

## Authors response

Dear editor, we would like to thank you for bringing the concerns of both referees on our revised manuscript. Also we would like to acknowledge you for bringing new suggestions which we think will help us to improve the quality and the readability of our manuscript. We answer the new concerns raised by referee #1 and 2 below.

We applied the following colour code in our response: Editor's comments are cited in **black** and referees' comments are cited in **blue**. Modifications in the manuscript are written in **pink**.

**1) Referee 1 has raised a small number of typos and minor clarifications. One point they raise that I would also be interested in hearing a response to is the runtime of your model – it does seem very slow for a 0D model, and it would be of interest to understand if there's an explanation for that.**

We took into account all the corrections suggested by Julien Palmieri. Concerning the runtime of our model, it is approximately between 45 and 50 minutes. This estimation includes compilation time (about 5 minutes), calculation time (about 40 minutes) and results files copy to a processing directory (about 2 minutes). It is important to note that Eco3M\_MIX-CarbOx is particularly complex, even in 0D as it includes an important number of variables (37), a high number of processes (646) and it produces multiple result files (one for each type of state variables, a file in which biogeochemical fluxes between state variables are detailed, and some diagnostic files in which organisms limitations and values of carbonate system variables other than the four main ones are detailed) which can explain that the model has such a long runtime.

However, we made these assessments for a run of the model performed sequentially on the "Cluster de calcul de l'institut OSU Pytheas". We do not exclude that run the model using another cluster can slightly modify this estimation.

**2) As you will see, they have also asked about the availability of the model code, but I have already appraised them of its availability via Zenodo.**

Thank you for this. Indeed, the version of Eco3M\_MIX-CarbOx 0D used in this study is available and downloadable on Zenodo website. We provided a link to the corresponding webpage in the section CODE AVAILABILITY, at the end of our manuscript.

---

**3) Referee 2 has made a several suggestions for further revision that are relatively limited in scope and that I think would improve your final manuscript. Points #2 and #3, in particular, should be addressed :**

**Point #2 : My second comment was on the lack of consistency in the treatment of Alkalinity and DIC (and as later mentioned also nutrients), when effect of Rhone water intrusions on alkalinity is modelled with a salinity-alkalinity relationship. I don't buy the argument that the inputs of DIC and nutrients from Rhone water are 'diluted', as stated in the author's reply, because dilution acts equally on DIC, Alkalinity and nutrients. But I see the point that, while alkalinity is mainly affected by freshwater fluxes, DIC and nutrients are much stronger affected by biological uptake, and DIC additionally by air-sea gas exchange, so that the riverine signal can be lost before the intrusion reaches the modelled site. That this is probably case is shown by the authors by referring to data. The authors should nevertheless**

probably replace the erroneous explanation by 'dilution' from their modified manuscript in this part ("which means that these values are significantly diluted before reaching SOLEMIO"), as it cannot be the physical process of dilution, which would equally dilute the alkalinity signal.

We agree that the word diluted was inappropriate in our revised manuscript. As suggested, we replaced (l.578) : [For the studied events, linking measured surface salinity to measured DIC (Appendix E) showed that the four events are not systematically associated to a DIC increase at SOLEMIO even though the Rhône River mouth DIC value ( $2877 \mu\text{mol kg}^{-1}$ , value calculated by using TA and pH from Schneider et al. (2007) and Aucour et al. (1999) respectively) is much higher than the mean value at the station ( $2294.9 \mu\text{mol kg}^{-1}$ ) which means that these values are significantly diluted before reaching SOLEMIO.] by : [For the studied events, linking measured surface salinity to measured DIC (Appendix E) showed that the four events are not systematically associated to a DIC increase at SOLEMIO even though the DIC value obtained at the Rhône River mouth ( $2877 \mu\text{mol kg}^{-1}$ , value calculated by using TA and pH from Schneider et al. (2007) and Aucour et al. (1999) respectively) is much higher than the mean value at the station ( $2294.9 \mu\text{mol kg}^{-1}$ ). Based on this observation, we can assume that, for DIC, the riverine signal is quickly lost when moving away from the Rhone River mouth and is not reaching SOLEMIO station. Contrary to TA which is mainly affected by Rhone River inputs in the area, DIC is impacted by air-sea  $\text{CO}_2$  exchanges and biological processes which can explain this pattern.]

**Point #3: Concerning my comments on choosing an arbitrary volume of 1 cubic metre as modelling domain (which was also a major criticism by referee 1), I am happy to see that the authors have made an additional run using a fixed water column of the average depth of the mixed layer at the site. While this is still a step away from using a seasonally varying mixed layer, it at least removes a systematic bias in the relation between the air-sea flux and the change of DIC concentration. I must, however, say that I probably would then have simply replaced all model runs with that choice, rather than treating it as a further sensitivity study, buried in the appendix, given that it leads to a somewhat better annual air-sea flux in the model.**

We understand that treating this run as a further sensitivity study and, therefore, placing it in supplementary material can be a bit frustrating for the reader. We considered other ways to integrate it to the manuscript and at the end, we chose to do as it because, to us, it is the easiest and most suitable way to integrate this run within the manuscript. We considered to replace our reference simulation by this one, as you suggested it above and, in your recommendation, however this replacement would result in several changes. To be consistent, it would require to re-do all the other runs to modify the considered layer thickness and consequently, re-do the entire study to consider these new simulations (statistical indicators calculation,  $\Delta p\text{CO}_2$  decompositions, simulations comparisons). We think that it represents a lot of work for a result which is still quite far from what is observed in the literature since the main problem of OD comes from the fact that, as you specify it in the following, we do not consider all the processes that impact the fluxes in the water column.

**This however, brings me to a weak point of the study that I had somehow overlooked in my last review: I had not realized that the model is indeed completely closed in its nutrient inventory in the model box, because it neglects sinking out of organic matter; everything produced is remineralized there. I am pretty sure that this is the reason that even with assuming a deeper box the model fails to represent the overall annual air-sea flux of carbon**

at the station: What happens in reality is very likely that over summer a negative  $p\text{CO}_2$  difference to the atmosphere is maintained because the biomass that was build up is at least partially exported before being remineralized. During winter mixing then, higher DIC and nutrient concentrations are entrained back into the surface layer. Without these vertical fluxes it is no wonder that  $p\text{CO}_2$  can always stay close to equilibrium. The simplest way how that effect could be implemented into the model would be to assume the mixed layer to be homogeneous but allow mixed layer depth to vary; deepening of the mixed layer then leads to entrainment of water (with DIN and DIC) from below, while shallowing leads to no concentration change. And then also to allow sinking, i.e. loss of organic matter. Such a model setup has been done e.g. for the BATS station, in a paper, I think by Scott Doney in the early nineties, I didn't find it quickly, though.

We understand your concerns but, as we specified it in our previous response, in this study we relied on Eco3M-CarbOx (Lajaunie-Salla et al., 2021) for the calculation of carbonate system variables. We used this model as a starting point to implement them in Eco3M\_MIX-CarbOx and then, bring some answers to the concerns raised by the previous study. By using the same concept in both studies (a closed volume of water of  $1\text{m}^3$  at the surface), we were able to compare the results of both models consistently. Even if we did not manage to obtain a realistic annual mean value and seasonality of air-sea  $\text{CO}_2$  fluxes, the model still manages to provide a good representation of the carbonate system variables.

Correct this pattern by using the method you proposed above requires a complete review of our OD configuration. As specified in our previous response, we decided to focus directly on the coupling of Eco3M\_MIX-CarbOx, in 3D to obtain a better representation of air-sea  $\text{CO}_2$  fluxes by considering all types of processes which occur in the water column, especially vertical mixing and matter transfer to the bottom of the water column.

**I do not argue that the authors have to do that; but if they don't, they should probably acknowledge that it is impossible with their model to represent the annual cycle of air-sea  $\text{CO}_2$  flux, although the model might still get the carbonate system in the water approximately right.**

We agree with that. Even if we somewhat approach this subject, it must be stated in a clearer way. Consequently, we added in the discussion section (l.657): [In fact, to represent the air-sea  $\text{CO}_2$  fluxes, especially their annual mean value in a more realistic way, we must consider, on the one hand, a realistic volume of water on which the aeration process is applied and on the other hand, all the processes that take place in the water column and impact this flux, **especially vertical mixing and matter transfer to the bottom of the water column. Consequently, in the present state, Eco3M\_MIX-CarbOx is unable to represent the annual cycle of air-sea  $\text{CO}_2$  fluxes.** Overcoming this problem requires the switch to a 3D configuration, which is planned for our future work.]

We also specified it in the conclusion by changing the sentence (l.697): [However, in winter, the model was unable to reproduce the undersaturation seen in seawater  $p\text{CO}_2$  measurements at SOLEMIO station and rather overestimate it. As a result, the commonly observed seasonality of air-sea  $\text{CO}_2$  fluxes in the north-western Mediterranean was not reproduced by our model which directly impacted our estimates of the overall yearly air-sea  $\text{CO}_2$  flux. While correctly identifying the BoM as an overall sink of  $\text{CO}_2$ , our model significantly underestimated the magnitude (our model :  $-0.21 \text{ mmol m}^{-2}$  per year,

Wimart-Rousseau et al., (2020):  $-803 \text{ mmol m}^{-2}$  per year).] to: [However, in winter, the model was unable to reproduce the undersaturation seen in seawater  $p\text{CO}_2$  measurements at SOLEMIO station and rather overestimate it. **As a result, the present configuration of Eco3M\_MIX-CarbOx is unable to reproduce the commonly observed seasonality of air-sea  $\text{CO}_2$  fluxes in the north-western Mediterranean. This pattern directly impacts our estimates of the overall yearly air-sea  $\text{CO}_2$  flux, as, even if the model clearly identifies the bay as a  $\text{CO}_2$  sink, it does not allow to reproduce the observed mean annual value of air-sea  $\text{CO}_2$  fluxes (our model :  $-0.21 \text{ mmol m}^{-2}$  per year, Wimart-Rousseau et al., (2020):  $-803 \text{ mmol m}^{-2}$  per year).]**

And in the abstract by changing (l. 23): [While our model was able to correctly represent the daily range of air-sea  $\text{CO}_2$  fluxes, we were unable to correctly estimate the yearly total air-sea  $\text{CO}_2$  flux. Although the model - consistent with observations - predicted the BoM to be a sink of  $\text{CO}_2$  on a yearly basis, the magnitude of this  $\text{CO}_2$  sink was underestimated which may be an indication of the limitations inherent in dimensionless models for representing air-sea  $\text{CO}_2$  fluxes.] to: [While we were able to correctly represent the daily range of air-sea  $\text{CO}_2$  fluxes, the present configuration of Eco3M\_MIX-CarbOx does not allow to correctly reproduce the annual cycle of air-sea  $\text{CO}_2$  fluxes observed in the area. This pattern directly impacts our estimates of the overall yearly air-sea  $\text{CO}_2$  flux, as, even if the model clearly identifies the bay as a  $\text{CO}_2$  sink, its magnitude was underestimated which may be an indication of the limitations inherent in dimensionless models for representing air-sea  $\text{CO}_2$  fluxes.]

#### **4) The referee's wider point (#4 and Recommendation) about manuscript length is also worth considering:**

**I think it is good that the authors have tested how much their assumed diagnostic relation of TA with salinity gives an improved carbonate system, by comparing with a run with constant alkalinity. It is shown that the prescribed variable alkalinity gives a somewhat better fit to data than the constant alkalinity. I am unsure, though, whether the details of that run really then need to be shown in the paper; I would probably just add the statistics of that run to a table with statistical indicators, without adding new figures.**

As you raised this point in your previous report, we thought that other readers might also have this question when reading our manuscript, which is why we saw this run and the associated results as an interesting addition to the manuscript. However, we agree that values of statistical indicators are enough to show that simply using a mean value to represent TA in the model does not allow to represent it in the best way. Consequently, we delete the figure S2 from the supplementary material.

**[...] One example in question is the new supplement S1.1 and Figure S1. If all recycling is done within the box, and assuming that the model is written correctly, then the fact that the model conserves total nitrogen and phosphorous does not need to be shown. A short statement in the main text would be enough.**

We agree with that. We already specified it in the manuscript (l.141): [As a result, when the water column is impacted by a hydrodynamic event which modifies its properties (i.e., which bring nutrients, organic matter, impact salinity or temperature for example), the event impacts only temperature and salinity of the volume, [...], and total N, and P are supposed to be conserved within the volume as,

contrary to C, we do not consider any external source or sink from/to the water column or the atmosphere.]

We delete the corresponding part from the supplementary material and the sentence which refers to it in the manuscript (l.146).

**And maybe it would make sense, instead of adding another appendix with the model run with modified mixed layer depth, to make that the new standard, and rather re-do the other runs. That would again save some discussion in the main text and the appendix. These are just suggestions, but I think that a bit more conciseness would help this manuscript to become noticed.**

As specified in point #3, we think that this change represents a lot of work for a result which is still quite far from what is observed in the literature since the main problem of OD comes from the fact that, as you specify it in the following, we do not consider all the processes that impact the fluxes in the water column. Moreover, we think that such a modification may raise questions from the reader. In the first part of the study (Barré et al., 2023a) we considered an arbitrary volume of  $1\text{m}^3$  then defining it as a feature of our configuration. To be consistent with this first part it makes sense to continue the study with the same water volume. We then decided to keep this part as it.

However, we agree with the fact that some parts of the manuscript, especially in the materials and methods section can be summarized or move to appendices. We detail the changes made below.

**For instance, if material can be summarised straightforwardly and / or be moved to an appendix, that will help with the readability of your manuscript.**

To help with the readability of our manuscript we propose:

- to reduce the section study area, as a description of the study area, and especially of forcings can be found in the first part of the study:

We delete the Table 1 and refer the reader to the first part of the study instead (l.115): **[A detailed description of forcings used by the model and a map of the study area showing the location of stations where measurements were carried, and places of interests can be found in Section 2.1 of Barré et al. (2023) (Table 1 and Fig. 1 respectively).]**

- to move section 2.2.4 to Appendix B:

To do so, we bring together sections 2.2.2 and 2.2.3, then create a new section “2.2.2 Carbonate system variables calculation” (l.187, in the following we cut the parts which have not been modified for more readability):

### **[2.2.2 Carbonate system variables calculation**

**In Eco3M\_MIX-CarbOx, we consider the four main carbonate system variables: TA, DIC,  $\text{pH}_T$  and  $\text{pCO}_2$ . We describe their calculation by the model in this section.**

In Eco3m-CarbOx, TA representation lacks variations during the year. Eco3m-CarbOx did not account for TA inputs by rivers, especially by the Rhône River which has an average alkalinity of  $2885 \mu\text{mol kg}^{-1}$  (Schneider et al., 2007). [...] We implemented both TA-S formulations in our Eco3M\_MIX-CarbOx model, and the formulation to be used was chosen based on the salinity : if salinity value used by the

model for the time step considered  $\leq 37.8$ , the TA-S dilution (Eq.6) was applied; else for salinity value  $> 37.8$  the TA-S correlation was applied (Eq. 5, Fig. 2c,d). With this method, TA only depends on salinity (i.e., biological processes are neglected).

The DIC formulation used in our Eco3M\_MIX-CarbOx model is very similar to the formulation used in Eco3M-CarbOx except that we added the mixotroph organisms' processes to our equation. As a result, DIC depends on phytoplankton, mixotrophs, zooplankton and bacterial respiration, air-sea CO<sub>2</sub> fluxes (aeration process), dissolution of CaCO<sub>3</sub>, phytoplankton and mixotrophs photosynthesis and precipitation of CaCO<sub>3</sub> (Eq.7). [...] By convention, we will consider negative aeration values (i.e.,  $pCO_{2,atm} > pCO_{2,sw}$ ) to represent fluxes from the atmosphere into the ocean and vice versa. Furthermore, we will express air-sea CO<sub>2</sub> fluxes in the more frequently used units of mmol m<sup>-2</sup> per unit time.

**pH<sub>T</sub> and pCO<sub>2</sub> are then obtained using the value of TA and DIC. Their calculation is detailed in appendix B.** Simulations were conducted using both TA formulations (autochthonous and allochthonous) for the year 2017 (Table 1, SIMC0 and SIMC1). In addition, we ran a simulation in which TA is set to a constant (TA = 2591.2 μmol kg<sup>-1</sup>, Table 1, SIMCSTE). This simulation and its results are detailed in supplementary material.]

and we reorganized Appendix B (l.714, in the following we cut the parts which have not been modified for more readability):

## [Appendix B: pH<sub>T</sub> and pCO<sub>2</sub> calculation

The calculation method performed in the Eco3M\_MIX-CarbOx model to obtain pH<sub>T</sub> and pCO<sub>2</sub> is detailed below. As specified in Sect. 2, we used the method introduced by Lajaunie-Salla et al. (2021), which is based on CO2SYSv3 (Sharp et al., 2020), a software originally developed by Lewis and Wallas (1998) to perform the resolution of carbonate system, to perform this calculation. This appendix aims to complete Appendix A from Lajaunie-Salla et al. (2021) by providing some corrections. **It also introduces the possibility to choose between two types of TA formulation (autochthone or allochthone) to perform the calculation of pH<sub>T</sub> and pCO<sub>2</sub>.**

[...]

### B.2 pH<sub>T</sub> and pCO<sub>2</sub> calculation

**Solving the equations of the carbonate system requires knowledge of TA and DIC. Depending on the TA formulation used, the steps followed by the model to issue the new pH<sub>T</sub> and pCO<sub>2</sub> are described on Fig B.1. If TA is calculated using the Eq. (4), biogeochemical and aeration processes are applied as described in Eqs. (4) and (7) in order to deliver new ([t] time step) TA and DIC : Air-sea CO<sub>2</sub> fluxes are calculated from temperature, salinity, wind speed, atmospheric pCO<sub>2</sub> and seawater pCO<sub>2</sub>, and biogeochemical processes required, at least, temperature to be computed and solar irradiance. When calculated, processes are applied in the form of fluxes to the previous TA and DIC ([t-1] time step values) to solve their respective state equation. The pH<sub>T</sub> and pCO<sub>2</sub> calculation is, then, performed using in addition to TA and DIC, temperature and salinity data.**

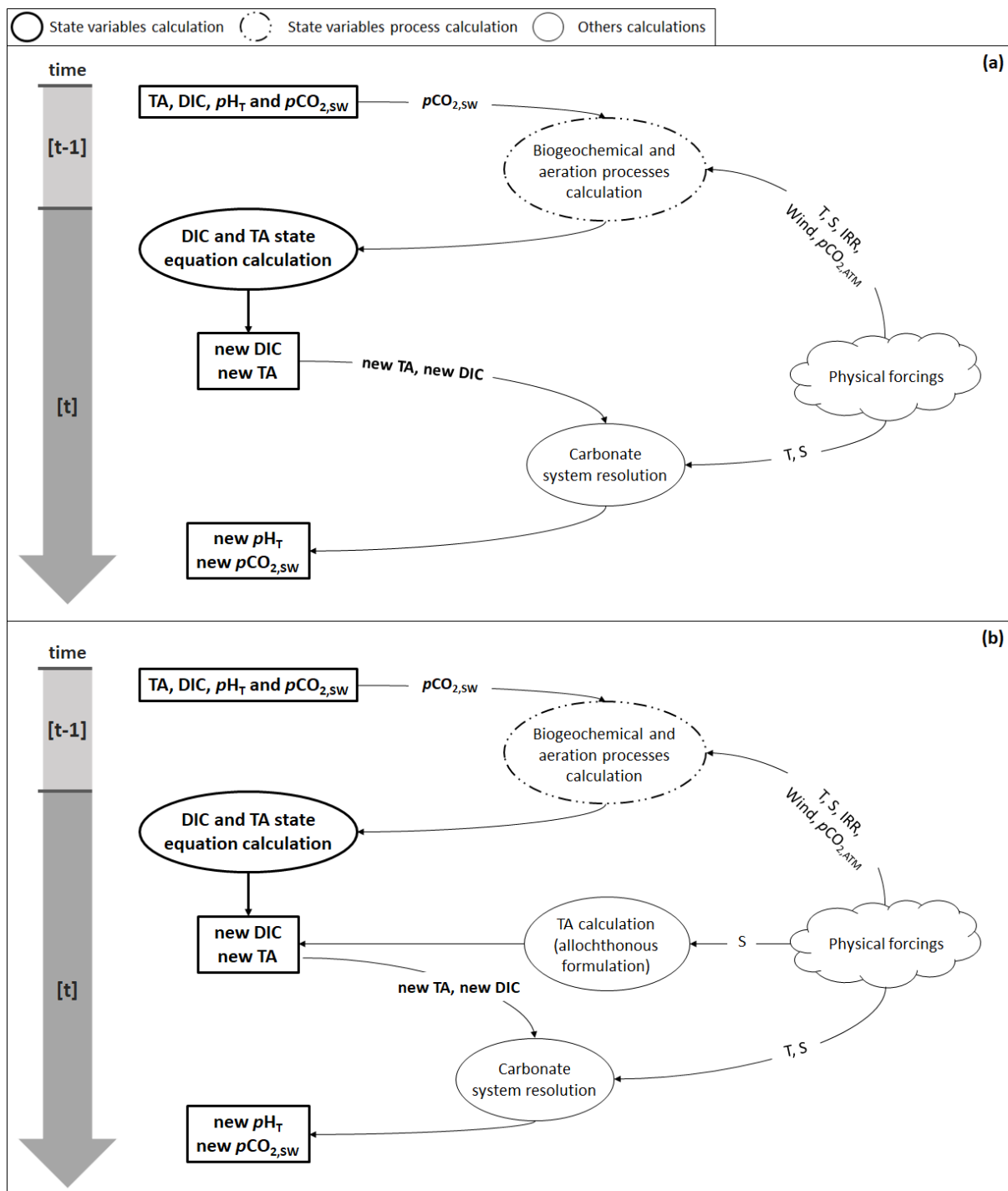


Figure B1. Flow diagram illustrating the steps needed to calculate  $pH_T$  and  $pCO_2$  (a) using the autochthonous formulation (Eq. 4) and (b) with the allochthonous formulation (Eq. 5 and 6). Physical forcings include temperature ( $T$ ), salinity ( $S$ ), solar irradiance ( $IRR$ ), wind speed ( $Wind$ ) and atmospheric  $pCO_2$  ( $pCO_{2,ATM}$ ).

When  $TA$  is calculated using Eqs. (5) and (6), the biogeochemical and aeration fluxes computed during the first stage are only applied to  $DIC$  from the preceding time step, while  $TA$  is calculated after  $DIC$  based on the salinity data from the current time step. All subsequent steps are unchanged (Fig. B1b)

### B.2.1 $pH_T$ calculation

pH<sub>T</sub> is calculating using a buffering value (B) defined as the pH variation induced by an addition of acid or base to a specific solution (Van Slycke, 1922). In seawater, B can be expressed in terms of TA (Middelburg, 2019) which yields:

$$B = \frac{\partial TA}{\partial pH_T} \Leftrightarrow \Delta pH_T = \frac{\partial TA}{\sum_{i=1}^n Bi} \quad (B17)$$

where i represents a chemical species contributing to TA.

Accordingly, we calculate the pH<sub>T</sub> difference between two model time steps (ΔpH<sub>T</sub>) using an iterative method. We set the pH<sub>T</sub> initial value to 8.0. We chose this value by considering the Mediterranean and Rhône River pH<sub>T</sub> which are respectively close and equal to 8.0...]

- to move Section 2.4 to appendix C:

We added the following sentence at the beginning of Section 3.1 (l.353): [First, we performed an initial qualitative evaluation of Eco3M\_MIX-CarbOx, comparing the output of SIMC0 (using the autochthonous TA formulation) and SIMC1 (using allochthonous TA formulation) for TA, DIC, pCO<sub>2</sub> and pH<sub>T</sub> to the corresponding SOLEMIO surface data for 2017 (Figs. 4a-d). Next, we used four statistical indicators to compare model outputs and SOLEMIO data quantitatively: the percentage bias (%BIAS), the average error (AE), the average absolute error (AAE) and the root mean square deviation (RMSD, also refer as root mean square error in the literature - RMSE). They were used with both Eco3M\_MIX-CarbOx simulations, SIMC0 and SIMC1 (Table 2), and the reference Eco3M-CarbOx simulation (Lajaunie-Salla et al., 2021). By comparing the statistical indicators obtained for SIMC0, SIMC1 and Eco3M-CarbOx we obtained an indication of how changes in the carbonate formulation affected the results. Statistical indicators calculation is detailed in appendix C.]

And added Section 2.4 to Appendix C (l.816):

### [Appendix C: Statistic indicators calculation and application to H<sup>+</sup> concentrations

We used four statistical indicators for the comparison between simulation and SOLEMIO data: the percentage bias (%BIAS), the average error (AE), the average absolute error (AAE) and the root mean square deviation (RMSD, also refer as root mean square error in the literature - RMSE). They were used with two Eco3M\_MIX-CarbOx simulations (SIMC0 and SIMC1) and the reference Eco3M-CarbOx simulation (Lajaunie-Salla et al., 2021). The %BIAS is calculated as follow:

$$\%BIAS = \frac{\sum_{i=1}^N (O_i - M_i)}{\sum_{i=1}^N O_i} * 100 \quad (C1)$$

where O represents the observations and M the model results (Allen et al., 2007). This indicator allows to quantify the model's tendency to under- or overestimate the observations. The closer the value is to 0, the better the model. Here, a positive %BIAS means that the model underestimated the in situ observations and vice versa. On an indicative basis, the %BIAS can be interpreted according to Marechal (2004): Absolute values of %BIAS allow to assess the overall agreement between the model results and observations and the agreement is considered: excellent if %BIAS < 10 %, very



good if  $10 \% \leq \%BIAS < 20 \%$ , good if  $20 \% \leq \%BIAS < 40 \%$  and poor otherwise. We based our calculation of AE, AAE and RMSD on Stow et al. (2009). Together, these three statistical indicators provide an indication of model prediction accuracy.

$$AE = \frac{\sum_{i=1}^N (O_i - M_i)}{N} \quad (C2)$$

$$AAE = \frac{\sum_{i=1}^N (|O_i - M_i|)}{N} \quad (C3)$$

$$RMSD = \sqrt{\frac{\sum_{i=1}^N (O_i - M_i)^2}{N}} \quad (C4)$$

The three of them aim to measure the size of the discrepancies between model results and observations, the closer the value is to 0, the better the agreement between model results and observations. However, when interpreting AE, it is important to note that value near zero can be misleading because negative and positive discrepancies can cancel each other. That is why it is important to calculate, in addition to AE, AAE and RMSD which allow to overcome this effect (Stow et al., 2009). Such as %BIAS, a positive value of AE means that the model underestimated the in situ observations and vice versa. The model data is averaged using the mean of the output from the date in question  $\pm$  five days. Using temporal mean and standard deviation of model results allowed us to better account of variability at SOLEMIO station.

In addition to TA, DIC,  $pH_T$  and  $pCO_2$ , statistical indicators were calculated for  $H^+$  concentrations. ]

---

We hope that our explanations and the changes that we propose will clarify your latest concerns and improve the readability of our manuscript. Again, we would like to thank you and both referees for your evaluation of our revised manuscript and helpful comments and suggestions.