

Reviewer 1

This study is an important example of analysis of oceanic carbonate systems based on observation data from the western Mediterranean Sea, and the measurement methods and data processing are generally appropriate. However, the structure of the Discussion and Conclusion is poor, and it is very difficult to understand the novelty that should be claimed in this paper. The authors should significantly revise the structure of the Discussion and Conclusion to clarify the appeal points of this paper to the readers.

Thank you very much for your thoughtful and constructive feedback on our manuscript. We greatly appreciate your recognition of the significance of our observation-based analysis of the ocean carbonate system in the Mediterranean Sea. We have carefully considered your comments and suggestions, which have contributed to enhancing the quality and reliability of the manuscript. Below, we provide a point-by-point response to each of your comments.

Major comments

Most description in the Discussion and Conclusions are repetitions of the Result. For example, Chapters 4.1 and 4.2 are unnecessary and should be deleted. The current description that merely lists data is redundant, and make it difficult to understand new findings that should be claimed in the paper. The structure of these sections should be substantially revised by deleting unnecessary descriptions.

We have thoroughly revised and modified these sections. The descriptive part has been relocated to a new subsection in the methodology titled "Study Area," and we have aimed to be more concise in discussing the main results presented in Sections 4.1 and 4.2. Additionally, we have modified Section 3: the results are now presented more succinctly, as they will be analysed in depth in the discussion section. In the conclusion, we have removed certain numerical results that contributed to noise and could confuse the reader, as well as some redundant phrases previously addressed in earlier sections. After implementing these changes, the new version of the manuscript is much clearer and can be better understood by the reader.

The multivariable Taylor expansion is performed in Equation (6), but in this paper, TA is calculated as a linear equation of salinity, so there should be very strong multicollinearity between SSS and TA. Therefore, I am very suspicious of the results of this equation. We have to clear the problem of multicollinearity by removing one of the variables or by using methods to avoid multicollinearity (e.g., PLS regression).

We agree that calculating alkalinity from salinity is a relevant point of this paper and significantly influences subsequent calculations, requiring special attention and detailed explanation. Due to limitations in autonomously collecting simultaneous seawater samples for A_T and C_T determination alongside xCO_2 measurements, we manually collected discrete samples at different times of the year along the vessel track (102 discrete samples in total with in situ SST and SSS measurements taken during February 2020, March 2021, and October 2023; see Section 2.3 for details). With these empiric

data, we obtained a statistically significant linear AT-SSS relationship (Eq. 1) at the 99% confidence level with a high correlation ($r^2 = 0.92$), which we used to calculate alkalinity at the time, latitude, and longitude of the surface $x\text{CO}_2$, SST, and SSS observations. We have previously applied this procedure in the Northeastern Atlantic (Curbelo-Hernández et al., 2021a) and the Strait of Gibraltar (Curbelo-Hernández et al., 2021b), both regions also monitored by CanOA-VOS. However, in those cases, AT fitted better with SSS using a second-degree polynomial equation, consistent with relationships reported for the Atlantic by Lee et al., 2006. In contrast to Lee et al. (2006), a multiparametric regression incorporating SST as a second variable (see Table 1 in Lee et al., 2006) did not yield satisfactory results in our case. After extensive analysis, we determined that our AT observations are correlated the best only with SSS. We attribute this outcome to the fact that our measurements were taken in coastal transition zones, where SST is highly variable and extends beyond the SST ranges established by Lee et al. (2006), who developed their relationships using observations in open-ocean Atlantic areas with more stable temperatures (see Zones 1 and 3 in Figure 1 of Lee et al., 2006).

Although reconstructing A_T through its relationship with SSS has been widely applied to calculate other variables of the Marine Carbonate System and to derive conclusions on oceanic CO_2 and pH levels and trends (e.g., Takahashi et al., 2014), we recognize that this method has certain limitations. Primarily, it does not consider biological processes that alter A_T and cannot be traced by salinity (Wolf-Gladrow et al., 2007) as well as the input of dissolved carbonate minerals and bicarbonate-carbonate species from river runoff, sediments and water mixing. Consequently, A_T -SSS relationships provide a useful general approximation in regions with stable conditions and less influenced by these processes but carry uncertainties in areas subject to variability.

In our study area along the western boundary of the Mediterranean Sea, surface A_T dynamics is primarily governed by the influx of fresher, low- A_T Atlantic waters and the significant role of evaporation/precipitation (Cossarini et al., 2015). In contrast, terrestrial and riverine contributions of A_T to the Alboran Sea and Eastern Iberian coast were found to have minimal influence on A_T distribution compared to marginal and coastal areas in the eastern Mediterranean Basin (see Table 2 and Figure 1 in Cossarini et al., 2015). Additionally, in the eastern Mediterranean, limited nutrient inflow and reduced water renewal amplify the role of biological processes in regulating carbon and alkalinity cycles. Conversely, in the western Mediterranean, the effect of these biological cycles on alkalinity is relatively diminished due to the influx of cooler, nutrient-rich Atlantic waters, which reduces the relative importance of local biological contributions to alkalinity dynamics. These processes explain the pronounced west-to-east surface gradient in A_T across the Mediterranean basin (Cossarini et al., 2015) and the relatively homogenous A_T distribution along the Iberian coast (see Figure 2a in Cossarini et al., 2015). In fact, the linear A_T -SSS relationships presented by Cossarini et al., 2015 (see Figure 4 and Table 3) showed a lower correlation and greater residual dispersion in the eastern basin, indicative of greater variability compared to the western basin.

Following Cossarini et al., 2015, and due to the weaker influence of non-salinity factors on A_T variation along the western boundary, we reconstructed A_T using a salinity-based empirical relationship developed specifically for our study transect. The new equation presented in this paper (Eq. 1) aligns with the linear relationships proposed in various

zones of this basin (Schneider et al., 2007, Copin-Montégut and Bégovic, 2002, Jiang et al., 2014, Cossarini et al., 2015).

Considering the limitations of the methodology applied for A_T calculation, we have exercised caution in interpreting and inferring conclusions from results involving this variable. Although A_T and NA_T values are presented in Figures and Tables throughout the manuscript and supplementary materials, we have avoided direct discussion of these results. Instead, we used these results to support discussions related to the spatio-temporal variability of other physical and biogeochemical variables. In studying factors controlling $fCO_{2,sw}$ seasonality, Takahashi et al., 2014 applied Taylor decomposition (Eq. 6) to examine drivers of seasonal changes in pCO_2 , pH, and Ω using A_T data reconstructed from salinity relationships. However, we normalized A_T values prior to including them in the Taylor decomposition using the most recent equation (Eq. 7) provided by Pérez et al., 2021, and extending trying to remove collinearity between A_T and SSS. In Figure 5, we represented seasonal changes in $fCO_{2,sw}$ due to changes in SSS ($\left(\frac{\partial pCO_2}{\partial SSS} + \frac{NC_T}{SSS_0} \frac{\partial pCO_2}{\partial C_T} + \frac{NA_T}{SSS_0} \frac{\partial pCO_2}{\partial A_T}\right) \frac{dSSS}{dt}$) and in A_T ($\left(\frac{SSS}{SSS_0} \frac{\partial pCO_2}{\partial A_T} \frac{dNA_T}{dt}\right)$), demonstrating an arbitrary relationship between them across all locations of interest during the study period. Moreover, seasonal changes in pCO_2 explained by SSS and A_T are often below 5 μatm , significantly lower than those induced by SST and DIC (in agreement with Takahashi et al., 2014). This mean that changes in $fCO_{2,sw}$ explained by SSS and A_T have minimal impact on the seasonal cycle of pCO_2 and are not crucial in quantifying changes driven by the two main drivers (temperature primarily, followed by DIC), which is the main conclusion we infer from this analysis.

I would also like to know how SSS and TA, which are less accurate in Equation (10), affect the results of the Taylor expansion. The author should calculate the error and clarify whether the Taylor expansion results are significant or not.

We have reviewed the Taylor deconvolution applied. The most important issue, which was not explicitly stated in the previous version of the manuscript and may be the main source of controversy, is that we did not use Equation 10 to calculate the seasonal amplitudes of the variables controlling the $fCO_{2,sw}$ changes. After a series of discussions, we decided to avoid using this equation for that purpose for the reason you pointed out: primarily, SSS and A_T do not show a high correlation with Equation 10 because they lack a pronounced seasonal cycle compared to the other variables. This is because they are influenced by a set of processes that can be regional or local and occur over much longer timescales, without being directly driven by seasonal factors. In this transitional coastal area of the Western Mediterranean, these processes mainly include evaporation/precipitation, river runoff, and geochemical interactions with the coast and marine sediments in shallow areas that promote mineral dissolution. Based on these premises, we can expect that SSS and A_T play a less relevant and more variable role, both interannually and spatially, in the seasonal change of in $fCO_{2,sw}$ compared to SST and C_T .

Therefore, given that the temporal changes in SST, SSS, A_T , and C_T in Equations 6 and 7 do not necessarily coincide with those of in $fCO_{2,sw}$ on an annual scale, we assumed the seasonal variation as the difference in each of these variables between the times when in $fCO_{2,sw}$ reaches its maximum and minimum (this difference give the seasonal amplitudes),

divided by the months elapsed. Seasonal amplitudes were calculated between monthly means (based on observations and computed data, not estimated through Equation 10) for February and September (where minimum and maximum $f\text{CO}_{2,\text{sw}}$ were observed). An error propagation based on standard deviations was performed to calculate the uncertainty of associated with the difference between February and September means for each term and year. The results of solving Eq. 7 are presented in Figure 5 and the uncertainties associated to the seasonal changes of each term are shown in Table Sup 3.

The Taylor expansion applied to the seasonal cycle of $f\text{CO}_{2,\text{sw}}$ has been validated by direct comparison between the seasonal rate of change in $f\text{CO}_{2,\text{sw}}$ $\frac{df\text{CO}_{2,\text{sw}}}{dt}$ derived from the sum of each individual component $(\frac{\partial f\text{CO}_{2,\text{sw}}}{\partial X} \frac{\partial X}{dt})$ in Eq. 6 and 7, referred to in the manuscript with the subscript “sum,” and the rate derived from the difference between the monthly averages of $f\text{CO}_{2,\text{sw}}$ observations in February and September, which we assume as the seasonal reference value for $f\text{CO}_{2,\text{sw}}$ and denote with the subscript “obs.” Both seasonal rates are presented with their uncertainties, calculated via error propagation (Figure 5, Supplementary Table 3). The $\frac{df\text{CO}_{2,\text{sw}}}{dt}_{(sum)}$, considering its uncertainty range, falls within the uncertainty range of $\frac{df\text{CO}_{2,\text{sw}}}{dt}_{(obs)}$ (see errorbars in Figure 5). Additionally, a high degree of concordance is observed between both values, particularly across section S in the Alboran Sea. This consistency is highlighted in the manuscript and confirms the robustness of the seasonal change values obtained, thereby installing confidence in the methodology applied.

In the revised manuscript, we provide a much more detailed discussion of the methodology and its robustness to ensure clarity for readers and to facilitate an accurate interpretation of the results.

We have included in section 2.3.3 the following paragraphs:

“The seasonal changes of each driver (SST, SSS, C_T and A_T) in Eq. 7 $(\frac{dX}{dt})$ were assumed as their difference between the times of the year in which $f\text{CO}_{2,\text{sw}}$ was at its minimum and maximum (seasonal amplitudes) per months elapsed. Seasonal amplitudes were calculated between monthly means (based on observations and computed data) for February and September (where minimum and maximum $f\text{CO}_{2,\text{sw}}$ were observed). An error propagation based on standard deviations for February and September was performed to calculate the error of the seasonal change.”

The first paragraph of section 4.4 was also modified as follows:

“To infer the causes of variations in the seasonal cycle of $f\text{CO}_{2,\text{sw}}$ among the study period, the seasonal rates of change of $f\text{CO}_{2,\text{sw}}$ $(\frac{df\text{CO}_{2,\text{sw}}}{dt}$, hereinafter $df\text{CO}_2$) were decomposed into their individual components $(\frac{\partial f\text{CO}_{2,\text{sw}}}{\partial X} \frac{\partial X}{dt}$, hereinafter $df\text{CO}_2^X$) as described in section 2.3.3 (Eq. 6 and 7). The results of solved Eq. 7 for each year at S1-S5 and E1-E6 are depicted in Figure 5. The positive values indicate an increase in $f\text{CO}_{2,\text{sw}}$ from February to September, while negative values the opposite. The uncertainty associated with the difference between the monthly means for each term

and year was obtained through error propagation considering their individual standard deviations and presented in Table Sup 3. The $\Delta f\text{CO}_2$ resulted from the cumulative sum of the individual terms in Eq. 7 (indicated with subscript “sum”) matched the $\Delta f\text{CO}_2$ directly calculated from observations between both seasons (indicated with the subscript “obs”), which renders confidence to the methodology (Figure 5).”

The discrete description of the study area is difficult to understand for those who are not familiar with this area. Thus, a "Study area" or similarly named subchapter should be added in Chapter 2 to describe the contents at Line 56-124, the hydrographical conditions, and previous studies of carbonate observations.

We agree that this study area has specific hydrodynamic characteristics that can be challenging for those unfamiliar with it, necessitating a detailed description. Following the journal's template and structure, we initially decided to include this description in the introduction, as observed in other regional/local scale articles published in Biogeoscience. We have now created a new subsection in the methodology titled "Study Area," which includes a description of the study area and the properties that may serve as potential sources of variability. This change has resulted in a much more concise and organized introduction and facilitate the comprehension of the entire study.

Line 287 Since river water does not reach zero alkalinity even with zero salinity (see Friis et al., 2003), the effect of river cannot be excluded with this method.

We have reviewed this point and agree we did not express it correctly. The traditional normalization method we are employing, which has also been utilized in prior studies applying Taylor deconvolution as outlined in Section 2.3.3, effectively removes the influence of salinity. This approach eliminates the effects of primary surface salinity-altering processes, such as evaporation, precipitation, and freshwater fluxes. However, this normalization still accounts for the influence of transport processes, including also vertical mixing and lateral advection, which can impact A_T and C_T concentrations.

In the specific case of river discharge, this normalization effectively removes the changes in A_T and C_T expected due to the decrease in salinity caused by freshwater input from river runoff near the mouth. However, we still account for changes in A_T and C_T that result from the input of dissolved carbonate minerals and bicarbonate-carbonate species.

Therefore, this normalization allows for the direct comparison of A_T and C_T , as well as their influence on changes in $f\text{CO}_{2,\text{sw}}$ across the region. It also enables the identification of areas where advection and/or river discharges become significant and introduce modifications to the seasonal cycle of $f\text{CO}_{2,\text{sw}}$, which aligns with the objectives of this study.

Minor comments

Line 56 Abbreviations that appears for the first time in the maintext should be explained in the maintext.

Done in the new version of the manuscript.

Line 187 Is the error in the instrument itself or is it due to the temperature difference between the ocean and the intake?

It is the error in the instrument itself, in the new version of the manuscript is indicated as “instrumental error”.

Line 226 One extra comma.

Typo. Removed in the new version of the manuscript

Line 295 What is different between S and SSS?

There was a typo in Eq. 7. As the study focuses on the surface, the salinity data is referred to throughout the manuscript as Sea Surface Salinity (SSS). Therefore, S was replaced with SSS in Eq. 7. We also noticed some inconsistencies in the explanation of the normalization procedure for A_T and C_T in the previous lines due to potential discrepancies in the terminology, and that SSS_0 was not defined in the text.

We have reformulated these lines as follows:

“...the most recent equation (Eq. 7) given by Pérez et al., (2021) with salinity-normalized C_T and A_T (NC_T and NA_T) was used. The normalization was performed to a constant salinity (SSS_0) of 37.4 ($NX_T = SSS_0 * X_T / SSS$), which is the average SSS for the entire monitored area”.

Line 318 The first paragraph of this chapter should be moved to the beginning of chapter 2.3. Also, if equation (10) is being applied to the data used in equations (6)-(9), it should be listed before those equations.

We have moved this paragraph to section 2.3.1. In the updated version of the manuscript, section 2.4 titled "Data adjustments and statistical procedures" only includes the procedure used for studying seasonal and interannual variability. In the case of Equation 10, it is applied to the average values along each route completed by the CanOA-VOS for each of the measured and computed variables. This procedure aim of study the temporal evolution of each variable and describe seasonal cycles that fits the observations. This equation was not used for calculating the drivers of $fCO_{2,sw}$ seasonality (Section 2.3.3, Eq. 6 and 7), but it was applied to the FCO_2 values calculated as described in Section 2.3.4 (Eq. 8 and 9). Therefore, after careful consideration, we believe that Equation 10 is listed in the text in a position consistent with the data processing workflow and the topic of section 2.4.

Line 399 Is this mean that the 11 points were determined by the seasonal variation of related parameters? If so this section should be moved to the second paragraph of the Result.

No, the selection of stations was based on the location of points of interest along sections S and E that were potential sources of variability. In making this selection, we considered factors such as the hydrodynamics, proximity to geographic features such as gulfs and capes where surface currents diverge and/or recirculate, and the bathymetry. The variability in seasonal amplitude across the two sections is already visible in Figure 2, as shown by the spatial differences between winter and summer, and is further analysed through the strategic positioning of these stations. We have explained that in a better way in the new version.

Line 557 The description about the SST reanalysis data should be moved to the Material and Method.

Done. The third paragraph in section 2.2 was modified as follow:

“The sea surface temperature (SST, in °C) was monitored by using a SBE38 thermometer placed at the primary seawater intake in the engine room, with a reported instrumental error of $\pm 0.01^\circ\text{C}$. The high sensitivity of $x\text{CO}_2$ to temperature fluctuations required to measure the temperature at different locations along the system. A SBE45 thermosalinograph and a Hart Scientific HT1523 Handheld Thermometer, with reported instrumental errors of $\pm 0.01^\circ\text{C}$, were used to monitor the temperature at the entrance of the wet box and inside the equilibrator, respectively. The measured SST was analysed in conjunction with SST reanalysis monthly data ($0.042^\circ \times 0.042^\circ$; with dates spanning 24 years within 01/01/2000 and 01/03/2024) from the Med MFC physical multiyear product (Escudier et al., 2020; 2021; Nigam et al., 2021), available at Copernicus Marine Data Store (<https://data.marine.copernicus.eu/products>). The SST reanalysis data was interpolated to the coordinates of the CanOA-VOS data to perform direct comparison in their dynamics.”

Line 657 The description should be moved to the Material and Method, or the Result.

We have moved some descriptive lines into section 2.3.2.

Figure 2 It would be better to make the $f\text{CO}_2$ and pH graph in Fig. 2 the Supplementary and $n\text{CT}$ and $n\text{AT}$ in the maintext.

Initially, we considered including the NA_T and NC_T plots alongside the other variables in Figure 2. However, this would have resulted in a figure with excessive information that could distract the reader. Since the main focus of the text is on the changes in $f\text{CO}_{2,\text{sw}}$ (and pH) in relation to SST changes, we deemed the inclusion of these variables in Figure 2 to be essential. Given the non-thermal processes that occur in the area and introduce spatial differences, we included a fourth plot for C_T , which supports the discussion of the results for the other variables, though it is not a primary focus of this article. Due to its lesser relevance in the discussion, but considering its importance in presenting these results to inform the reader about the variations in the other MCS variables, we decided to include the A_T , NA_T and NC_T plots in the supplementary material.