Response to anonymous 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.

Although the manuscript has been already revised by a professional English native person, we submitted the revised manuscript for another 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: “T*he most significant outgassing was in lower order streams while peaks were simulated downstream of the major wastewater treatment effluent.*” [L32-34]

’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 pCO2 (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.

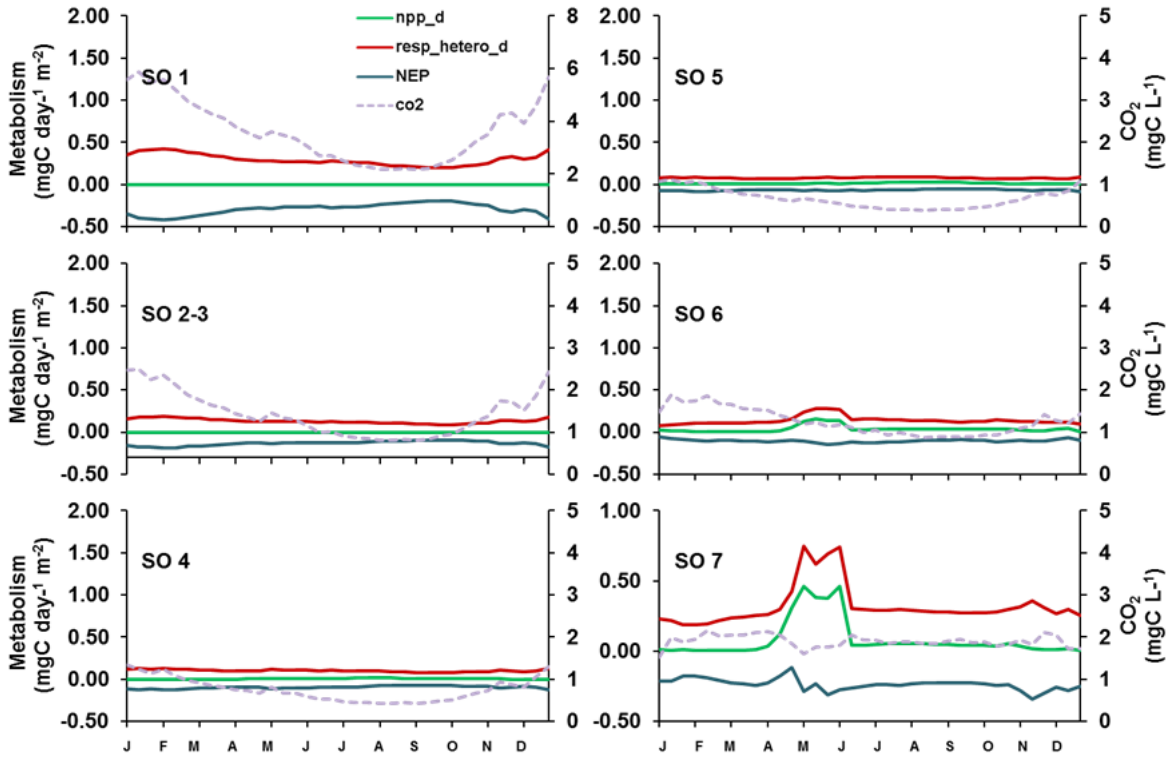
A13. The whole paragraph has been reorganised:

"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].

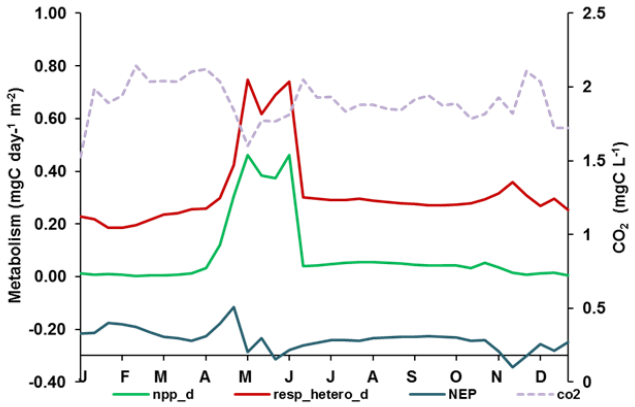
Line 624: left bracket is missing in citation;
A14. Thanks, we added it.

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]