

Interactive comment on “Modeling inorganic carbon dynamics in the Seine River continuum in France” by Audrey Marescaux et al.

Anonymous Referee #2

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

Major comments:

#1: Writing

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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.

#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 your model, to see which ions are actually taken into account. Last but not least, I find it very strange that you report TA in $\mu\text{mol L}^{-1}$, and not in $\mu\text{eq L}^{-1}$ like it is normally done.

#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

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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).

#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

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in the water column). Similarly, when a too high k is chosen, the total CO₂ emission 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?

When comparing to your earlier study to estimate the CO₂ emissions from the Seine (e.g. L607-611), you should also discuss the estimate total river surface area as source of uncertainty. Similar to k , this uncertainty won't significantly affect your simulated total CO₂ emission. However, when you calculate the CO₂ emission rate per water surface area from your simulation results, the uncertainty related to river surface area estimate does have a direct and proportional effect on the uncertainty of emission rates. That means in this case, if the simulated CO₂ emission rate per water surface area is too high, this is maybe because your estimate of the total stream surface area is too low!

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?

L20: Remove the commata around pyNuts-Riverstrahler

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

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

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

L25: Remove “In average,”.

L26: WWTP has not been defined.

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

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?).

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”.

L64: Delete “sources”!

L67-69: That doesn't make any sense.

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

Materials and methods

L111: Degree signs needed.

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

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

L216-219: You state that you could use two variables, DIC and TA, to calculate all other

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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.

L229: “CO₂ gradient concentrations” should be “CO₂ concentration gradients”

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.

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

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.

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

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 mean μeq L⁻¹? Also, you should report DIC in μmol L⁻¹ to be consistent, even if you report alkalinity in μeq L⁻¹ (which you definitely should!).

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

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

Results

L420: What do you mean by “good levels”?

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.

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.

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>.

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.

L492-493: I assume that “ventilation” means CO₂ emissions from water surface. Any-

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way, you should use a more consistent terminology to not confuse the reader.

Discussion

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

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.

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.

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.

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.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2019-601>, 2019.

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