



Supplement of

Implementation and assessment of a model including mixotrophs and the carbonate cycle (Eco3M_MIX-CarbOx v1.0) in a highly dynamic Mediterranean coastal environment (Bay of Marseille, France) – Part 2: Towards a better representation of total alkalinity when modeling the carbonate system and air–sea CO₂ fluxes

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Supplementary materials

S1. Supplementary simulations

S1.1 Simulation with constant TA

In addition to simulations with autochthonous and allochthonous TA formulations, we ran a simulation in which TA is set to a constant (mean of surface SOLEMIO measurements for the year 2017: 2591.2 $\mu\text{mol kg}^{-1}$). Statistical indicators (%BIAS, AAE, AE and RMSD) for this simulation are presented in Table S1.

Table S1. Statistical indicators calculation for the simulation with a constant TA (TA = 2591.2 $\mu\text{mol kg}^{-1}$). Mean, SD, AE, AAE and RMSD are in the same unit than the considered variable, i.e.: $\mu\text{mol kg}^{-1}$ for TA and DIC, μatm for $p\text{CO}_2$ and mmol m^{-3} for $[\text{H}^+]$. %BIAS is without unit.

		TA	DIC	$p\text{CO}_2$	pH_T	$[\text{H}^+]$
N	Observation	20	20	20	20	20
Mean \pm SD	Observation	2591.2	2294.9	391.0	8.09	8.08×10^{-9}
		± 19.4	± 24.0	± 31.0	± 0.03	$\pm 5.52 \times 10^{-10}$
Mean \pm SD	Model	2591.2	2305.7	418.0	8.07	8.48×10^{-9}
		± 0.22	± 26.1	± 28.9	± 0.03	$\pm 2.64 \times 10^{-10}$
%BIAS	Model	-0.002	-0.50	-5.79	0.26	-4.95
AAE	Model	16.5	19.7	35.5	0.03	6.26×10^{-10}
AE	Model	-0.06	-11.5	-22.6	0.02	-4.00×10^{-10}
RMSD	Model	18.90	26.14	38.45	0.03	6.78×10^{-10}

10 S1.2 Simulation with modified aeration process

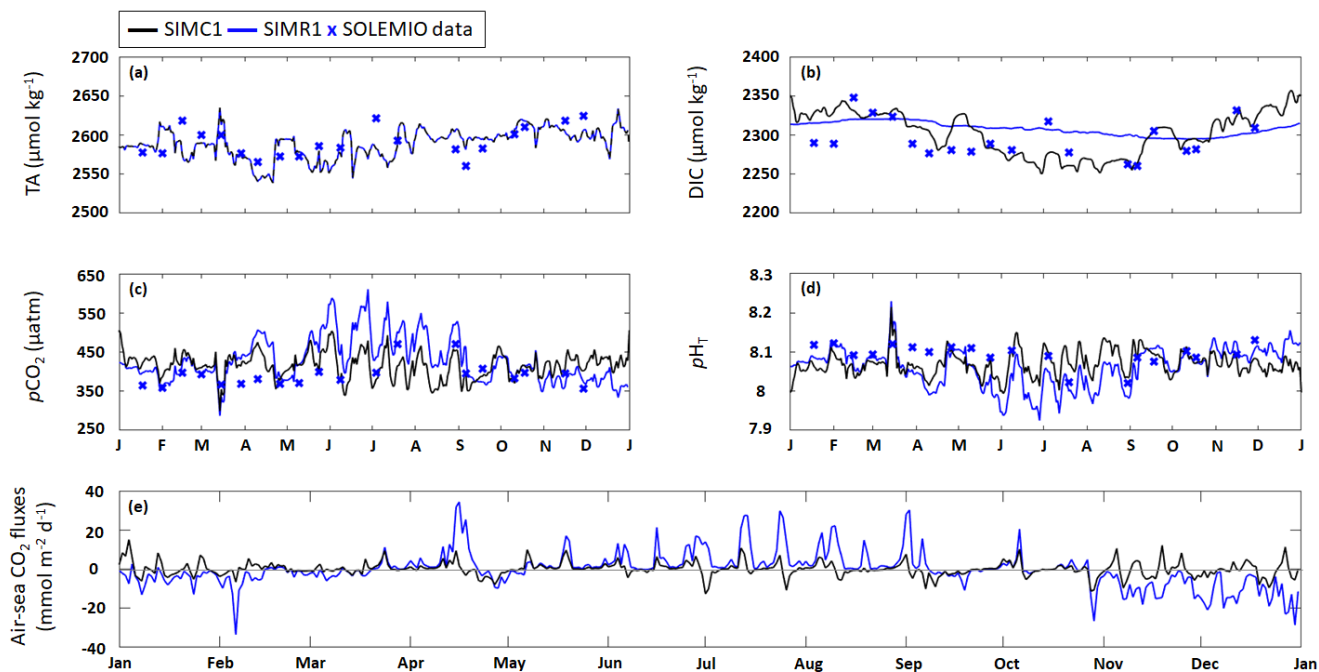
By considering a small volume of 1 m^3 at the surface, Eco3M_MIX-CarbOx fail to represent seasonality and annual mean value of air-sea CO_2 fluxes. To better understand this feature, we ran a simulation with a modified version of aeration process (Eq. S1).

$$Aera = \frac{K_{ex}}{30.5} * \alpha * (p\text{CO}_{2,sw} - p\text{CO}_{2,atm})$$

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(S1)

where Aera is in $\text{mmol m}^{-3} \text{s}^{-1}$. Kex represents the gas transfer velocity (Wanninkhof, 2014) in cm h^{-1} , α the CO_2 solubility coefficient (Weiss, 1974) in $\text{mol L}^{-1} \text{atm}^{-1}$, $p\text{CO}_{2,sw}$ the seawater $p\text{CO}_2$ modelled at the previous time step in μatm , $p\text{CO}_{2,atm}$ the atmospheric $p\text{CO}_2$ from CAV in μatm . The process is now applied to a larger thickness of water which represents the mean value of mixed layer depth in the area ($H = 30.5 \text{ m}$, Wimart-Rousseau et al., 2020).



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Figure S1. Comparison of model outputs from SIMC1 (aeration process apply on a 1 m layer, Table 2 of the manuscript) and SIMR1 (aeration process apply on 30.5 m layer, model runs showing daily average (a) TA, (b) DIC, (c) $p\text{CO}_2$, (d) pH_T , and air-sea CO_2 fluxes for 2017. SOLEMIO data are represented by blue markers.

This new simulation (SIMR1) is compared to the simulation in which allochthonous formulation of TA is used (SIMC1, Table 1 of the manuscript). The representation of the variables of carbonate system and air-sea CO_2 fluxes for both simulations are presented in figure S1. A comparison of annual mean values of air-sea CO_2 fluxes for both simulations and Wimart-Rousseau et al. (2020) study is available in Table S2.

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Table S2: Comparison of annual mean value and daily value range obtained for the SIMC1 ($H = 1$ m), SIMR1 ($H = 30.5$ m) and in Wimart-Rousseau et al. (2020) study.

	Annual mean value ($\text{mmol m}^{-2} \text{ yr}^{-1}$)	Daily value range ($\text{mmol m}^{-2} \text{ d}^{-1}$)
SIMC1	-0.21	[-13, 15]
SIMR1	-113.6	[-33, 34]
Wimart-Rousseau et al. (2020)	-803	[-15, 10]

30 S2. Supplementary figures

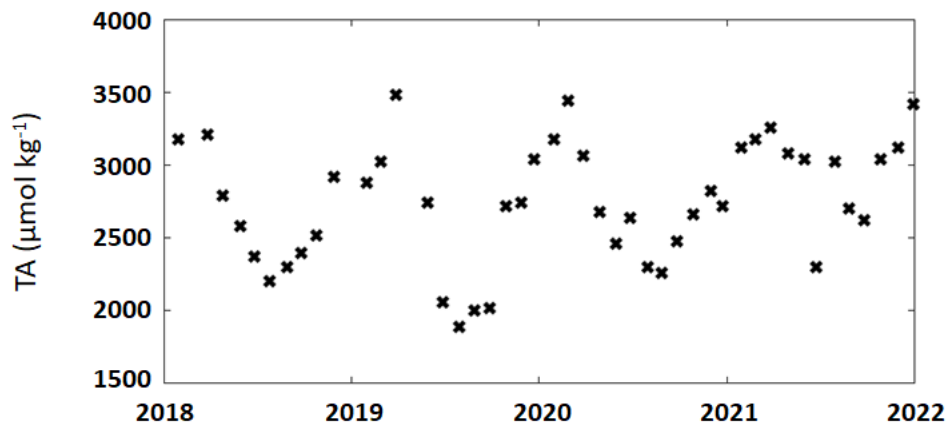


Figure S2: TA measurements in the Rhône River (data: Naiades, <https://naiades.eaufrance.fr>, first data available: January 2018).

S3. Supplementary tables

Table S3. Salinity-TA couples for LSE events measured at SOLEMIO between 6 June 2016 and 26 June 2019 (last data available).

	Salinity	TA ($\mu\text{mol kg}^{-1}$)
6 June 2016	37.11	2603.0
4 July 2016	37.78	2579.6
2 November 2016	37.30	2585.5
15 March 2017	36.82	2600.6
5 September 2017	37.18	2560.8
31 May 2018	37.66	2568.4
26 June 2019	37.32	2520.7

35 References

- Frayse, M., Pinazo, C., Faure, V. M., Fuchs, R., Lazzari, P., Raimbault, P. and Peyraud, I.: Development of a 3D Coupled Physical-Biogeochemical Model for the Marseille Coastal Area (NW Mediterranean Sea): What Complexity Is Required in the Coastal Zone? PLoS ONE, 8(12): e80012, <https://doi.org/10.1371/journal.pone.0080012>, 2013.
- Frayse, M., Pairaud, I., Ross, O. N., Faure, V. M. and Pinazo, C.: Intrusion of Rhone River diluted water into the Bay of Marseille: Generation processes and impacts on ecosystem functioning, Journal of Geophysical Research: Oceans, 119, <https://doi.org/10.1002/2014JC010022>, 2014.
- Gatti, J., Petrenko, A., Devenon, J. -L., Leredde, Y. and Ulses, C.: The Rhone River dilution zone present in the northeastern shelf of the Gulf of Lion in December 2003, Continental Shelf Research, 26, 1794-1815, <https://doi.org/10.1016/j.csr.2006.05.012>, 2006.

45 Lajaunie-Salla, K., Diaz, F., Wimart-Rousseau, C., Wagener, T., Lefevre, D., Yohia, C., Xueref-Remy, I., Nathan, B., Armengaud, A., and Pinazo, C.: Implementation and assessment of a carbonate system model (Eco3m-CarbOx v1.1) in a highly dynamic Mediterranean coastal site (Bay of Marseille, France), *Geoscience Model Development*, 14, 295–321, <https://doi.org/10.5194/gmd-14-295-2021>, 2021.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean revisited, *Limnology and Oceanography: Methods*, 12 (6), 351-362, <https://doi.org/10.4319/lom.2014.12.351>, 2014.

50 Wimart-Rousseau, C., Lajaunie-Salla, K., Marrec, P., Wagener, T., Raimbault, P., Lagadec, V., Lafont, M., Garcia, N., Diaz, F., Pinazo, C., Yohia, C., Garcia, F., Xueref-Remy, I., Blanc, P. E., Armengaud, A., and Lefèvre, D.: Temporal variability of the carbonate system and air–sea CO₂ exchanges in a Mediterranean human-impacted coastal site, *Estuar. Coast. Shelf S.*, 236, <https://doi.org/10.1016/j.ecss.2020.106641>, 2020.

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