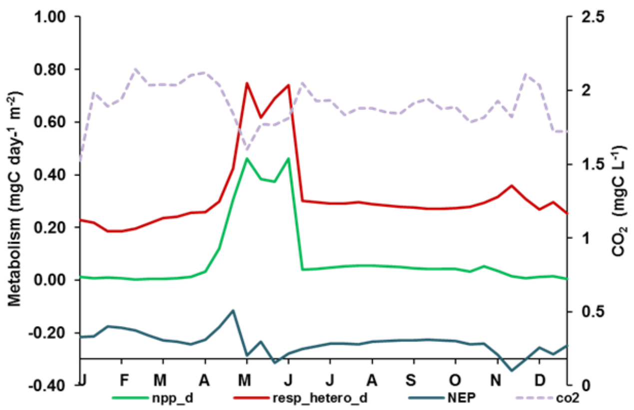
Line 624: left bracket is missing in citation;
**A14.** Thanks, we added it.

Section 4.3: is there a relationship between the river eutrophic state and the metabolism activity, and CO2 outgassing?

**A15.** Eutrophic state of the river indeed changes the metabolism activity (see Garnier & Billen, 2007). We observe that the influence of the metabolism activities on the $CO_2$ outgassing is low. Indeed, in the carbonated Seine River, the IC originating from groundwater supports the $CO_2$ outgassing along the network (figure 8). Nevertheless, instream metabolism activities produce or consume $CO_2$. In high stream Strahler orders, river metabolism activities (as NPP and heterotrophic respiration) influence seasonal variations of $CO_2$ concentrations (see figures below).




NB: SO7 with a scale change for $CO_2$:




We added this remark in the manuscript:

*"We observe that the influence of the metabolism activities on the $CO_2$ outgassing is low. Indeed, in the carbonated Seine River, the IC originating from groundwater supports the $CO_2$ outgassing along the network (Figure 8). Nevertheless, instream metabolism activities produce or consume $CO_2$."* [L684-687]

## 2. Response to Referee #2

Received and published: 14 January 2020

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. We submitted the revised manuscript for a complete proofreading 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).

*Additional answers of A3:*

We completed new simulations and recalculated the CO2 emissions to take into account the remarks on the TA. Indeed, we removed ammonium and phosphate from the total alkalinity when calculating the pH.

| Scenario | $CO_2$ emissions (See Table 4) |
|---|---|
| | *$kgC\ km^{-2}\ yr^{-1}$* |
| Reference (see Table 4 of the MS) | 5619 |
| Using (CA = Total alkalinity – ammonium – phosphate) to calculate the pH | 5733 |

The new simulation showed that taking into account TA or "TA-ammonium -phosphate" to calculate pH (Culberson, 1980) led to a difference in CO2 emissions of less than 2%. This small difference is related to the fact that the Seine basin is a highly carbonated basin where carbonate alkalinity can be approximated by total alkalinity.

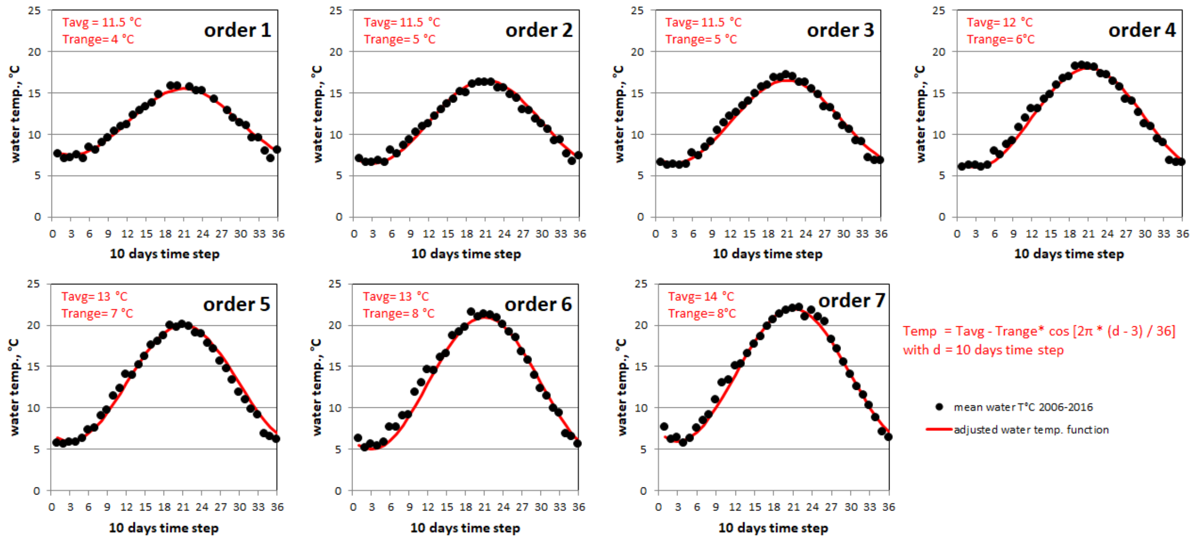
Regarding the reviewer remark about units used for alkalinity. In biogeochemistry modeling, total alkalinity used to be described in meq/L however more and more manuscripts described it now in µmol/L since chemical formula enable to make the conversion (among others: Borges, A. V. and Abril, G.: Carbon 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.

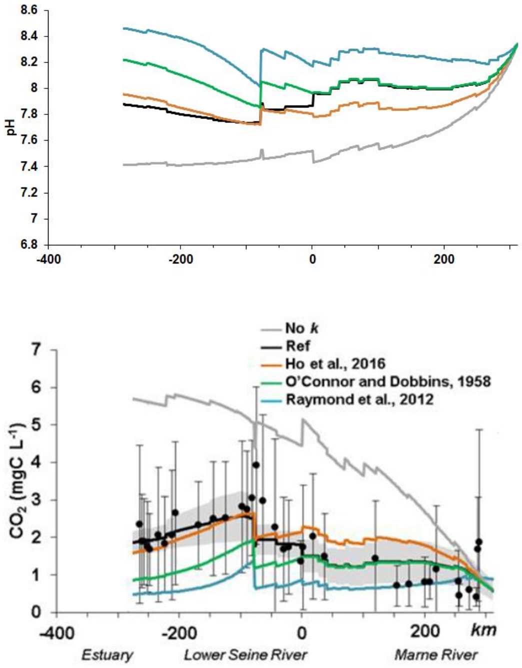
When you use observed (or calculated) CO2 concentrations (or better partial pressures) to estimate the total CO2 evasion flux, you will first calculate the water-air CO2 gradient and multiply that by the estimates of k and the total stream surface area. That Means that uncertainties related to the estimates 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 <u>367 km out of the 24,306 km</u> 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.** Yes it was diffuse sources but we reformulated the abstract.

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 now clearly stated as:
*"For the period studied (2010–2013) ..." [L22 and L32]*

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).

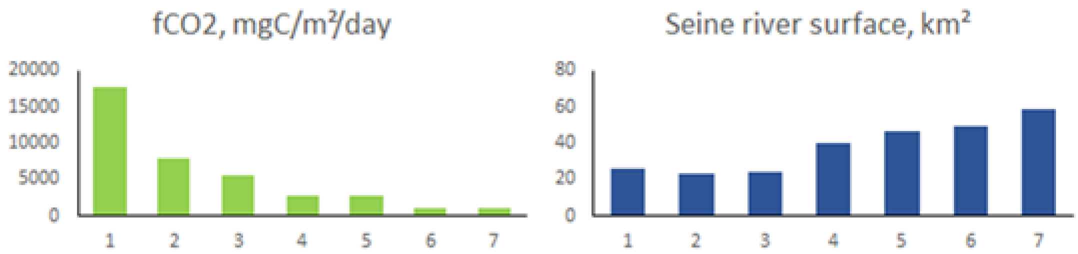
*"Regarding gas transfer velocity values, an equation for large rivers with no tidal influence using wind speed could be more appropriate (Alin et al., 2011) and could decrease NRMSE in these downstream sections of the river."* [L572-574]

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.

## 3. Response to Referee #3

**Modeling inorganic carbon dynamics in the Seine River continuum in France by Marescaux et al.**

The authors present a modeling effort of inorganic carbon dynamics in the Seine River. It is done in the pyNuts-Riverstrahler model. With the new module, the outgassing of CO2 is calculated for the time period 2010-2013. Also a budget for inorganic and organic carbon including alkalinity for the whole Seine river basin is presented. The manuscript is well structured. The model performance from small orders to higher orders is reasonable at first sight. However, considering how sensitive the balance between alkalinity – CO2 – pH is, the model performance from small orders to higher orders is impressive. I recommend to publish this paper after major revision.

**Specific comments**

- There are many well tested and well described inorganic carbon modules readily available (see for a review: Orr et al., 2015, https://www.biogeosciences.net/12/1483/2015/bg-12-1483-2015.pdf). Is there a specific reason to develop an own implementation for pyNuts-riverstrahler?

**A0.** This excellent review by Orr et al. 2015 is based on ten packages that aim at calculating ocean carbonate chemistry. The aim of our own implementation was to propose a process-based approach of the modeling $CO_2$ in relationship with the aquatic cycling of nutrients and organic matter, and taking into account the development of micro-organisms (phytoplankton, zooplankton, bacteria) all involved in the aquatic dynamics of $CO_2$ concentrations in the river. A second aim was to route such an inorganic module in an existing drainage network model to calculate $CO_2$ emissions by river.

- In paragraph a kind of sensitivity analyses is presented for the gas transfer velocity. It is not clear to me, why this parameter is chosen. I miss a more extended model sensitivity analyses to determine which input parameters are sensitive to CO2 emissions or carbon export to the sea. Which model parameter contributes most to variability of CO2 emissions?

**A0.** We realized that the tests carried out on the formulation of the k-coefficients (Figure 7), which concern only a very limited downstream part of the Seine system, were not presented in sufficient detail. We have therefore revised the text to better explain these tests on k-formulation, and their impact on total CO2 emissions. see Lines [L463-466], [L580-587] and [L635-639].

We have also carried out additional simulations evaluating the sensitivity of $CO_2$ emissions to different formulations of *k*-values applied to the entire Seine river system. These tests are presented in detail in our A32 answer. In particular, they have allowed a better discussion of the total emissions values obtained, with respect to previous work on the Seine (Marescaux et al., 2018a), and finally strengthen the value of 364 +/- 99 GgC/yr put forward.

**Technical corrections main text**

1. Double equation numbers. Equation numbers in SI and in main article overlap. Please give them different names.

**A1.** Equations in supplementary material are now numbered with S- prefix to prevent overlap.

2. Line 46: The first highlight of a successful implementation. I was surprised by this highlight. There is no word on the implementation details in this article. I think the model itself is never a highlight. The model is a tool to show some of your findings (as you do in this article). So remove.

**A2.** This highlight has been removed and replaced by:

*"$CO_2$ emission from the Seine River was estimated at 364 ± 99 GgC $yr^{-1}$ with the Riverstrahler model." [L46-47]*

3. Line 101: Again purpose of this study is an implementation. I don't think this journal is suited for this purpose.

**A3.** The sentence has been modified as follows:

*"The purpose of the present study was to quantify the sources, transformations, sinks and gaseous emissions of inorganic carbon using the Riverstrahler modelling approach (Billen et al., 1994; Garnier et al., 2002; Thieu et al., 2009)." [L102-104]*

4. Line 102: "pyNuts modeling environment" I would like to have a reference to this. To me it is not clear what the difference is between RiverStrahler, RIVE pyNuts-Riverstrahler. All names are used here. Please elaborate this.

**A4.** We do not refer to "pyNuts modeling environment" in this section anymore. Please refer to our previous answer see A3.

For the differences between RIVE, Riverstrahler and pyNuts modeling environment is now better explained in section 2.2, with adequate references quoted in the text.

For the reviewer information :

- The **RIVE model** aims at representing the biogeochemical functioning of aquatic systems, by simulating concentrations of oxygen, carbon and nutrients (multiple forms) in relationship with the development of phytoplankton, zooplankton and bacteria. The model also takes into account benthic variables.
- The **Riverstrahler approach** is based a lagrangian description of the circulation of waterbodies within the drainage network. It allows the calculation of geographical and seasonal variations (with a 10 days period resolution) of water flow, water quality and ecological function of a river system based on the biogeochemical RIVE model.
- The **pyNuts modeling environment** is a python framework (with the “Nuts” suffix standing for NUTrientS ) that brings together the biogeochemical modeling code, raw spatially explicit data describing natural and anthropogenic constraints for input calculation, a collection of pre-processing methods and a set of databases structured in a database-management system.

A detailed information could also be found at https://www.fire.upmc.fr/rive/

5. Line 106: remove s from works

**A5.** The sentence has been removed.

6. Line 111: Add unit to the decimal numbers.

**A6.** The decimal coordinates have been changed into degrees, minutes and seconds.

7. Lines 147 – 154: This footnote is unclear. Last line: calculation of stream velocity. How? Is something fallen of the page here? Use of parameter WSA is confusing. It could mean: mean_width * Slope * Area (not defined here). Change name or put bracket around name.

**A7** Table 1 has been reviewed. It now introduces characteristics of the Seine drainage network until its fluvial outlet (at Poses). The presentation of the formulas for the calculation of mean widths and depths was awkward here, since it has to be done all along the network and not on values averaged by Strahler order. For these two metrics we now use respectively the references Thieu et al. 2009 and Billen et al. 1994.

see the new Table 1 here after :

*Table 1: Hydro-morphological characteristics of the Seine drainage network, (*) averaged by Strahler order (SO) and (**) over the time period 2010-2013. Hydrographic network provided by the Agence de l'Eau Seine Normandie and water discharges by the national Banque Hydro database. Depth and flow velocity calculated according to Billen et al 1994; width calculated according to Thieu et al 2009.*

| SO | Draining area *km²* | Cum. length *km* | Width (*) *m* | Depth (**) *m* | Slope (*) *m m⁻¹* | Discharge (**) *m3 s⁻¹* | Flow velocity (**) *m s⁻¹* |
|---|---|---|---|---|---|---|---|
| 1 | 36083 | 12759 | 2.4 | 0.14 | 0.01442 | 0.13 | 0.34 |
| 2 | 12354 | 5231 | 5.2 | 0.29 | 0.00540 | 0.66 | 0.36 |
| 3 | 7067 | 2871 | 10.6 | 0.45 | 0.00300 | 2.17 | 0.47 |
| 4 | 4054 | 1548 | 20.2 | 0.79 | 0.00212 | 6.35 | 0.33 |
| 5 | 2649 | 943 | 46.0 | 1.11 | 0.00060 | 25.87 | 0.46 |
| 6 | 2094 | 636 | 77.8 | 2.51 | 0.00029 | 82.22 | 0.42 |
| 7 | 1354 | 318 | 168.3 | 2.61 | 0.00037 | 416.16 | 0.81 |

8. Line 161: Please make figure captions consistent. Figures 1,5,6,.. ends with a dot, but other figure captions not.

**A8.** Figure captions have been homogenized with a systematic dot at the end.

9. Lines 192-197: Message in this paragraph is unclear

**A9.** The Riverstrahler approach applied to any river basin allows to subdivide this basin in sub-basins connected to main axes. Depending on the quality and quantity of available data, the number of simulated objects can vary. For example, the major tributary of the Seine are the upstream Seine Basin, the Marne, and the Oise which could be branched to one axe. But here, because the Seine Basin in well documented, we were able to identify 69 sub-basins, connected to six axes, described per km of stretch.

The paragraph has been re-written as follows:

*"Geomorphology. A drainage network can be described as subbasins (tributaries) connected to one or several main axes, that define a number of modelling units. The modelling approach considers the drainage network as a set of river axes with a spatial resolution of 1 km (axis-object), or they can be aggregated to form subbasins that are idealized as a regular scheme of tributary confluences where each stream order is described by mean characteristics (basin-object). 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." [L182-190]*

10. Line 210: Which module? I only see RIVE in figure 2, including TA and DIC. Highlight the IC module in figure 2.

**A10.** This is exact. We rephased the paragraph as the carbonate system is now fully integrated in the RIVE model.

*"The carbonate system was described by a set of equations (named $CO_2$-module) based on a previous representation provided by Gypens et al. (2004) and adapted for freshwater*

*environments (N. Gypens and A.V. Borges, personal communication). This $CO_2$-module was fully integrated in the RIVE model (Figure 2)." [L212-215]*

11. Line 236: Eq 3 is referred to as eq 1 in SI

**A11.** Yes, the equation of $CO_2$ equilibrium at the air-water is duplicated in the supplementary material in order to facilitate the reading of section S3. We numbered equations in supplementary material with S- prefix to prevent overlap.

12. Line 238: Table 2: It is not clear how column TA is made out of the formulas 3 – 8. Please explain.

**A12.** We calculated for one mole of carbon, how many mole of H+, HCO3- are consumed or produced.

13. Line 258: values and constants are given in Table 2. Is this reference correct? I don't see them.

**A13.** Thank you, we now refer to table S3-1

14. Line 263: Where are the subsurface and groundwater flow components described? Is this in line 201 and further?

**A14.** Exactly, hydrology is described in the paragraph from line 198 to 206. Sub-titles have been added for a better structuration of the section 2.2.

15. Line 296: Are pH values measured? From HCO3- and pH, the CO2 concentrations could be calculated.

**A15.** pH in groundwater is actually measured on a regular basis by French water authorities, but reliability of these measurements seems weak, in particular because we do not have information on pH-meter types used and their calibration, and the way of how piezometers are sampled. . For these reasons, we decided not to use the available pH measurements and to recalculate the pH from DIC and TA concentrations according to Culberson (1980), see S3.4.

16. Line 318: S3. Is this the right reference?

**A16.** Sorry, this is indeed not the right reference. The numbering of the figures and tables was confusing and has been revised.

17. Line 343-351: Reservoirs are an integrated component of the river network itself. They are not point sources, they are receivers of alkalinity. This is a strange paragraph. There is no module with DIC module for reservoirs, so measurements from one reservoir are taken. Does this mean that reservoirs are not part of the module? This can't be true….

**A17.** Thank you for this remark. The title of the section "Point sources from the reservoirs" was poorly chosen. We have changed it by *"Impact of the reservoirs*".

We indeed have a model of reservoirs using the version of RIVE without the integration of the CO2-module, as we measured only $CO_2$ at 3 occasions in one of the reservoirs. When realizing that the reservoirs have such an impact on the downstream Seine River, not only for nutrients and organic carbon, but also for TA, DIC and hence for $CO_2$ and pH, we used the few reservoir measurements of TA, DIC we measured as forcing variables contrary to the other RIVE variables which were calculated.

One of the sentence of this paragraph has been modified as follows:

*"Owing to the absence of an inorganic carbon module in the modeling of reservoirs yet, we used mean measurements of TA and DIC in reservoirs as forcing variables to the river network." [L354-356]*

18. Line 400: Figure 4: missing x-axes like for example "Strahler order".

**A18.** "Strahler order" has been added as x-axe of figure 4

19. Line 402: Change mgC- CO2 L-1 to mgC L-1

**A19.** Done

20. Line 409: were followed in were followed.

**A20.** Done.

21. Line 438: Figure 6 is too small to see the results.

**A21.** The legends of Figure 6 have been enlarged

22. Line 439: Subscript of CO2 (twice)

**A22.** This is done.

23. Line 440: What is simulation envelope? Can I see this? What is the gray area?

**A23.** Simulation envelope corresponds to standard deviations (gray area). It has been put in evidence in the figure 6 caption.

24. Line 448: Here a time lag is mentioned. But size is total different as well. I don't see any explanation for this.

**A24.** It is true, that phytoplankton dynamics is not well reproduced, although that overall the simulations by the model are in the range of the observations (0.05 to 5 mgC/l, i.e. about 2 to 20 µgChla /l). Tentative explanations are provided in the discussion (line 610-621).

*"Phytoplankton development strongly results from a compromise between dilution rate by the river water and phytoplankton growth rates. But it also depends on nutrients and light availability. Observed water flows are split into two components (runoff and base flow) so*

*that are water flows taken into the model are close to the observations. Nutrients are well reproduced by the model and rarely limiting. However, phytoplankton compartment comprises only 3 groups with their own physiological characteristics (growth rates specifically) and we use empirical relationships for mean daily photosynthetically active radiation (PAR) received per day. Due to major changes in the water quality of the Seine River after the implementation of the Water Framework Directive (from 2000 onwards), phytoplankton biomass was reduced by a factor of 5 to 10, with possibly new groups of phytoplankton not taken into account in the RIVE model. Also instead of using empirical formula for light, observed values of PAR, would certainly improve phytoplankton simulations, especially in February or March when light quickly increase. This could explain the delay in phytoplankton development, which could be probably moved forward while taking into account e.g. a phytoplankton group of small species with a high growth rate (r-strategy), during a short sunny period in winter, often observed".*

25. Line 451: There is a four (number with dot) shown. Delete.

**A25.** Deleted !

26. Line 461: to = too

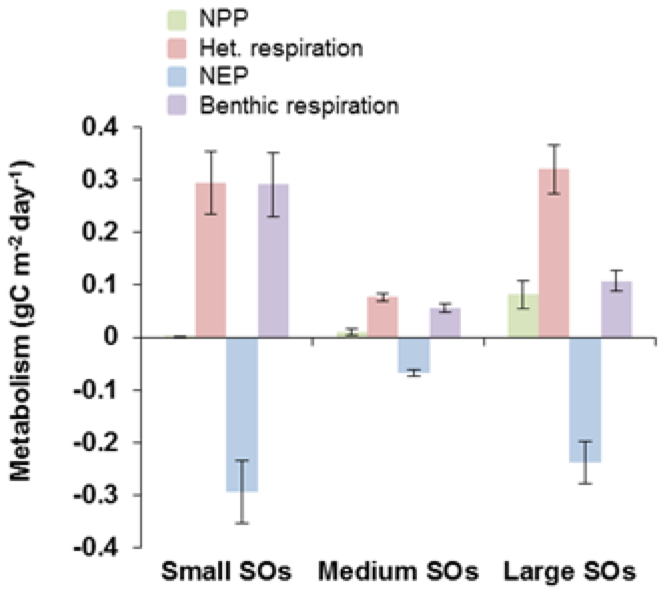
**A25.** Corrected !

27. Line 522: Subscript of CO2

**A25.** Done !

28. Line 545: Figure 9, to show the spatial dynamics of the ecology in the continuum, it might be interesting to explicitly present the relative contribution of benthic primary producers and the planktonic primary producers to the total primary production.

**A28.** We make the graphic suggested. Indeed, we can observe that benthic respiration is very high in small stream orders and then decrease in medium SOs to re-increase in large SOs. This pattern is described and discussed Lines [543-544]. We did not change the figure in the manuscript because the information is redundant with Figure 8 and we prefer to keep this Figure 9 simple,benthic respiration being included in heterotrophic respiration.




29. Line 563: Did you test the performance of the model with the wind speed parameterization suggested by Alin et al. 2011?

**A29.** Indeed, the wind may have a big influence on *k*-values. 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 requires new developments that we will investigate in future works.

Nevertheless, we calculated that using different *k*-formulations (namely Raymond, Ho and O'Connor equation) in these sectors (less than 1.5% of the cumulative length of the Seine network) will lead to a 6.2% change in $CO_2$ emissions from the overall Seine River drainage network.

30. Line 584: Any sense of direction which specific algae parameter(s) / trophic condition(s) has/have changed that causes the temporal variability not matching?

**A30.** Please refer to our answer A24.

31. Line 594: Dot at end of line.

**A31.** Done

32. Line 602-604: What is the contribution of estimated k-value to the uncertainty of the total basin CO2 emissions? You slightly touch upon in figure 7, but basin total CO2 emissions are not mentioned.

**A32.** 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 if the *k* 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 simulations vs. Marescaux et al (2018)**

Our estimates of simulated $CO_2$ outgassing (364 GgC/yr) are lower than our previous estimate based on observation (590 GgC/yr, Marescaux et al. 2018a). This difference is explained below:

- Marescaux et al (2018a) use k- formulation 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.

33. Line 604-606: I would not compare outgassing by surface area to global studies. Reference to temperate rivers are relevant.

**A33.** Thanks, we remove the part on global studies. We rephrased as:

*"The outgassing found for the Seine River by surface area of river of 1400 ± 381 gC $m^{-2}$ $yr^{-1}$ is in the middle range of the average estimates of outgassing from temperate rivers (70-2370 gC $m^{-2}$ $yr^{-1}$), including the St. Lawrence River (Yang et al., 1996), Ottawa River (Telmer and Veizer, 1999), Hudson River (Raymond et al., 1997), US temperate rivers (Butman and Raymond, 2011) and Mississippi River (Dubois et al., 2010).*" [L641-645]

34. Lines 613-614: Sentence is not correct.

**A34.** This is right, sorry! We have deleted the incorrect sentence.

35. Line 620-624: The OC export estimate by Meybeck is higher, but the detail and scale of his study is incomparable to yours. How do you know erosion in the Seine is limiting for OC export compared other temperate rivers? Also, what makes the trophic state of the Seine other than other temperate rivers?

**A35** Thanks for your remark, we tried to provide a clearer explanation:

*"Compared with other temperate rivers, the rivers of the northern France, and specifically the Seine River here, are rather flat, their low altitude limiting erosion (Guerrini et al., 1998). In addition, since the implementation of the European Water Framework Directive in the 2000s, decreasing nutrients and carbon in wastewater effluents discharged into the rivers (Rocher and Azimi, 2017), together with a decrease in phytoplankton biomass development (Aissa Grouz et al., 2016; Romero et al., 2016) can explain this difference in DOC fluxes for the Seine, a change probably valid for many other western European rivers (Romero et al., 2013)." [L658-665]*

36. Line 622: change ": )".

**A36.** Done. See new sentence **A35**

37. Line 624: Add ( before Rocher.

**A37.** Done. See new sentence **A35**

38. Line 646: I would add benthic information to figure 9 too

**A38.** Please refer to our previous answer A28

39. Line 660-661: I don't see benthic respiration explicitly mention in figure 9.

**A39.** Indeed, we made a mistake, we refer to figure 8

40. Line 668: Figure8 add blank.

**A40.** Done.

41. Line 693-694: Where do you show small orders are driven by groundwater discharges?

**A41.** We changed the formulation:

"*In small orders, concentrations are mainly driven by diffuse sources*."

This new sentence is clearly supported but Table 4 and figure 8.

**Technical corrections SI**

42. Page 1 and 8 : broken link.

**A42.** Done.

43. Page 2 : *** Now it is added to model RIVE ??

**A43.** Yes these are the new state variable added to the RIVE model when implementing the inorganic carbon module.

44. Figure S1 : I see nine red hatching areas. Not eight. Please change this also in main text (if 9 is the correct number).

**A44.** These numbers have been corrected and we now provided a new map removing part of the Seine River basin flowing downstream it fluvial outlet.

45. Eq 6 does not make sense here. Remove. Will be given in eq 14 and 15.

**A45.** Eq 6 has been removed and the following equations renumbered.

46. Eq 11 : Remove C from K2C

**A46**. This typo has been removed from Eq. 11 (now Eq. S10)

47. Section 3: Eq 17 to 19: What is CA? Carbonic Acid? Carbonate Alkalinity?

**A47.** In section 3, we wrongly refer to carbonate alkalinity (CA) instead of Total Alkalinity (TA). This error has been corrected.

48. Eq. 28 should be k600 = 13.82 + 0.35v

**A48.** In the Eq 28 : k600 = (13.82 + 0.35 * v * 100) / 100

The multiplication by 100 applies only to v to get water velocity in cm/s. The division by 100 applies to the whole Alin formula to convert the k600 obtained in cm/h into m/h. But thanks to your remark we correct a typo in this section for k600 units (in m/h instead of m/day)

49. Reference list: I would like to have one for the SI and one for the main text. Please also check the reference list. I was looking for Milero et al. 2006. It is used in the text (Table S1), but not mentioned in reference list.

**A49.** This has been done.

## 4. List of all relevant changes made in the manuscript

- We restructured the abstract and the introduction.
- We clarify the difference between RIVE, Riverstrahler and pyNuts-Rivestrahler
- We added a table in the supplementary information 2 with the list and morphological characteristics of the PyNuts-Riverstrahler modeling objects.
- We clarify the used of total alkalinity in the pH calculation
- We have tried to replace our finding for the Seine River system to a broader context of aquatic $CO_2$ evasion from temperate and/or human impacted river systems, providing comparative values.
- Thanks to the suggestion of the reviewer 2, we compared our work with that of Lauerwald et al. (2017)
- We now go further in the discussion on the *k* value (see 4.1. Evaluation of the model )
- We revised our results and the evaluation of the model to be more critical (see “3.1.1. Seasonal variations” and “4.1. Evaluation of the model”)
- We go further in the explanation of the difference between our previous observations based estimate in Marescaux et al. (2018) and our modelling results (“4.2. Export fluxes”)
- We strongly reformulated the sections “4.1. Evaluation of the model”, “4.2.Export fluxes” and, “5.Conclusion” as suggested by the reviewers.
- The manuscript has been revised by a professional proofreader.

## 5. Revised manuscript with track changes

## Title page

# Modeling inorganic carbon dynamics in the Seine River continuum in France

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Article revised to be submitted to Hydrology and Earth System Sciences

# Abstract


Inland waters ~~have been~~are ~~recognized as~~ an active component of the carbon cycle where transformations and transports are associated with carbon dioxide ($CO_2$) outgassing.

This study estimated $CO_2$ emissions from the human-impacted Seine River (France) and provided a detailed budget of aquatic carbon transfers for organic and inorganic forms, including in-stream metabolism along the whole Seine River network. The existing process based~~We propose a modeling approach by formalizing an inorganic carbon module integrated into the~~ biogeochemical~~ model,~~ pyNuts-Riverstrahler model was supplemented by a newly developed inorganic carbon module and simulations were ~~, to~~ performed for the recent period 2010-2013.~~estimate the carbon fate in the aquatic continuum. Our approach was~~ developed ~~on the human-impacted Seine River (France) taking into account point sources (including the largest wastewater treatment plant~~ (WWTP) ~~in Europe, reaching a treatment capacity of 6 10^6 inhab eq),~~ New input constraints for the modelling of riverine inorganic carbon were documented by field measurements and complemented by analysis of ~~and diffuse constraints to the model. Both sources were characterized by field measurements in groundwater and in wastewater treatment plants~~WWPTs~~, and by~~using existing databases. The resulting ~~In average, we calculated~~ dissolved inorganic (DIC) concentrations in the Seine aquifers ranged from 25 to 92 mgC $L^{-1}$ ~~depending of on the aquifers~~ while in wastewater treatment plant (WWTP) effluents our measurements of DIC averaged 70 mgC $L^{-1}$.

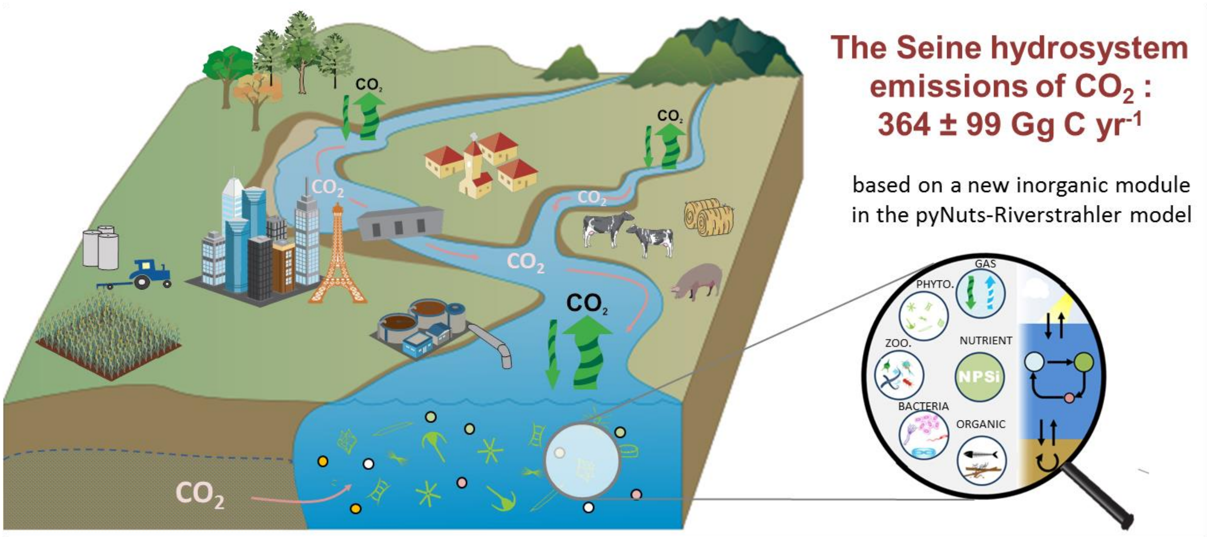
~~On~~ During ~~the period studied (2010–2013), yearly averaged simulated $CO_2$ emissions from the hydrosystem were estimated at 364 ± 99 Gg C $yr^{-1}$.~~ Along the main stem of the Seine River, ~~S~~simulations of ~~dissolved inorganic carbon~~DIC, total alkalinity, pH, and $CO_2$ concentrations ~~showed good agreement~~ were ~~in~~ of the same order of magnitude as ~~with~~ the observations, ~~and~~ but seasonal variability ~~could be~~was not always well reproduced. Our

simulations demonstrated the $CO_2$ supersaturation with respect to atmospheric concentrations over~~f~~ the entire Seine ~~basin~~River network.~~was shown at all locations.~~ ~~everywhere~~ The most significant ~~. O~~outgassing was ~~the most important~~ in lower order streams while peaks were simulated downstream of the major ~~wastewater treatment~~WWTP effluent. For the period studied (2010–2013), the annual average of simulated $CO_2$ emissions from the Seine drainage network were estimated at 364 ± 99 Gg C $yr^{-1}$.

Metabolism in the Seine hydrographic network highlighted the importance of benthic activities in ~~ small~~ headwaters~~ streams~~ while planktonic activities ~~were~~ occured mainly ~~observed~~ downstream in larger rivers. ~~In contrast to the 1990s, t~~The net ecosystem productivity remained negative throughout ~~all~~ the 4 simulated~~of the~~ years and over the entire drainage~~at every place~~ site ~~within the river~~ network, highlighting the heterotrophy of the basin. ~~In parallel, $CO_2$ supersaturation with respect to atmospheric concentrations of the basin was shown. Outgassing was the most important in lower order streams while peaks were simulated downstream of the major wastewater treatment effluent.~~

**Keywords:** $CO_2$ outgassing; inorganic carbon modeling; instream metabolisms; waste- and ground water inputs; carbon budget ; temperate Seine River

**Graphical abstract:**




**Highlights:**

- $CO_2$ emission from the Seine River was estimated at 364 ± 99 GgC $yr^{-1}$ with the Riverstrahler model.
- $CO_2$ riverine concentrations are modulated by groundwater discharge and instream metabolism.
- $CO_2$ emissions account for 31% of inorganic carbon exports, the rest being exported as DIC.

# Introduction

Rivers have been demonstrated to be active pipes for transport, transformation, storage and outgassing of inorganic and organic carbon (Cole et al., 2007). Although there are large uncertainties ~~on flux~~in the ~~quantification~~ quantification of flux from inland waters, carbon dioxide ($CO_2$) outgassing has been estimated to be a significant efflux to the atmosphere, subjected to regional variabilities (Cole et al., 2007; Battin et al., 2009a; Aufdenkampe et al., 2011; Lauerwald et al., 2015; Regnier et al., 2013; Raymond et al., 2013a; Sawakuchi et al., 2017; Drake et al., 2017). These variabilities are ~~controlled~~ determined by regional climate and watershed characteristics and are related to terrestrial carbon exports under different forms, from organic to inorganic, and dissolved to particulate. 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 ~~synthesized~~ produced instream by photosynthesis or brought by dust particles (Prairie and Cole, 2009; Drake et al., 2017). Inorganic carbon ~~sources~~ originate from groundwater, soil leaching and exchange by diffusion at the air–water interface, depending on the partial pressure of $CO_2$ ($pCO_2$) at the water surface with respect to atmospheric $pCO_2$ (Cole et al., 2007; Drake et al., 2017; Marx et al., 2018). Beside air-water exchanges, carbon exchanges occur at the water–sediment interface, through biomineralization and/or burial ~~Additional carbon exchanges, e.g., incorporation into biomineralized structures or resuspension, occur at the water–sediment interface and can be buried~~ (Regnier et al., 2013b). As a whole, oligo- and mesotrophic lotic hydrosystems generally act as a source of carbon while surface water of lentic eutrophic systems ~~can~~ may be undersaturated with respect to atmospheric $pCO_2$ (Prairie and Cole, 2009; Xu et al., 2019; Yang at al., 2019).

Direct measurements of $pCO_2$ or isotopic surveys (~~although as by example, completed by~~ as realized by Dubois et al. 2010 in the Mississippi River) along the drainage network are still too scarce to accurately support temporal and spatial analyses of $CO_2$ variability. While calculations from pH, temperature and alkalinity may help reconstruct spatiotemporal patterns of $CO_2$ dynamics (Marescaux et al., 2018b), ~~only~~ modeling tools can predict the fate of carbon in whole aquatic systems. Indeed, modeling approaches have made it possible to simulate and quantify carbon fluxes between different reservoirs: atmosphere, biosphere, hydrosphere and lithosphere (e.g., Bern-SAR, Joos et al., 1996; ACC2, Tanaka et al., 2007; TOTEM, Mackenzie et al., 2011; MAGICC6, Meehl et al., 2007). In addition to these box approaches, a number of more comprehensive mechanistic models, describing biogeochemical processes involved in carbon cycling and $CO_2$ evasion, have been set up for oceans (e.g., Doney et al., 2004; Aumont et al., 2015), coastal waters (e.g., Borges et al., 2006; Gypens et al., 2004, 2009, 2011) and estuaries (e.g., Cai and Wang, 1998; Volta et al., 2014, Laruelle et al., 2019). In inland waters, the NICE-BGC model (Nakayama, 2016) accurately represents $CO_2$ evasion at the global scale. However, to our knowledge, ~~whereas~~ while several process-based river models~~, including~~ ~~Riverstrahler (Billen et al., 1994; Garnier et al., 2002)~~ describe the carbon cycle through organic matter input and degradation by aquatic microorganisms (e.g., PEGASE, Smitz et al., 1997; ProSe, Vilmin et al., 2018; QUAL2Kw, Pelletier et al., 2006; QUAL-NET, Minaudo et al., 2018, QUASAR, Whitehead et al., 1997; Riverstrahler, ~~(~~Billen et al., 1994; Garnier et al., 2002~~)~~), none of them describes the inorganic carbon cycle including carbon dioxide outgassing.

The Seine River (northwestern France) has long been studied using the biogeochemical riverine Riverstrahler model (Billen et al., 1994; Garnier et al., 1995)~~-~~, a generic model of water quality and biogeochemical functioning of large river systems. ~~is a generic model of water quality and biogeochemical functioning of large river systems.~~

~~The Seine River (northwestern France) has long been studied using the Riverstrahler model.~~ For example, the model has made it possible to quantify deliveries to the coastal zone and understand eutrophication phenomena (Billen and Garnier, 2000; Billen et al., 2001; Passy et al., 2016; Garnier et al., 2019), nitrogen transformation and $N_2O$ emissions (Garnier et al., 2007; Garnier et al., 2009; Vilain et al., 2012) as well as nitrate retention (Billen and Garnier, 2000; Billen et al., 2018), and organic carbon metabolism (Garnier and Billen, 2007; Vilmin et al., 2016).

It is only recently that we investigated $pCO_2$ and emphasized the factors controlling $pCO_2$ dynamics in the Seine River (Marescaux et al., 2018b).

The purpose of the present study was to quantify the sources, transformations, sinks and gaseous emissions of inorganic carbon using the Riverstrahler modelling approach (Billen et al., 1994; Garnier et al., 2002; Thieu et al., 2009). ~~e purpose of the present study is the implementation of a generic module of inorganic carbon into the newly developed pyNuts modeling environment for the Riverstrahler model in order to quantify the sources, transformations, sinks and gaseous emissions of inorganic carbon.~~ A further aim in newly implementing this $CO_2$ module was to quantify and discuss autotrophy versus heterotrophy patterns in regard to $CO_2$ concentrations and supersaturation in the drainage network. ~~In future works, a systematic coupling with an estuary model could enable to accurately calculate carbon delivery fluxes to the ocean as already proposed for the year 2010 by Laruelle et al. (2019).~~

# Material and methods

## 2.1. Description of the Seine basin

Situated in northwestern France, ~~within 46.950~~46°57’ – ~~50.0167~~50°55’ north and 0~~.~~° ~~117~~ 7’ 1” – ~~4.000~~4° east, the Seine basin (~76,285 km²) has a temperate climate and a pluvio-oceanic hydrologic regime (Figure 1). The mean altitude of the basin is 150 m above sea level (ASL) with 1% of the basin reaching more than 550 m ASL in the Morvan (Guerrini et al., 1998). The ~~annual~~ water flow at Poses (stream order 7, basin area 64,867 km²), the most downstream monitoring station free from tidal influence, averaged 490 $m^3$ $s^{-1}$ ~~in~~ during the 2010–2013 period (the HYDRO database, http://www.hydro.eaufrance.fr, last accessed 2019/03/26). The major tributaries include the Marne and upper Seine rivers upstream from Paris, and the Oise River downstream from Paris (Figure 1a). Three main reservoirs, storing water during winter and sustaining low flow during summer, are located upstream on the Marne River and the upstream Seine and its Aube tributary (Figure 1a). The total storage capacity of these reservoirs is 800 $10^6$ $m^3$ (Garnier et al., 1999).

The maximum water discharge of these tributaries occurs during winter with the lowest temperature and rate of evapotranspiration; the opposite behavior is observed during summer (Guerrini et al., 1998).

Except for the crystalline rocks in the north and from the highland of the Morvan (south), the Seine basin is for the most part located in the lowland Parisian basin with sedimentary rocks (Mégnien, 1980; Pomerol and Feugueur, 1986; Guerrini et al., 1998). The largest aquifers are in carbonate rock (mainly limestone and chalk) or detrital (sand and sandstone) material separated by impermeable or less permeable layers.

The concept of Strahler stream order (SO) (Strahler, 1957) was adopted for describing the geomorphology of a drainage network in the Riverstrahler model (Billen et al., 1994). The smaller perennial streams are order 1. Only confluences between two river stretches with the same SO produce an increase in Strahler ordination (SO+1) (Figure 1). The mean hydrophysical characteristics of the Seine River are aggregated by stream orders shown in Table 1.

The Seine basin is characterized by intensive agriculture (more than 50% of the basin, CLC - EEA, 2012)~~. The Seine basin is densely populated (~ 230 inhabitants km$^{-2}$). The population~~ is mostly concentrated in the Paris conurbation (12.4 million inhabitants in 2015) (Figure 1) (INSEE, 2015). Located 70 km downstream of Paris, the largest wastewater treatment plant in Europe (Seine Aval, SAV WWTP) can treat up to 6 $10^6$ inhab eq per day, releasing 15.4 m$^3$ s$^{-1}$ into the lower Seine River (*Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne*; French acronym SIAAP, http://www.siaap.fr/, last accessed 2019/03/04).

*Table 1: Hydro-morphological characteristics of the Seine drainage network, (*) averaged by Strahler order (SO) and (**) over the time period 2010-2013. Hydrographic network provided by the Agence de l'Eau Seine Normandie and water discharges by the national Banque Hydro database. Depth and flow velocity calculated according to Billen et al 1994; width calculated according to Thieu et al 2009.*

| SO | Draining area | Cum. length | Width (*) | Depth (**) | Slope (*) | Discharge (**) | Flow velocity (**) |
|---|---|---|---|---|---|---|---|
| | *km²* | *km* | *m* | *m* | *m m$^{-1}$* | *m3 s$^{-1}$* | *m s$^{-1}$* |
| 1 | 36083 | 12759 | 2.4 | 0.14 | 0.01442 | 0.13 | 0.34 |
| 2 | 12354 | 5231 | 5.2 | 0.29 | 0.00540 | 0.66 | 0.36 |
| 3 | 7067 | 2871 | 10.6 | 0.45 | 0.00300 | 2.17 | 0.47 |
| 4 | 4054 | 1548 | 20.2 | 0.79 | 0.00212 | 6.35 | 0.33 |
| 5 | 2649 | 943 | 46.0 | 1.11 | 0.00060 | 25.87 | 0.46 |
| 6 | 2094 | 636 | 77.8 | 2.51 | 0.00029 | 82.22 | 0.42 |
| 7 | 1354 | 318 | 168.3 | 2.61 | 0.00037 | 416.16 | 0.81 |

~~[1] The hydrographic network and the slopes (S, m m$^{-1}$) were provided by the Agence de l'Eau Seine Normandie (French acronym AESN, http://www.eau-seine-normandie.fr/, last accessed 2019/03/04); water discharges by the national Banque Hydro database (http://www.hydro.eaufrance.fr/, last accessed 2019/03/04); mean width (W, m) is assumed to follow the empirical relationship with the upstream watershed area (WSA, km$^2$) (see Eq. 1; Billen et al., 1994):~~

$$\cancel{W = 0.8\,WSA^{\frac{1}{2}}}$$ ~~Eq. 1~~

~~The mean depth (D, m) is related to the slope (S, m m~~$^{-1}$~~) and water flow (Q, m~~$^{3}$ ~~s~~$^{-1}$~~) by the relationship derived from Manning's formula (see Eq. (2), Billen et al., 1994):~~

$$\cancel{D = [0.045Q(W(S^{1/2}))^{-1}]^{3/5}}$$ ~~Eq. 2~~

~~The stream velocity (m s~~$^{-1}$~~) is calculated from the water discharge and the wetted area.~~

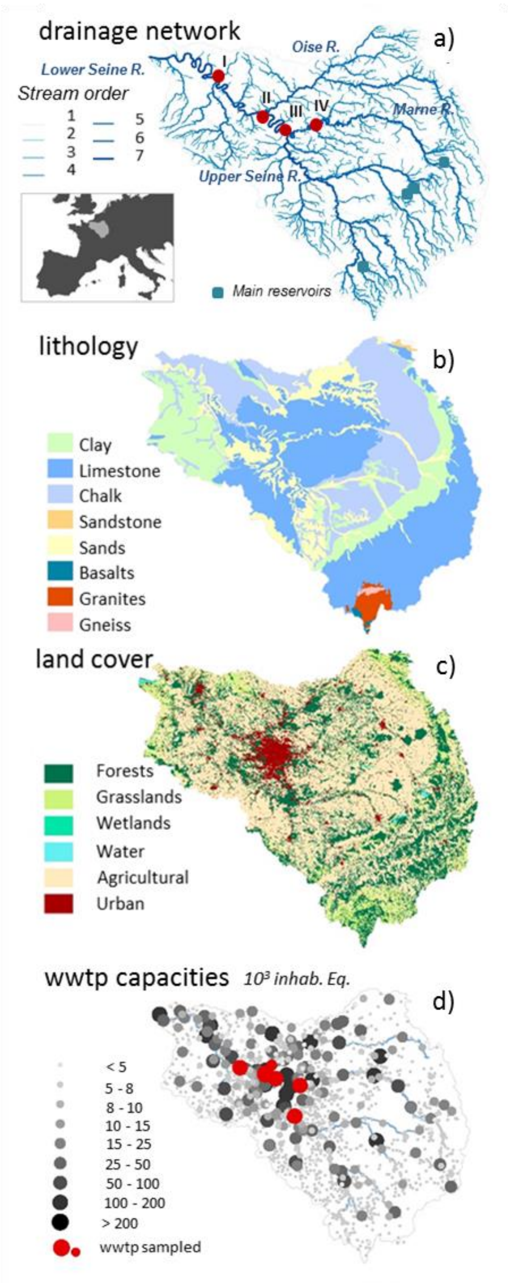


*Figure 1 Characteristics of the Seine basin: a) drainage network according to Strahler stream orders (Strahler, 1952, 1957), monitoring stations (I: Poses, II: Poissy (Downstream Paris), III: Paris, IV: Ferté-sous-Jouarre (Upstream Paris); b) the lithology according to Albinet, (1967); c) land use according to the Corine Land Cover database, with six simplified classes (EEA, 2012); d) wastewater treatment plants (WWTPs) of the basin. Red dots are the WWTPs sampled in 2018.*

## 2.2. The pyNuts-Riverstrahler model and its biogeochemical model, RIVE

*The biogeochemical model, RIVE.* The core of the biogeochemical calculation of the pyNuts-Riverstrahler model (described hereafter) is the RIVE model (e.g., Billen et al., 1994; Garnier et al., 1995; Garnier et al., 2002; Servais et al., 2007) (https://www.fire.upmc.fr/rive/), which simulates concentrations of oxygen, nutrients (nitrogen (N), phosphorus (P) and silica (Si)), particulate suspended matter, and dissolved and particulate organic carbon (three classes of biodegradability) in a homogeneous water column. Biological compartments are represented by three taxonomic classes of phytoplankton (diatoms, Chlorophyceae and Cyanobacteria), two types of zooplankton (rotifers with a short generation time and microcrustaceans with a long generation time), two types of heterotrophic bacteria (small autochthonous and large allochthonous with a higher growth rate than the small ones), as well as two types of nitrifying bacteria (ammonium-oxidizing bacteria and nitrite-oxidizing bacteria).

The model also describes benthic processes (erosion, organic matter degradation, denitrification, etc.) and exchanges with the water column with the explicit description of benthic organic matter, inorganic particulate P and benthic biogenic Si state variables. The benthic component does not explicitly represent all the anaerobic reduction chains, denitrification being the major anaerobic microbial process.

A detailed list of the state variables of the RIVE model is provided in S1. Most of the kinetic parameters involved in this description have been previously determined through field or laboratory experiments under controlled conditions and are fixed a priori (see detailed description of all kinetics and parameters values in Garnier et al., 2002). To date, there has been no explicit representation of inorganic carbon in the RIVE model (see this new input in S1).

~~PyNuts is a modeling environment that can calculate the constraints (diffuse and point sources) to the Riverstrahler model (Raimonet et al., 2018; Desmit et al., 2018). As Riverstrahler manages the calculation of the RIVE model according to a Lagrangian routing of water masses along the hydrographic network (Billen et al., 1994), PyNuts-Rivertrahler is a generic model of water quality and biogeochemical functioning of large drainage networks that simulates water quality within entire drainage networks.~~

~~In PyNuts-Riverstrahler,~~ Riverstrahler allows for the calculation of water quality variables at any point in the aquatic continuum based on a number of constraints characteri~~s~~zing the watershed, namely, the geomorphology and hydrology of the river system and the point and diffuse sources of nutrients.

*Geomorphology*. A drainage network~~modeling units~~ can be described as subbasins (tributaries) connected to one or several main axes, ~~which~~that define a number of modelling units. ~~as~~ The modelling approach considers the drainage network as a set of river axes with a spatial resolution of 1 km (axis-object), or they can be aggregated to form ~~upstream~~ subbasins that are idealized as a regular scheme of tributary confluences where each stream order is described by mean characteristics (~~stream order~~basin-object). Here, the Seine drainage network starts from headwater until it fluvial outlet (Poses) and was divided into 69 -modeling units, including ~~6~~ 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.

~~Here, the Seine basin was divided into 80 modeling units, including eight nine axes (axis-object) and 72 upstream basins (stream order-object) (S2)~~.

*Hydrology.* Runoffs were calculated over the whole Seine basin using water discharge measurements at 48 gauged stations (source: Banque Hydro database, http://www.hydro.eaufrance.fr/, last accessed 2019/08/29). Surface and base flow contributions were estimated applying the BFLOW automatic hydrograph separation method (Arnold and Allen, 1999) over the recent time series of water discharges (2010–2017). For the study period (2010–2013), the mean base flow index (BFI = 0.71) of the Seine basin indicates the extent of the groundwater contribution to river discharge, with spatial heterogeneity following the main lithological structures (Figure 1b), but ~~not significant differences~~ when summarizing the BFI criteria by Strahler order, significant differences did not appear (not shown).

*Water temperature.* 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-day time step (s~~S~~ee S2).

*Diffuse and point sources.* Riverstrahler manages the calculation of the RIVE model according to a Lagrangian routing of water masses along the hydrographic network (Billen et al., 1994) and is a generic model of water quality and biogeochemical functioning of large drainage networks that simulates water quality. PyNuts is a modeling environment that can calculate the constraints (diffuse and point sources) ~~to~~on the Riverstrahler model at a multiregional scale (Desmit et al., 2018 for the Atlantic façade).

~~As Riverstrahler manages the calculation of the RIVE model according to a Lagrangian routing of water masses along the hydrographic network (Billen et al., 1994), PyNuts-Rivertrahler is a generic model of water quality and biogeochemical functioning of large drainage networks that simulates water quality within entire drainage networks.~~

### 2.2.1. Development of an inorganic carbon module

**Introducing the carbonate system**

The carbonate system was described by a set of equations (named $CO_2$-m~~M~~odule) based on a previous representation provided by Gypens et al. (2004) and adapted for freshwater environments (N. Gypens and A.V. Borges, personal communication). This $CO_2$-module was fully integrated in the RIVE model (Figure 2).~~This module represented in Figure 2 was developed based on the model described in Gypens et al. (2004) and adapted for freshwater environments (N. Gypens and A.V. Borges, personal communication)~~. It aims at computing the speciation of the carbonate system based on two new state variables: dissolved inorganic carbon (DIC) and total alkalinity (TA), making it possible to calculate carbon dioxide ($CO_2$). The module uses three equations (see S3: Eqs. 1, 2, 3) that also calculate bicarbonate ($HCO_3^-$), carbonate ($CO_3^{2-}$) and hydronium ($H_3O^+$). Indeed, two variables of the carbonate system are sufficient to calculate all the other components (Zeebe and Wolf-Gladrow, 2001). Here, DIC and TA were selected because the biological processes involved in their spatiotemporal variability along the aquatic continuum were already included in the RIVE model (Figure 2). We calculated pH as a function of ~~total alkalinity~~TA and ~~dissolved inorganic carbon~~DIC using the Culberson equation (Culberson, 1980) (S3.4).

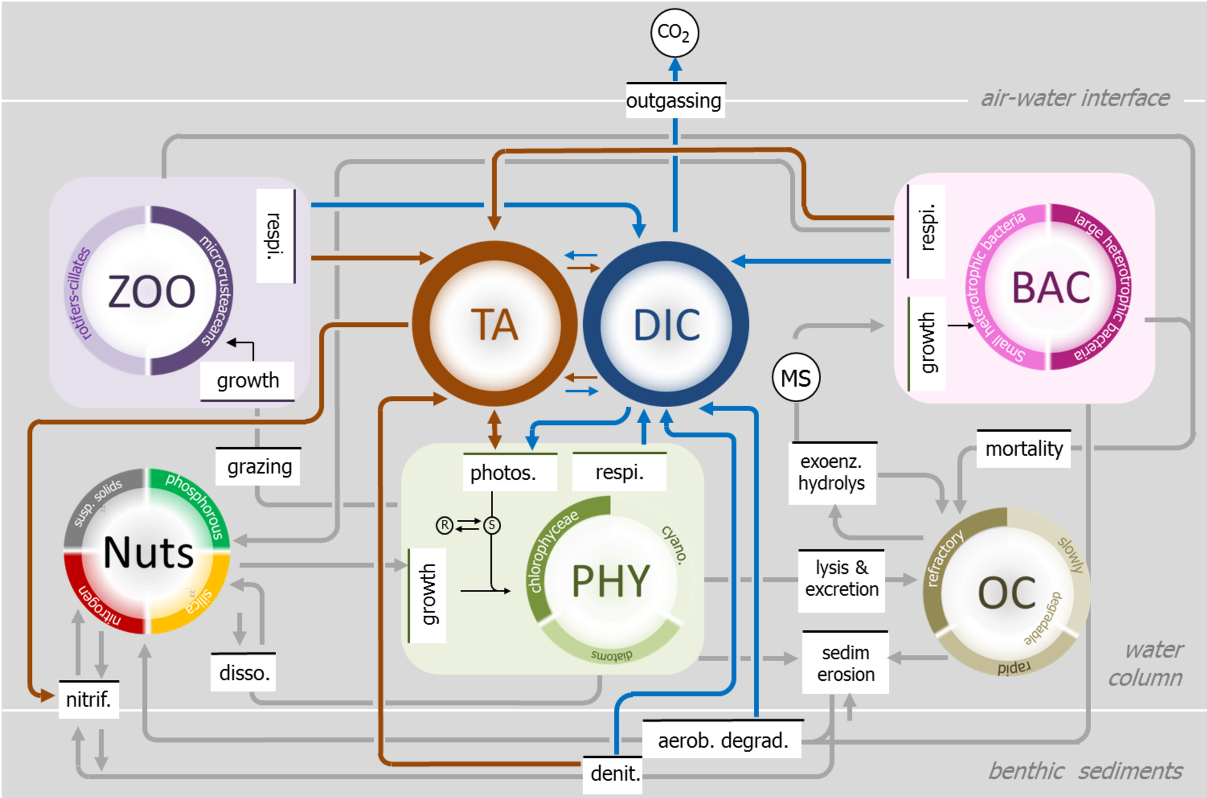



*Figure 2 Schematic representation of the ecological RIVE model (inspired from Billen et al. 1994, Garnier & Billen, 1994), with grey lines indicating the main processes simulated in the water column and at the interface with sediment (oxygen not shown), and implementation of the new inorganic module, based on total alkalinity (TA, ~~(~~maroon) and dissolved inorganic carbon (DIC, ~~(~~ blue) ~~lines~~.*

**Aquatic processes affecting TA and DIC**

The exchange of $CO_2$ between the water surface and the atmosphere~~-~~ depends, respectively, on the gas transfer velocity (k-value) and ~~of~~on the sign of the $CO_2$ concentration~~s~~ gradient at the water surface–atmosphere interface (S3.5). Change in $pCO_2$ will ~~affect~~ in- turn affect DIC concentrations (see Table 2, Eq. 1). ~~increases or decreases DIC, depending on the gas transfer velocity (k-value) and the $CO_2$ gradient concentrations gradient at the water surface–atmosphere interface (Table 2, Eq. 3 and S3.5)~~. Dissolved or particulate organic matter is mostly degraded by microbial activities (more or less quickly depending on their biodegradability), resulting in $CO_2$ and $HCO_3^-$ production (Servais et al., 1995), thus inducing a change in DIC and TA concentrations in the water column (Table 2, Eq. ~~4~~2, Figure 2). Photosynthesis and denitrification processes also affect DIC and TA (Table 2, Eqs. ~~5~~3–~~7~~5), while instream nitrification only influences TA (Table 2, Eq. ~~8~~6, Figure 2).

*Table 1 Stoichiometry of the biogeochemical processes, influencing dissolved inorganic carbon (DIC) and total alkalinity (TA) in freshwater, as~~s~~ taken into account in the new inorganic carbon module. TA and DIC expressed in mol:mol of the main substrate (either C or N).*

| Process | Equation | DIC | TA | Eq. |
|---|---|---|---|---|
| $FCO_2$ | $CO_2(aq) \leftrightarrow CO_2(g)$ | ±1 | 0 | ~~3~~1 |
| Aerobic degradation | $C_{106}H_{263}O_{11}N_{16}P + 106O_2 \rightarrow 92CO_2 + 14HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 92H_2O$ | +1 | +14/106 | ~~4~~2 |
| Photosynthesis ($NO_3^-$ uptake) | $106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow C_{106}H_{263}O_{11}N_{16}P + 138O_2$ | -1 | +17/106 | ~~5~~3 |
| Photosynthesis ($NH_4^+$ uptake) | $106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \rightarrow C_{106}H_{263}O_{11}N_{16}P + 106O_2 + 15H^+$ | -1 | -15/106 | ~~6~~4 |
| Denitrification | $5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$ | +1 | +4/5 | ~~7~~5 |
| Nitrification | $NH_4^+ + 2O_2 \rightarrow 2H^+ + H_2O + NO_3^-$ | 0 | -2 | ~~8~~6 |

## State equations and parameters of the inorganic carbon module

These processes affecting TA and DIC result in equations governing inorganic carbon dynamics as:

$$TA = TA_{t-1} + dt.\frac{dTA}{dt} + \mathrm{TA_{inputs}}$$

Eq. 7~~9~~

with:

$$\frac{dTA}{dt} = (\frac{14}{106}\frac{(respbact + respZoo + respBent)}{M(C)} + \left(\frac{4}{5}Denit - 2.nitr[\text{‘}AOB\text{’}]\right).\ M(N)^{-1} + (\frac{17}{106}\frac{uptPhyNO_3^-}{uptPhyN} - \frac{15}{106}\frac{uptPhyNH_4^+}{uptPhyN}).phot\ .M(O_2)^{-1})1000$$

Eq. 8~~10~~

where $TA_{t-1}$ is the value of ~~total alkalinity~~TA (µmol $L^{-1}$) ~~at~~ in the previous time step (t−1). $Respbact$, $RespZoo$, and $respBent$ are respectively the heterotrophic planktonic respiration of bacteria, zooplankton and benthic bacteria already included in RIVE (mgC $L^{-1}$ $h^{-1}$). $M(C)$ is the molar mass of the carbon (12 g $mol^{-1}$). $Denit$ and $nitr[\text{‘}AOB\text{’}]$ are respectively the processes of denitrification and nitrification by ammonia-oxidizing bacteria (AOB) as implemented in the RIVE model (mgN $L^{-1}$ $h^{-1}$); $M(N)$ is the molar mass of the nitrogen (14 g $mol^{-1}$). $phot$ is the net photosynthesis (mg$O_2$ $L^{-1}$ $h^{-1}$). $uptPhyN$ is the nitrogen uptake by phytoplankton (mgN $L^{-1}$ $h^{-1}$) which is differentiated for nitrate ($uptPhyNO3^-$, mgC $L^{-1}$ $h^{-1}$) and ammonium ($uptPhyNH4^+$, mgC $L^{-1}$ $h^{-1}$), and $M(O_2)$ is the molar mass of the dioxygen (32 g $mol^{-1}$). $\mathrm{TA_{inputs}}$ is TA (µmol $L^{-1}$) entering the water column by diffuse sources (groundwater and subsurface discharges) and point sources (WWTPs).

$$DIC = DIC_{t-1} + dt.\frac{dDIC}{dt} + \mathrm{DIC_{inputs}}$$

Eq. 9~~11~~

with:

$$\frac{dDIC}{dt} = (respbact + respZoo + respBent) + denit\,.\,M(C).\,M(N)^{-1} + phot.\,M(C).\,M(O_2)^{-1} + \frac{F_{CO_2}}{depth}$$ Eq. 1~~2~~0

where $DIC_{t-1}$ is the value of ~~dissolved inorganic carbon~~DIC (mgC $L^{-1}$) ~~at~~ in the previous time step (t−1). $F_{CO_2}$ is the $CO_2$ flux at the water–atmosphere interface in mgC $m^{-2}$ $h^{-1}$ described in S3.5; depth is the water column depth (m).

The different values of constants and parameters used in the inorganic carbon module are introduced in Table 1 of S3.6~~2~~. The full inorganic carbon module is described in S3 (3.1 to 3.5).

### 2.2.2. Input constraints of the pyNuts-Riverstrahler model

**Diffuse sources from soil and groundwater**

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 ~~r~~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. These concentrations are then combined with a 10-day time step description of surface and base flows to simulate the seasonal contribution of diffuse emissions to the river system. For nutrients, several applications of the Riverstrahler on the Seine River basin refined the quantification of diffuse sources: e.g., Billen and Garnier (2000) and Billen et al. (2018) for nitrogen; Aissa-Grouz et al. (2016) for phosphorus; Billen et al. (2007), Sferratore et al. (2008) and Thieu et al. (2009) for N, P and Si. In this study we revised our estimates for diffuse organic carbon sources and propose TA and DIC values for the Seine basin. The summary of all the ~~model's~~ carbon-related inputs of the model~~are~~ is ~~shown~~ provided in Table 3.

Dissolved organic carbon (DOC) input concentrations were extracted from the AESN database (http://www.eau-seine-normandie.fr/, last accessed 2019/03/04) and averaged by land use for subsurface sources (mean, 3.13 mgC $L^{-1}$; sd, 4.56 mgC $L^{-1}$; 3225 data for 2010–2013). For groundwater sources, concentrations were extracted from the ADES database (www.ades.eaufrance.fr, last accessed 2019/03/04) and averaged by MESO waterbodies (French acronym: Masse d'Eau SOuterraine, see S4; mean, 0.91 mgC $L^{-1}$; sd, 0.8 mgC $L^{-1}$; 16,000 data for 2010–2013). These concentrations were ~~similarly~~ separated into three pools of different biodegradability levels, with 7.5% rapidly, 17.5% slowly biodegradable and 75% refractory DOC for subsurface sources and 100% refractory DOC for groundwater flow (Garnier, unpublished).

Total POC inputs were calculated based on estimated total suspended solid (TSS) fluxes, associated with a soil organic carbon (SOC) content provided by the LUCAS Project (samples from agricultural soil, Tóth et al., 2013), the BioSoil Project (samples from European forest soil, Lacarce et al., 2009) and the Soil Transformations in European Catchments (SoilTrEC) Project (samples from local soil data from five different critical zone observatories (CZOs) in Europe, Menon et al., 2014) (Aksoy et al., 2016). TSS concentrations were calculated using fluxes of TSS provided by WaTEM-SEDEM (Borrelli et al., 2018) and runoffs averaged over the 1970–2000 period (SAFRAN-ISBA-MODCOU, SIM; Habets et al., 2008). The POC mean was 8.2 mgC $L^{-1}$; sd, 10.4 mgC $L^{-1}$ in subsurface runoff, and 0.8 mgC $L^{-1}$; sd, 1.0 mgC $L^{-1}$ in groundwater discharge. The same ratio of DOC reactivity was applied for three classes of POC degradability. The k~~K~~inetics for POC and DOC hydrolysis and parameters ~~are~~ however are different (Billen and Servais, 1989; Garnier et al., 2002).

DIC and TA are brought by subsurface and groundwater discharges (Venkiteswaran et al., 2014). DIC is defined by the sum of bicarbonates ($HCO_3^-$), carbonates ($CO_3^-$) and $CO_2$. Unlike $HCO_3^-$ and $CO_3^-$ measured in groundwater on a regular basis by French authorities (ADES, www.ades.eaufrance.fr, last accessed 2019/03/04), $CO_2$ concentrations were not measured in their survey. TA values are also provided in the ADES database.

To calculate DIC concentrations in groundwaters, we therefore used our own $CO_2$ measurements, equaling on average 15.92 mg~~C-~~ ~~$CO_2$~~C $L^{-1}$; sd, 7.12 mgC $L^{-1}$ ~~mgC-$CO_2$ $L^{-1}$~~ (55 measurements in six piezometers in the Brie aquifer ~~in~~ during 2016–2017) (see methodology in Marescaux et al., 2018a). DIC and TA were averaged for the 48 unconfined hydrogeological MESO units of the basin (see concentrations in S4) ~~on~~ during the recent period (2010–2015), including the simulation period. In Figure 3, a summary of TA and DIC inputs by MESO units is shown by grouping MESO units according to lithology and geological ages.

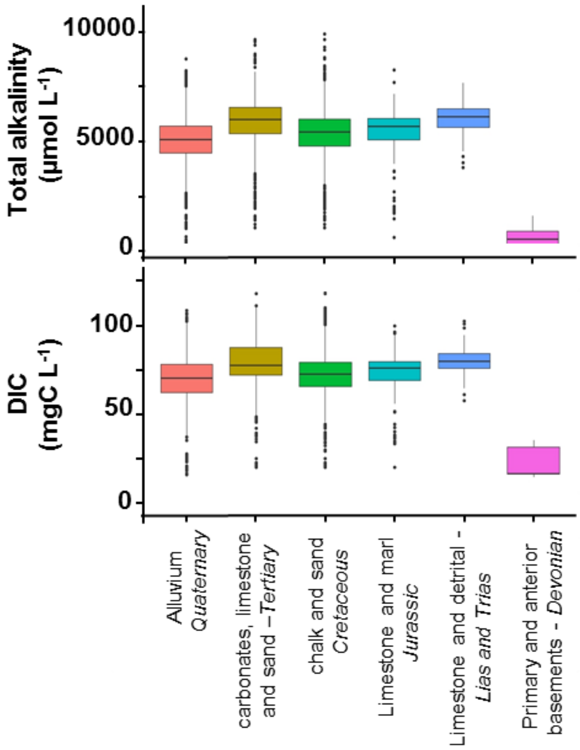



*Figure 3 Boxplots of total alkalinity (µmol $L^{-1}$) and dissolved inorganic carbon (DIC, mgC $L^{-1}$) groundwater concentrations by grouping the MESO units. The lower, intermediate and upper parts of the boxes represent, respectively, the 25th, 50th and 75th percentiles and the circles represent the outlier values (source: ADES). The color code is the same as the one in S4 spatially representing the MESO units of the basin.*

Documenting TA and DIC diffuse sources based on MESO units ensures ~~good~~ a representation of their spatial heterogeneity in the Seine River basin. Carbonate waters showed higher TA and DIC mean concentrations while crystalline waters had the lowest mean concentrations in TA and DIC (primary and anterior basements from Devonian, Figure 3). Aquifers from Tertiary and alluvium ~~of~~ from Quaternary ~~showed~~ had a more heterogeneous distribution of their concentrations (Figure 3). TA and DIC by MESO units were then spatially averaged at the scale of each modeling unit of the pyNuts-Riverstrahler model (~~80~~ 69 modeling units, subdivided according to Strahler ordination, ~~S3~~S2), thus forming a semi-distributed estimate of groundwater concentrations.

TA and DIC measurements in lower order streams cannot be considered as representative of subsurface concentrations because lower order streams are expected to ~~strongly~~ degas strongly in a few hundred meters, as shown for $N_2O$ ~~in~~ by Garnier et al. (2009) and for $CO_2$ in Öquist et al. (2009). We have considered similar concentrations and spatial distribution for subsurface components ~~that~~ to those obtained for groundwater (from 25 to 92 mgC $L^{-1}$ DIC, and from 663 to 5580 µmol $L^{-1}$ TA, Figure 3).

**Point sources from WWTP effluents**

The pyNuts-Riverstrahler model integrates carbon and nutrient raw emissions from the local population starting from the collection of household emissions into sewage networks until their release after specific treatments in WWTPs. In the Seine River basin, most of these releases are adequately treated before being discharged to the drainage network. DOC discharge from WWTPs was described according to treatment type, ranging from 2.9 to 9.4 gC $inhab^{-1}$ $day^{-1}$ while POC discharge ranged from 0.9 to 24 gC $inhab^{-1}$ $day^{-1}$ based on the sample of water purification treatment observed in the Seine basin (Garnier et al., 2006; Servais et al., 1999).

TA and DIC were measured at eight WWTPs selected to reflect various treatment capacities (from 6 $10^3$ inhab eq to 6 $10^6$ inhab eq) and different treatment types (activated, sludge, Biostyr® Biological Aerated Filter) in the Seine River basin. Sampling and analysis protocols are provided in S5. This sampling did not allow us to highlight differences in per capita TA and DIC emissions. Consequently, we used a fixed value of 3993 µmol $L^{-1}$ for TA and 70 mgC $L^{-1}$ for DIC, which correspond to the weighted mean by WWTP capacity of our measurements and are in agreement with values from Alshboul et al. (2016) found in the literature.

### Impact of the ~~Point sources from~~ **reservoirs**

Nutrients and organic carbon cycling within the three reservoirs of the Seine River network were simulated using the ~~same~~ biogeochemical RIVE model adapted for stagnant aquatic systems (Garnier et al., 1999). ~~Despite~~ ~~Due~~Owing to the absence of an inorganic carbon module in the modeling of reservoirs yet, we used mean measurements of TA and DIC in reservoirs as ~~occasional inputs~~forcing variables to the river network. The Der lake reservoir was sampled three times (2016/05/24, 2016/09/12, 2017/03/16) and among others, TA and DIC were measured (see Table 3). Recent sampling campaigns showed that TA and DIC are similar for the three reservoirs (X. Yan, pers. comm.).

*Table 2 Summary of the carbon related inputs of the pyNuts-Riverstrahler model.*

| Input variables | Flow | Database | averaged | values | source |
|---|---|---|---|---|---|
| **DOC** | subsurface | AESN | land use | mean: 3.13 mgC $L^{-1}$; sd: 4.56 mgC $L^{-1}$; | http://www.eau-seine-normandie.fr/ |
| | groundwater | ADES | MESO units | mean: 0.91 mgC $L^{-1}$; sd: 0.8 mgC $L^{-1}$ | www.ades.eaufrance.fr |
| **POC** | subsurface | LUCAS, BioSoil and SoilTrEC Projects | based on estimated total suspended solids (TSS) fluxes, associated with a soil organic carbon (SOC) content | mean: 8.2 mgC $L^{-1}$, sd: 10.4 mgC $L^{-1}$ | (Aksoy et al., 2016) |
| | groundwater | | | mean: 0.8 mgC $L^{-1}$, sd: 1.0 mgC $L^{-1}$ | |
| **DIC** | subsurface | ADES | MESO units | from 25 to 92 mgC $L^{-1}$ | www.ades.eaufrance.fr |
| | groundwater | | | from 25 to 92 mgC $L^{-1}$ | |
| **TA** | subsurface | ADES | MESO units | from 663 to 5580 µmol $L^{-1}$ | www.ades.eaufrance.fr |
| | groundwater | | | from 663 to 5580 µmol $L^{-1}$ | |
| | | | | | |
| **DOC** | Point sources | Measurements | According to WWTP treatment and capacity | 2.9 to 9.4 gC $inhab^{-1}$ $day^{-1}$ | (Garnier et al. 2006; Servais et al. 1999) |
| **POC** | Point sources | Measurements | | 0.9 to 24 gC $inhab^{-1}$ $day^{-1}$ | |
| **DIC** | Point sources | Measurements | weighted mean by WWTP capacity | 70 mgC $L^{-1}$ | This study |
| **TA** | Point sources | Measurements | weighted mean by WWTP capacity | 3993 µmol $L^{-1}$ | This study |
| | | | | | |
| **DIC** | Reservoirs | Measurements in the Der Lake | by year | mean: 23 mgC $L^{-1}$, sd: 4 mgC $L^{-1}$ | This study |
| **TA** | Reservoirs | Measurements in the Der Lake | by year | mean: 1890 µmol $L^{-1}$, sd: 350 µmol $L^{-1}$ | This study |

## 2.2.3. Observational data

We selected the 2010–2013 timeframe for setting up and validating the new inorganic module. This period includes the year 2011, which was particularly dry in summer (mean annual water discharge at Poses, 366 $m^3$ $s^{-1}$) and 2013, which was wet (mean annual average water discharge at Poses, 717 $m^3$ $s^{-1}$) while 2010 and 2012 showed intermediate hydrological conditions (mean annual average water discharges at Poses, 418 $m^3$ $s^{-1}$ and 458, $m^3$ $s^{-1}$, respectively) (data source: Banque Hydro).

The $pCO_2$ values (ppmv) were calculated using CO2SYS software algorithms (version 25b06, Pierrot et al., 2006) based on existing data collected by the AESN. TA, pH, ~~total alkalinity~~ and water temperature data sets were used for the 2010–2013 selected period (8693 records ~~of~~

for these three variables, i.e., around 1209 stations distributed throughout the Seine basin, measurements that were taken at a fixed ~~day~~ time – 9:00-15:00 UTC–,~~)~~ and could not represent diurnal fluctuations). The carbonate dissociation constants (K1 and K2) applied were calculated from Millero (1979) with zero salinity and depending on the water temperature. Because $pCO_2$ calculations from pH and TA can lead to overestimation of $pCO_2$ (Abril et al., 2015), the $pCO_2$ calculated data were corrected by a relationship established for the Seine River and based on $pCO_2$ field measurements (Marescaux et al., 2018b). To compute the interannual average over the 2010–2013 ~~time~~ period, data were averaged monthly, then annually at each measurement station and then spatially averaged (i.e., by Strahler orders). Four stations offering sufficient data for the 2010–2013 ~~time~~ period were selected for appraising seasonal patterns. They are located along the main stem of the Marne-Lower Seine River: Poses (the outlet), Poissy (downstream of the SAV WWTP), Paris and Ferté-sous-Jouarre (upstream of Paris) (Figure 1a).

All data were processed using R (R Core team, 2015) and QGIS (QGIS Development Team, 2016). Kruskal-Wallis tests were used to compare simulated and measured $pCO_2$ averages.

#### 2.2.4. Evaluation of the model

Root m~~M~~ean s~~S~~quare e~~E~~rrors normalized to the range of the observed data (NRMSE) were ~~performed~~ used to evaluate the pyNuts-Riverstrahler model including the inorganic module, indicating the variability of the model results with respect to the observations, normalized to the variability of the observations. NRMSE analysis were performed on inter-annual variations per decade for the 2010-2013 ~~time~~ period, combining observations and simulations at four main monitoring stations along the longitudinal profile of the Seine River: Poses, Poissy (d~~D~~ownstream of Paris), Paris, and Ferté-sous-Jouarre (u~~U~~pstream of Paris).

# Results

## 3.1. Simulations of spatial and seasonal variations of $pCO_2$.

### 3.1.1. $CO_2$ from lower order streams to larger sections of the Seine River

Simulations of $CO_2$ concentrations averaged for 2010–2013 by Strahler orders showed that pyNuts-Riverstrahler succeeded~~s~~ in reproducing the general trends of $CO_2$ observations (7565 data) (Figure 4). Although differences in $CO_2$ concentrations between the different order streams were not significant, their means tended to decrease from ~~-~~lower order streams (SO1-) (width < 100 m) to SO5, and to finally increase in the higher order streams (width > 100 m) from SO6 to SO7, downstream of the Paris conurbation. Some discrepancy ~~appears~~ appeared for order 1, with simulations yielding higher values than the observations while for orders 2–7 simulation values~~s~~ were conversely lower than observation values~~s~~. The corresponding *k*-values calculated for the Seine ranged from 0.04 to 0.23 m $h^{-1}$ with higher values in the first streams and lower values in larger rivers (not shown), with $CO_2$ outgassing positively related to the *k*-value (S4.5 E~~e~~q. S25).

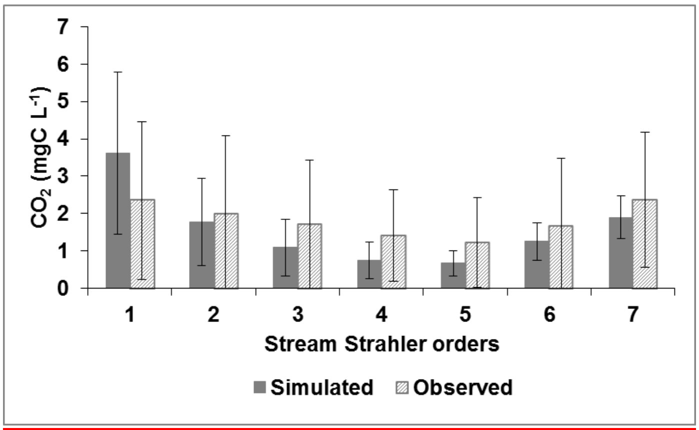


*Figure 4 Carbon dioxide concentrations in the Seine waters ($CO_2$, mg~~C-~~~~$CO_2$-~~C $L^{-1}$) simulated by the pyNuts-Riverstrahler model (dark ~~grey~~gray) and observed (light grey) as a function of the stream order averaged ~~on~~ over the 2010–2013 period (whiskers indicating standard deviations).*

### 3.1.2. Profiles of the main stem Marne ~~–~~and Lower Seine (at Poses)

~~On~~ In the same period (2010-2013), a focus on the main stem from the Marne River (SO6) until the outlet of the Seine River (Poses, SO7) showed that the model correctly reproduced longitudinal variations~~ are clearly represented by the model~~. Higher concentrations of $CO_2$ downstream of Paris, and a peak of $CO_2$ concentrations immediately downstream of the SAV WWTP were followed by a progressive decrease until the estuary (Figure 5). Note that the estuarine $CO_2$ concentrations were specifically modeled ~~in~~ by Laruelle et al. (2019), using these outputs of the Riverstrahler simulations.

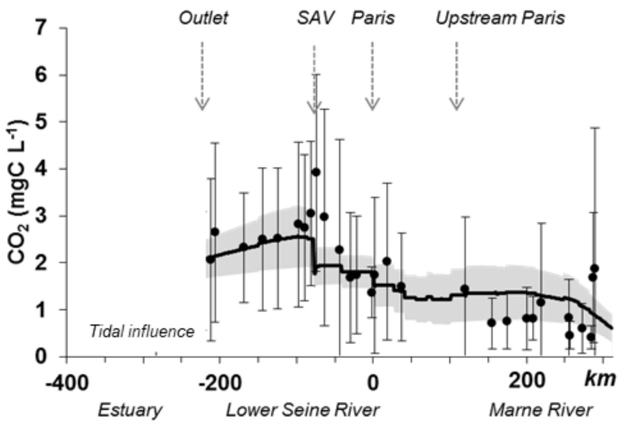



*Figure 5 Observed (dots) and simulated (line) mean carbon dioxide concentrations ($CO_2$, mgC $L^{-1}$) along the main stem of the Marne River (km −350 to 0) and the lower Seine River (km 0–350) averaged over the 2010–2013 period. The simulation envelope (~~grey~~ gray area) represents standard deviations of simulated $CO_2$ ~~simulated~~concentrations. Whiskers are standard deviations between observed $CO_2$ concentrations.*

### 3.1.3. Seasonal variations

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).

~~Upstream, within Paris, and downstream of Paris, simulations provided rather good levels of CO2, DIC, TA and pH (Figure 6). In addition to a satisfactory range of values, DIC and TA simulations showed 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 CO2 (Figure 4), CO2 highly varied seasonally (Figure 6). Although simulated CO2 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)~~.

For DIC, simulations upstream from Paris (Figure 6, right) seemed lower than the observations (but summer data are missing); however, downstream at the other three stations selected, simulations accurately represented the observations (Figure 6, NRMSE = 15%). Seasonal variations of TA were satisfactorily reproduced by the simulations, although they were slightly underestimated by the model at the stations upstream and downstream of Paris (Figure 6, NRMSE = 25%). Regarding pH, simulations were in a similar range as the observations (range, 7.5–8.5), and lower summer pH values in the lower Seine were correctly simulated by the model (Figure 6, NRMSE = 17%).

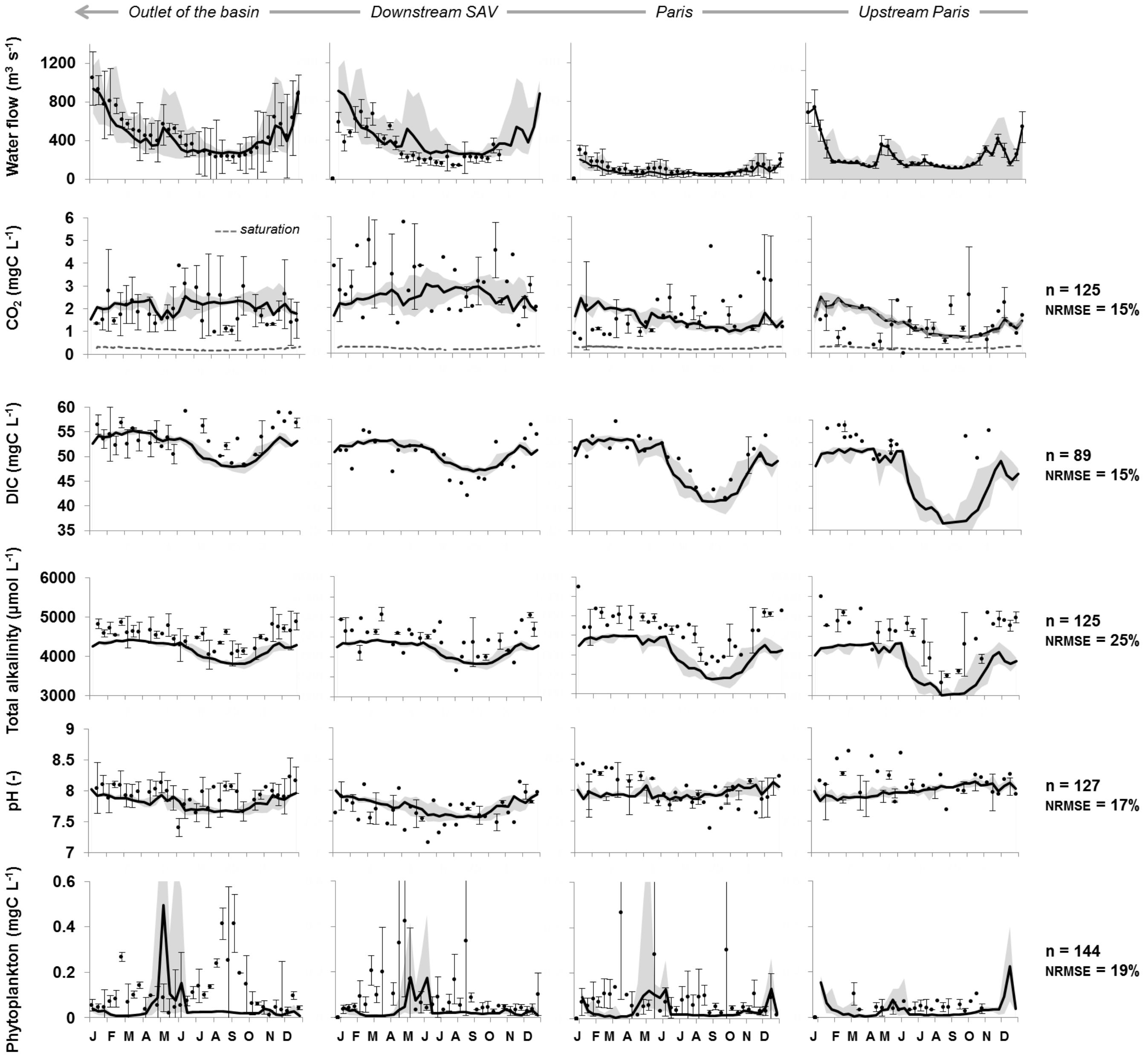



*Figure 6 Ten-day simulated (lines) and observed (dots) water discharges over the 2010–2013 period (Q, $m^3$ $s^{-1}$), concentrations of carbon dioxide ($CO_2$, mgC $L^{-1}$, and $CO_2$ sat, mgC $L^{-1}$), dissolved inorganic carbon (DIC, mgC $L^{-1}$), total alkalinity (TA, µmol $L^{-1}$), pH (-), and phytoplankton (mgC $L^{-1}$). ~~Simulation envelope corresponds to standard deviations. For observed data, whiskers are standard deviations.~~ Four monitoring stations of interest along the main stem of Marne-~~Poses~~ lower Seine are shown: Ferté-sous-Jouarre (upstream of Paris on the Marne River), Paris on the lower Seine (upstream at Charenton), downstream of the SAV WWTP, and at the outlet of the basin (Poses). NRMSE analysis were performed on inter-annual variations per decade for the 2010-2013 ~~time~~ period, combining observations and simulations at four main monitoring stations.*

*Simulation envelope corresponds to standard deviations (greay area). For observed data, whiskers are standard deviations.*.

Although the level of phytoplankton biomass was adequately simulated, the summer bloom observed at the outlet was not reproduced, whereas the early spring bloom observed in the lower Seine was simulated with a time lag compared to the observations (Figure 6, bottom, NRMSE = 19%).

### 3.1.4. Selection of a gas transfer velocity

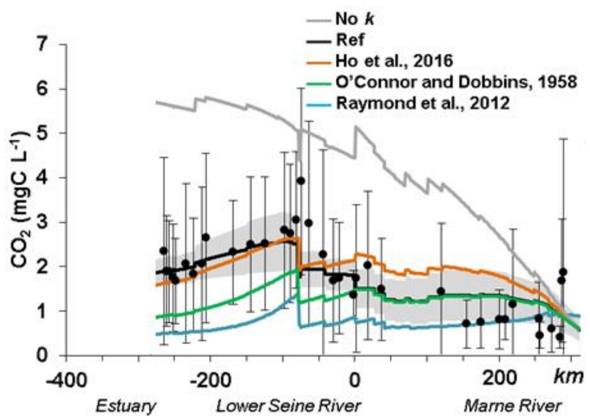



*Figure 7 Influence of the gas transfer velocity formalisms along the main stem of the Seine River basin (Marne – Lower Seine River) impacted riverine $CO_2$ concentrations.*

The way of taking into account the gas transfer velocity in the modeling approach could explain these discrepancies in SO6 and SO7 (Figure 4). 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). Indeed, the gas transfer velocity value reported by Alin et al. (2011) was used for streams and rivers up to 100 m wide, as they recommended. Whereas these *k*-values provided adequate simulations in the river up to 100 m wide, for river widths greater than 100 m, we tested different *k*-values. In larger stream orders, we showed that calculations of *k* according to the Eequation ~~5~~2 of Table ~~5~~2 ~~of~~ by Raymond et al. (2012), induced a too high outgassing while ~~without~~ when not using any *k*--value ~~or using Ho et al.~~

~~(2016)~~ for these larger rivers, the opposite behavior with a much too low outgassing of $CO_2$ was observed.

Therefore, for river widths greater than 100 m, a $k_{600}$ equation based on O'Connor and Dobbins, (1958) and Ho et al. (2016), neglecting the term related to the wind, and providing the most accurate $CO_2$ concentrations, was selected (see S3 ~~and S6~~ for more information's on the selection of $k$ and the tests performed):

Although these results can be improved, organic and inorganic carbon and total alkalinity budgets can be calculated at the scale of a whole drainage basin for the first time.

## 3.2. Alkalinity, inorganic and organic carbon budgets

We established an average inorganic and organic budget for the period studied (2010–2013) (Table 4). The budget of inorganic and organic carbon (IC and OC) of the entire Seine River basin (from headwater streams to the beginning of the estuary) ~~shows~~ showed the high contribution of external inputs (sum of point and diffuse sources accounted for 92% and 68% of IC and OC inputs, respectively) and riverine exports (68% and 66% of IC and OC outputs, respectively). These exports were at least one order of magnitude higher for the IC budget (Table 4). The substantial contribution of the Seine aquifer water flow led the IC flux brought by groundwater to dominate over those from the subsurface (respectively, 57.5% vs. 34% of total IC inputs, respectively), while for OC, the subsurface contributions were higher than the groundwater contributions (54% vs. 14% of the total OC fluxes).

Interestingly, the relative contributions of point sources to OC inputs were higher than for IC (23% and 7% of the OC and IC inputs, respectively) (Table 4).

Heterotrophic respiration by microorganisms accounted for only 1.5% of the IC inputs. Similarly, IC losses by net primary production also accounted for a small proportion, i.e., 0.6% of the IC inputs. For the OC budget, despite a contribution of autochthonous inputs from instream biological metabolisms (NPP and nitrification, 9% of inputs, and heterotrophic respiration, 7%), which was relatively high compared ~~to~~ with their proportion in IC fluxes (2.3%), allochthonous terrestrial inputs still dominated the OC budget (Table 4).

The Seine River, at the outlet, exported 68% of the IC entering or produced in the drainage network, and 66% of the OC brought to the river (including both particulate and dissolved forms) (Table ~~5~~4). Instream OC losses were related to heterotrophic respiration (7%) and to a net transfer to the benthic sediment compartment, including sedimentation and erosion processes (estimated at 28% of losses). In the IC budget, ~~ventilation of~~ $CO_2$ emissions w~~as~~ere a substantial physical process (31% of the overall losses) (Table 4).

A s~~S~~imilar calculation was performed for the total alkalinity (TA) budget. As for inorganic carbon, the contribution of internal processes remained relatively low compared ~~to~~ with the high levels of TA in lateral inputs (diffuse sources: 93 %; point sources: 6 %) and flows exported to the basin outlet (97 %). Indeed, instream production mostly relied on heterotrophic respiration (< 1%) while denitrification ~~appeared~~ was negligible. Photosynthesis might also produce or consume alkalinity whether $NO_3^-$ or $NH_4^+$ is the preferential N source of phytoplankton’s uptake, but in our budget it resulted in our budget in a net TA reduction ~~TA~~ (2%), while nitrification also contributed to less than 1% of TA output.

*Table 4 Budget of the Seine hydrosystem for inorganic and organic carbon (kgC km$^{-2}$ yr$^{-1}$) and ~~Total~~ total alkalinity (TA, mol km$^{-2}$ yr$^{-1}$) as calculated by the pyNuts-Riverstrahler model averaged ~~on~~ over the period 2010-2013. * TA input related to NPP refers to the net difference between TA produced by photosynthesis on $NO_3$ uptake and photosynthesis on $NH_4$ uptake (reducing alkalinity). **Net sediment loss is the difference between the erosion and the sedimentation calculated by the model.*

| 2010-2013 | **Processes involved in inorg C budget** | kgC km$^{-2}$ yr$^{-1}$ | % |
|---|---|---|---|
| **Input to river** | Diffuse sources from subroot | 5963 | 34.4 |
| | Diffuse sources from groundwater | 9968 | 57.5 |
| | Urban point sources | 1135 | 6.6 |
| | Heterotrophic respiration | 266 | 1.5 |
| | Denitrification | 0 | 0.0 |
| **Output from river** | Delivery to the outlet | 12483 | 68.4 |
| | ~~Ventilation~~ $CO_2$ emissions | 5619 | 30.8 |
| | Nitrification | 37 | 0.2 |
| | NPP | 105 | 0.6 |
| | | | |
| 2010-2013 | **Processes involved in TA budget** | mol km$^{-2}$ yr$^{-1}$ | % |
| **Input to river** | Diffuse sources from subroot | 360983 | *34.9* |
| | Diffuse sources from groundwater | 604145 | *58.4* |
| | Urban point sources | 66770 | *6.4* |
| | Heterotrophic respiration | 2972 | *0.3* |
| | Denitrification | 0 | *0.0* |
| **Output from river** | Delivery to outlet | 1004299 | *97.1* |
| | Nitrification | 6219 | *0.6* |
| | NPP * | 24352 | *2.4* |
| | | | |
| 2010-2013 | **Processes involved in org C budget** | kgC km$^{-2}$ yr$^{-1}$ | % |
| **Input to river** | Diffuse sources from subroot | 870 | 53.9 |
| | Diffuse sources from groundwater | 227 | 14.1 |
| | Urban point sources | 375 | 23.2 |
| | Nitrification | 37 | 2.3 |
| | NPP | 105 | 6.5 |
| **Output from river** | Delivery to the outlet | 1086 | 65.7 |
| | Heterotrophic respiration | 110 | 6.7 |
| | Net sedimentation ** | 456 | 27.6 |

## 3.3. Carbon aquatic processes

Whereas IC and OC budgets of the Seine hydrosystem were clearly dominated by external terrestrial inputs and outputs through deliveries at the coast, an attempt was made here to analyze instream processes involved in the IC and OC cycles (Figure 8, Figure 9).

The a~~A~~verage spatial distribution of IC processes, as calculated by the model, was mapped for the 2010–2013 period (Figure 8). Benthic activities were the greatest in smaller streams. ~~In~~ By contrast, net primary production and heterotrophic planktonic respiration, which both followed a similar spatial pattern, increased as Strahler order increased, reaching their highest values in the lower Seine River. All these biological processes involved in the IC cycle were therefore highly active in the main stem of the river, while on the other hand $CO_2$ outgassing ~~mainly~~ occurred mainly in the basin's small headwater streams (Figure 8~~9~~).

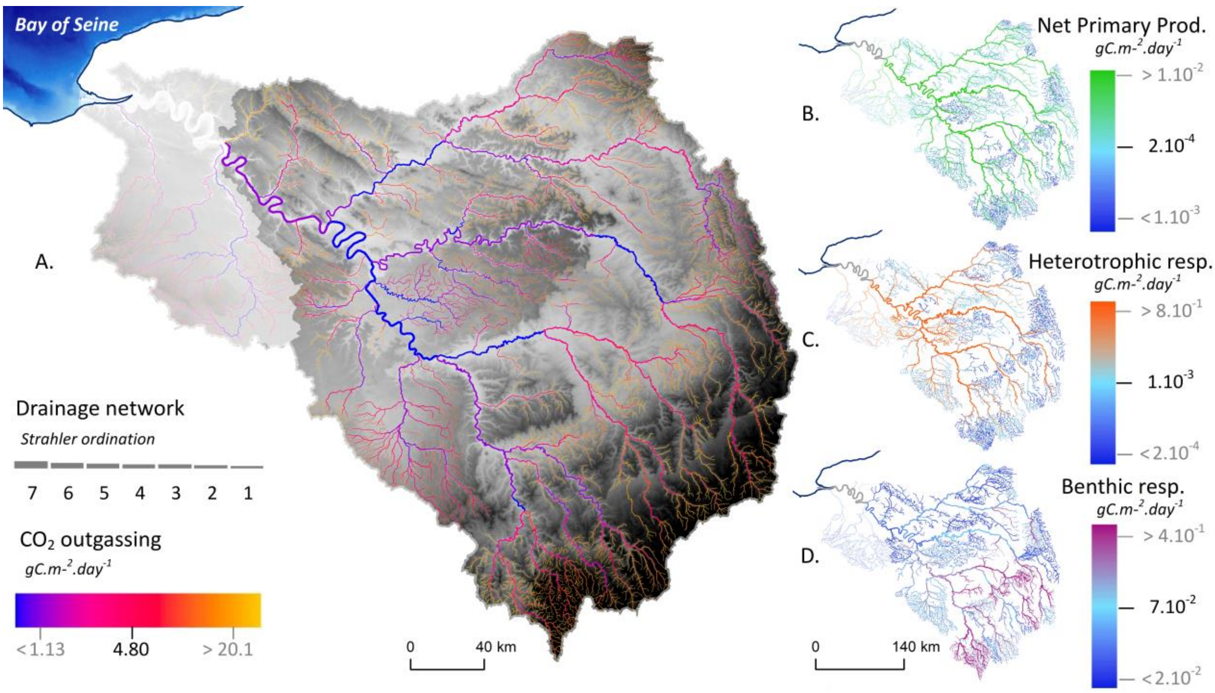



*Figure 8~~.~~ Instream processes involved in the inorganic carbon cycle simulated by pyNuts-Riverstrahler and averaged ~~on~~ over the 2010–2013 period for the ~~whole~~ Seine River network* *until its fluvial outlet at Poses~~-~~. a) $CO_2$ outgassing (blue–yellow, gC m$^{-2}$ day$^{-1}$); b) net primary production (blue–green, gC m$^{-2}$ day$^{-1}$); c) heterotrophic planktonic (blue–violet); d) benthic respiration (blue–orange, gC m$^{-2}$ day$^{-1}$) are represented in the hydrographic network.*

Regarding the OC processes, mostly linked to biological activity, they were analyzed in terms of ecosystem metabolism (Figure 9). The net ecosystem production (NEP, gC m$^{-2}$ day$^{-1}$) is defined as:

$$\text{NEP} = \text{NPP} - \text{Het. Respiration}$$

where NPP is the net primary production (gC m$^{-2}$ day$^{-1}$) depending on the growth of phytoplankton. NPP contributes to building phytoplankton biomass ~~building~~ that constitutes a stock of organic carbon, emitted in turn as $CO_2$ by respiration ~~-~~(Het. respiration, gC m$^{-2}$ day$^{-1}$).

Simulations showed that NEP would remain negative in the entire drainage network (Figure 9). However, NEP ~~has to~~must be analyzed with caution since the phytoplankton pattern was not adequately represented (see Figure 6). In SO1, this negative NEP was associated with almost no NPP, and heterotrophic respiration was dominated by benthic activities (see Figure 8). In SO5, NEP was less negative than in SO1 (Figure 9), and heterotrophic respiration was lower than in SO1 while NPP was higher. In the lower Seine River (SO7), NPP increased as ~~well as~~did heterotrophic respiration, which reached its highest value in this downstream stretch receiving treated effluents from WWTPs. Therefore, the increase in NPP did not result in positive NEP. The entire drainage network was thus supersaturated in $CO_2$ with respect to atmospheric concentrations, and constituted a source of $CO_2$. This supersaturation was the highest in smaller orders, lower in intermediate orders and increased again in the lower Seine River (Figure 4, see also Figure 8).

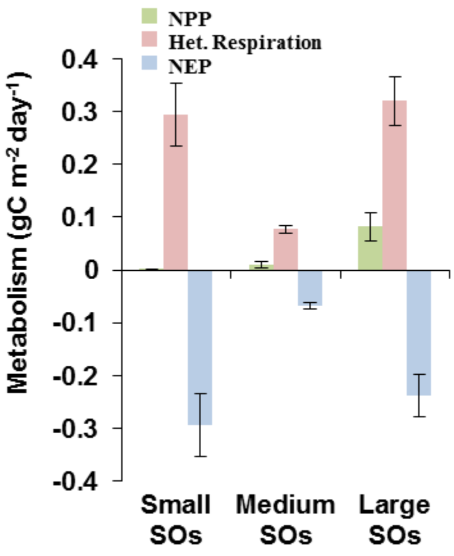



*Figure 9 Metabolism for small, intermediate and large stream orders (SO) (here ~~respectively~~ represented by SO1, SO5, and SO7, respectively) of the Seine basin simulated by pyNuts-Riverstrahler and averaged over the 2010–2013 period. Net primary production (NPP, gC m$^2$ day$^{-1}$), heterotrophic respiration (Het. respiration, gC m$^2$ day$^{-1}$), net ecosystem production (NEP, gC m$^2$ day$^{-1}$).*

# Discussion

## 4.1. Evaluation of the model

Simulated $CO_2$ concentrations tend to be higher than observed ones for SO1. These differences may be related to the high variability of $CO_2$ in SO1, and the scarcity of measurements in spring. However, Öquist et al. (2009) estimated that up to 90% of daily soil DIC import into streams was emitted to the atmosphere within 200 m. 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). ~~9)..~~ Since soil emissions were very difficult to capture, we considered that concentrations in groundwater (DIC and TA) closely reflect the composition of diffuse sources, much like soil composition. This assumption probably underestimates the DIC/TA ratio brought to the river in lower order streams. Differently from SO1, simulated concentrations in SO2–7 are lower than the observed values (Figure 4). Overall, the NRMSE indicating a percentage of variation was less than 20%, except for TA (25%).

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. However, the Riverstrahler model does not consider wind as an input variable, which would have required the model to have a much higher spatiotemporal resolution to reflect its spatiotemporal heterogeneity in the Seine basin, with for example, the diurnal cycle affected by phenomena such as breezes (Quintana-Seguí et al., 2008). ~~tindeed diding~~

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 result~~-~~s of~~by~~ Lauerwald et al (2007), who observed that a large variation ~~of~~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~~ing with~~to simulations on a natural network (Lauerwald et al., 2007).

Regarding seasonal patterns, DIC and alkalinity amplitudes ~~are~~ were suitably captured and the level of the values was correct. DIC and TA observations showed a strong decrease from June/July to November (maximum amplitude decrease, 10 mgC $L^{-1}$ and 1000 µmol $L^{-1}$), as illustrated by the model. For the Seine River, the water flow decrease in summer was mainly related to the decrease in runoff water, meaning that the groundwater contribution was comparatively higher at this time. According to our measurements, these groundwaters were more concentrated in TA, DIC, and $CO_2$ than runoff water. However, water released by upstream reservoirs (supporting low flow in the downstream section of the Seine network) account~~ed~~ for a significant proportion of the river discharge during summer and was characterized by lower TA, DIC and $CO_2$ concentrations. Then the decrease observed was related to the contribution of reservoirs. These results strongly encourage the implementation of an inorganic carbon module in the modeling of reservoirs, already coupled with Riverstrahler for nutrients and organic carbon (Garnier et al., 1999).

The model showed a weak performance ~~to~~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. However, it is worth mentioning that phytoplankton parameters in RIVE were determined through laboratory experiments at a time when the amplitude of algal blooms w~~ere~~as much higher than at present~~ly~~ (up to 4.5-6 mgC $L^{-1}$ i.e., chlorophyll *a* reaching 150 µgChla $L^{-1}$, Garnier et al., 1995). Indeed, the implementation of the European Water Framework Directive in the 2000s with ~~improvement~~enhancement of treatments in WWTPs ~~strongly~~greatly improved water quality (Romero et al., 2016). New laboratory experiments for possibly taking into account additional phytoplankton groups or species in these new trophic conditions and/or mixing stochastic and mechanistic modeling ~~could be~~are required to better represent phytoplankton temporal dynamics in the model. In addition, the observed incident light, instead of the empirical relationship used, would improve the early winter bloom, newly occurring in a changing environment.

~~For phytoplankton, although the biomass level is consistent with the observations, the seasonal pattern was not satisfactory reproduced by the model. However, algal blooms has been considerably reduced compared to those observed in the 1990s when chlorophyll a reached 150 µgChla L$^{-1}$ (Garnier et al., 1995). The RIVE model phytoplankton parameters were determined through laboratory experiments at that time when amplitude algal blooms were much higher than presently, after improvement of treatments in WWTPs strongly reducing river eutrophication (Romero et al. 2016). New laboratory experiments for possibly taking into account additional phytoplankton groups or species in these new trophic conditions and/or mixing stochastic and mechanistic modeling could be required to better represent phytoplankton temporal dynamics in the model. In addition, in future work, testing different pH calculation formulations (e.g. using Follows et al., 2006) could improve our pH simulations~~

## 4.2. Export fluxes

The new implementation of an inorganic carbon module in the pyNuts-~~Riverstrahler~~ Riverstrahler model allows us to estimat~~ing~~e $CO_2$ outgassing of the Seine River at 364 ±

~~100~~ 99 GgC $yr^{-1}$ ) (1.4 GgC $km^{-2}$ $yr^{-1}$ ~~from~~ taking into account a river surface area of 260 $km^2$). This is significantly lower than in our previous estimate of 590 GgC $yr^{-1}$ (2.2 GgC $km^{-2}$ $yr^{-1}$ from a river surface area of 265 $km^2$) using $CO_2$ measurements only ~~-~~(Marescaux et al., 2018a). This difference is explained by ~~different~~various factors. Marescaux et al (2018a) use *k* formulates according to Raymond et al. (2012, Eq. 5 in Table 2) all along the Seine drainage network and consequently, the ~~estimatio~~value ~~n~~ of $CO_2$ emissions was most likely overestimated (see 4.1. Evaluation of the model). We also acknowledged that the $CO_2$ outgassing estimate yielded by simulations might overall slightly underestimate emissions with respect to Figure 4, which showed that our simulated $CO_2$ concentrations were overestimated for SO1 but underestimated for SO2 to SO7. In the model, a better spatio-temporal resolution and description of the water temperature, the water velocity and a more accurate description of the *k*-value adopted here with different *k*-values for small and high stream orders would be ~~responsible for~~associated with less outgassing than in our previous study. For this reasons, we believe that our estimate of 364 ± 99 GgC/yr, using our process based model ~~would~~ is a more accurate value of $CO_2$ emissions from the Seine River.

~~This flux estimation difference could be also due to the fact that, in this previous study, we used the same *k*-value for all stream orders based on Eq. 5 in Table 2 in Raymond et al. (2012). The more accurate description of the *k*-value adopted here with different *k*-values for small and high stream orders would be responsible for less outgassing than in our previous study.~~

The outgassing found for the Seine River by surface area of river of 1400 ± 381 gC $m^{-2}$ $yr^{-1}$ is in the middle ~~of the~~ range of the average estimates of outgassing from temperate rivers (~~from~~ 70 ~~to~~ -2370 gC $m^{-2}$ $yr^{-1}$), including the St. Lawrence River (Yang et al., 1996), Ottawa River

(Telmer and Veizer, 1999), Hudson River (Raymond et al., 1997), US temperate rivers (Butman and Raymond, 2011) and Mississippi River (Dubois et al., 2010).

~~shows lower rates (from 70 to 1284 gC m$^{-2}$ yr$^{-1}$) than in the Seine River~~. This high variability for these temperate rivers is ~~highly~~ strongly dependent on whether or not the first-order streams were considered in the outgassing. Similar to our study, Butman and Raymond (2011) took into account lower order streams and rivers while lower estimates correspond to studies investigating large rivers, excluding lower order streams. ~~$CO_2$ concentrations (see Figure 2).~~ Indeed, outgassing are often greater in headwater streams than in large rivers ~~due~~ owing to higher $CO_2$ concentrations and headwater streams have higher gas transfer velocities (Marx et al., 2017; Raymond et al., 2012a). The mapping of $CO_2$ outgassing in the Seine basin clearly ~~shows~~ showed these spatial trends, with smaller streams releasing more $CO_2$ than median and larger rivers (see Figure 8). Indeed, first-order ~~rivers~~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.

Regarding organic carbon, Meybeck (1993) estimated the DOC export to the ocean for a temperate climate at 1.5 gC m$^{-2}$ yr$^{-1}$, a value that is higher than our OC estimate of 1.1 gC m$^{-2}$ yr$^{-1}$ for the Seine River basin, before entering the estuarine section. Compared ~~to~~ with other temperate rivers, the rivers of the northern ~~of~~ France, and specifically the Seine River here, are rather flat, their low altitude limiting erosion (Guerrini et al., 1998). In addition, since the implementation of the European Water Framework Directive in the 2000s, decreasing nutrients and carbon in wastewater effluents discharged into the rivers (Rocher and Azimi, 2017), together with a decrease in phytoplankton biomass development (Aissa Grouz et al., 2016; Romero et al., 2016) can explain this difference in DOC fluxes for the Seine, a change probably valid for many other western European rivers (Romero et al., 2013). ~~3). This might~~

~~be explained by the low altitude of the Seine River, limiting erosion (Guerrini et al., 1998; ) and by the change in the trophic state of rivers after the implementation of water directives in the late 1990s Rocher and Azimi, 2017; Romero et al., 2016)~~. ~~In addition~~Furthermore, the $CO_2$/OC ratio of the export to the estuary of the Seine hydrosystem is 5.2, which is higher than this ratio for the Mississippi River, for example (4.1; Dubois et al., 2010b; Li et al., 2013)~~, for example,~~ and may be related to considerable outgassing from headwater streams taken into account in our study. Note, however, that the small Seine River basin exports only 70 ± 99 GgC $yr^{-1}$ OC compared ~~to~~ with the large Mississippi River with exports amounting to 2435 GgC $yr^{-1}$ OC (Dubois et al., 2010), and with ~~its~~ a surface area more than 40 times greater than the Seine. Interestingly, the Seine River export ~~is~~ was estimated at three times less than the export calculated in 1979 (250 Gg C $yr^{-1}$ , Kempe, 1984). This difference ~~must be related to improvements in water treatments in the basin, within~~in DOC concentrations in the Seine River would be 2.8 times lower ~~since~~ than in the 1990s (Rocher and Azimi, 2017). ~~and to a remarkable reduction in phytoplankton blooms (Aissa Grouz et al., 2016).~~

We estimated the DIC export of the Seine River at 820 ± 220 GgC $yr^{-1}$, a value higher than basins of the same size or even larger (e.g., Ottawa River, drainage are, 149,000 $km^2$, 520 GgC $yr^{-1}$ , Telmer and Veizer, (1999); Li et al. (2013)). The high concentrations of $HCO_3^-$ in the Seine basin already documented and related to the lithology of the Seine basin (limestone and gypsum beds from Cretaceous and Tertiary) (Kempe, 1982; 1984) may explain this high export to the river outlet. With both high $CO_2$ and DIC exports, the ratio of $CO_2$/DIC exports from the Seine River is ~~here~~ the same as the overall ratio here (0.5, Li et al., 2013).

## 4.3. Metabolism

Model simulations with the new inorganic carbon module can be used to analyze spatial variations of $CO_2$ in regard to instream metabolism activities. We observe that the influence of the metabolism activities on the $CO_2$ outgassing is low. Indeed, in the carbonated Seine River, the IC originating from groundwater supports the $CO_2$ outgassing along the network (Figure 8). Nevertheless, instream metabolism activities produce or consume $CO_2$.

The model highlights the importance of benthic activities in headwater streams (Figure 8) that decreased downstream as heterotrophic planktonic activities increased in larger rivers, a typical pattern described by the river continuum concept (RCC, Vannote et al., 1980) and quantified for the Seine River (Billen et al., 1994; Garnier et al., 1995; Garnier and Billen, 2007). These results are also in agreement with those reported by Hotchkiss et al. (2015), ~~which~~ who suggested that the percentage of $CO_2$ emissions from metabolism increases with stream size while $CO_2$ emissions of lower-~~-~~order streams ~~were~~ are related to allochthonous terrestrial $CO_2$. Regarding headwater streams, Battin et al. (2009b) described benthic activities as the highest (as also observed in our study, Figure 8) where microbial biomass is associated with streambeds characterized by exchanges with subsurface flow bringing nutrients and oxygen and increasing mineralization.

Mean NEP would remain negative in the entire basin resulting from heterotrophic conditions producing $CO_2$ (Figure 8 and Figure 9). However, even though the level of phytoplankton biomass was correctly simulated, the summer downstream bloom, which was not reproduced by the model, could lead to some NPP underestimation. As expected, NPP in lower order streams was lower than in higher SOs ~~due~~ owing to shorter water residence times. Benthic respiration of lower order streams was significant (Figure 8~~9~~) and made NEP highly negative. Also, small SOs were the most concentrated in $CO_2$ ~~due~~ owing to the groundwater contribution. Intermediate stream orders showed the smallest $CO_2$ or heterotrophic respirations with NEP less than −0.1 gC m$^{-2}$ day$^{-1}$. This can be explained by an increase of NPP due to a lower dilution rate than the phytoplankton growth rate (Garnier et al., 1995), and to a reduced ratio of the bottom sediment-~~-~~to-~~-~~water column volume, decreasing heterotrophic respiration. In higher stream orders both NPP and heterotrophic respiration were the highest, however, they led ~~leading~~ to negative NEP lower than SO1 (Figure 8 and Figure 9). Despite photosynthesis ~~reduced~~ reducing the $CO_2$ concentrations (Figure 6), the highest SOs were affected by wastewater effluents, resulting in an overall negative NEP.

~~On~~ During the recent 2010–2013 period studied herein, and in all SOs, the NPP never exceeded heterotrophic respiration (ratio NPP:Het.-Resp or P:R < 1) (Figure 9). Whereas in the past~~,~~ the eutrophication of the Seine River led to a P:R ratio ~~above~~ greater than 1 in large rivers, at least during spring blooms, with P and R values increasing up to 2.5 gC $m^{-2}$ $day^{-1}$ (Garnier and Billen, 2007), the P:R ratio is now systematically ~~below~~ lesser than 1. These changes, linked to an overall decrease in biological metabolism, are explained by ~~the~~ improvements of treatments in WWTPs decreasing the organic carbon load discharged into rivers and the associated pollution, and hence decreasing the $CO_2$ concentration along the main stem of the Seine River (Marescaux et al., 2018b). Beside DOC, i~~I~~mprovements ~~of treatments in~~ wastewater treatments also reduced nutrient inputs to the river, especially phosphates, today a limiting nutrient to algal development in SO5 and 6, reducing algal peaks ~~from 150 µgChla $L^{-1}$ in the 1990s to often less than 50 µgChla $l^{-1}$ presently (Romero et al., 2016; Aissa-Grouz et al., 2016).~~ by a factor of 3~~three~~.

## Conclusion

The pyNuts-Riverstrahler model of biogeochemical river functioning ~~pyNuts-Riverstrahler~~ newly includes ~~The first simulations with~~ t~~The~~ ~~model of river biogeochemical river functioning pyNuts-Riverstrahler model newly including includes~~ the processes involved in the inorganic carbon cycle in order to represent the spatial dynamics and seasonal variations of $CO_2$ concentrations and outgassing along the Seine hydrosystem.~~, and represents the $CO_2$ concentrations and outgassing along the Seine hydrosystem quite accurately.~~

The sensitivity of simulations to different gas transfer velocity values highlighted the need for additional ~~measurements~~ refinement ~~in~~ for the Seine River so as to choose the best model equation~~ or to propose a new one~~. In addition, revisiting the phytoplankton description in the model could ~~enable~~ facilitate a better simulation of the temporal dynamics of phytoplankton. ~~In the future~~Further, an explicit representation of the anaerobic reduction chain of the benthos could enable us to specify the benth~~os~~ic impact on TA and DIC in a greater variety of ecosystems.

$CO_2$ concentrations appear to be controlled differently along the Seine hydrosystem. In small orders, concentrations were mainly driven by ~~groundwater discharges~~diffuse sources. In larger rivers, in addition to the influence of groundwater and low-flow support by upstream reservoirs, concentrations showed patterns linked to hydrosystem metabolisms. Indeed, blooms tended to decrease $CO_2$ concentrations, although the hydrosystem ~~remains~~ remained heterotrophic and supersaturated with respect to the atmospheric $CO_2$ concentrations. Heterotrophic respiration increased $CO_2$ concentrations with peaks downstream of WWTP effluents enriched in organic carbon.

Around 31% of the DIC inputs, widely dominated by soils, groundwater and/or WWTP effluents, are outgassed, while 68% are exported to the estuary. IC inputs and outputs are estimated at ~~ten~~ 10 times the OC inputs and outputs.

## Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

## Author contribution

All the authors contributed to the design of the study. J.G. and V.T. are co-supervisors of the PhD. A.M. participated as a PhD student in the field campaigns, lab chemical analyzes and implementation of the new inorganic carbon module. N.G. and M.S. provided technical and scientific support for the modelling. A.M. wrote the first draft of the manuscript, and all the co-authors helped to interpret the data and write the article.

## Competing interests statement

The authors declare no competing financial or non-financial interest.

## Acknowledgments

The project leading to this application received funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 643052. A PhD grant was attributed to Audrey Marescaux. Many thanks are due to Sébastien Bosc, Anunciacion Martinez Serrano and Benjamin Mercier for their kind participation in the fieldwork and for their assistance with chemical analyses in the lab. We thank Muriel Chagniot (Veolia Water, France), and the operators of the Veolia WWTPs for their precious help in organizing the field campaigns. The SIAAP (Vincent Rocher) is also sincerely acknowledged for their contribution to sampling the largest WWTP of the Paris

conurbation and the long-term view on treatments in the SIAAP WWTPs provided by their recent book (Rocher and Azimi, 2017). Vincent Thieu (assistant professor at the University Pierre and Marie Curie, Paris) and Josette Garnier (Research Director at the Centre National de la Recherche Scientifique, France) are co-supervisors of the PhD. Nathalie Gypens is Professor at the Université Libre de Bruxelles (Belgium). Marie Silvestre is GIS Engineer at the Centre National de la Recherche Scientifique (France).

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