Response to anonymous 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

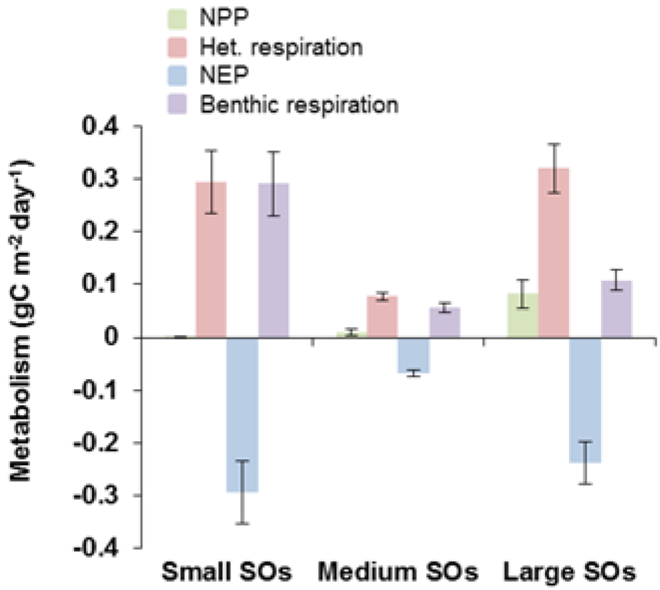
A25. Corrected !

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.