

Author Response to Interactive comment on “Concomitant ocean acidification and increasing total alkalinity at a coastal site in the NW Mediterranean Sea (2007–2015)” by Lydia Kapsenberg et al.

Overall author response: We thank the referees for their time and suggested improvements. We appreciate the positive reception of our study and have addressed all major comments below, point by point. Our major revisions include:

1. Removal of trend analyses on raw observations. We now only present statistical analyses on anomalies.

2. Use of the anomaly approach for the deconvolution analyses. This has resolved issues raised by the Referees and we were better able to attribute trends to specific drivers of change (e.g., warming, atmospheric CO₂). As a result, the Abstract, Results, and Discussion have been updated.

For the ease of reviewing our response, we have numbered the Referee Comments (RC) from 1 to 27. RC#1-21 are those from Referee #1 and RC#22-27 are those from Referee #2. We first list the comment in standard font and then our response followed by the change in the text, in italics.

Anonymous Referee #1, Received and published: 26 October 2016

In the present paper, the authors analyse two timeseries of carbonate system parameters (e.g. pH, alkalinity, CT and CO₂) collected in a coastal site of the NW Mediterranean Sea during the period 2006-2015. A valuable description of the temporal variability at different scales and of recent trends is provided along with a discussion about the possible driving processes. The analysis presented in the paper provides important elements that can shed some light on the dynamics of carbonate system in coastal areas of the Mediterranean Sea. Therefore, the paper is worthy of being published in OS after few major concerns. Statistical methods are mostly appropriate, however the deconvolution analysis, the presence of two trend analyses and the relationship between atmospheric CO₂ and sea water CO₂ needs some clarifications (see major comments 2, 3 and 4). Results about Point B timeseries are well presented but I would suggest exploiting better the high-frequency timeseries at EOL boy (see major comments 5). Few points of the discussion section seem questionable and need some clarifications: that one about the relationship between the study site and the Adriatic Sea (major comment 6) and that one on the potential drivers (major comment 7). Finally, abstract and conclusion do not summarise exhaustively the valuable work and findings presented in the paper (point 1). Major comments:

No response needed.

1) Abstract. I have found the abstract poorly informative, lacking to explain the main focus and the relevant findings. The first sentence is not clear to me. It is undoubtedly that monitoring in coastal area is important, however it seems to me that this sentence combines too many concepts. Please, review it.

We have extensively altered the abstract given the comments described below and updated results from an improved deconvolution analysis (see RC#2). The first sentence has been simplified and now reads, “Coastal time-series of ocean carbonate chemistry are critical for understanding how global anthropogenic change manifests in near-shore ecosystems”.

-Line 18. The concept “faster-than-expected based on atmospheric carbon dioxide forcing alone”, which is repeated twice (at lines 18 and 27), is not clear and needs some clarifications.

As part of the updated results presented in the abstract, we have removed this phrasing. Instead, we now directly describe the drivers of the observed trend in pH, which are atmospheric carbon dioxide and warming.

-Line 27. The sentence “localized biogeochemical cycling” should be made clearer. Line 22. The sentence “. . . its cause remains to be identified” is not consistent with the following “It seems therefore likely that changes in coastal AT cycling via a shallow coastal process gave rise to these observations”. Please, review consistently.

We have clarified the sentence with “localized biogeochemical cycling” to specify the “...importance of understanding changes in coastal carbonate chemistry through the lens of biogeochemical cycling at the land-sea interface.”

The sentence “its cause remains to be identified” has been updated to reflect that our dataset cannot identify the driver of A_T change, but we have some information as what it could be. These concepts which were previously separated in the abstract but are now combined: “The driving process of the interannual increase in A_T remains to be identified, but it has a seasonal and shallow component, which may indicate riverine or groundwater influence.”

-The sentence “Interesting, the increase . . .” (line 23) should be improved. Which “increases” is referred to? If the authors refer to the trends computed for each month, please make it clearer.

We have clarified the statement by specifying reference to “monthly means”. The edited sentence now reads: “Based on the analysis of monthly trends, concomitant increases in C_T and A_T were fastest in the spring-summer transition.”

-Last sentence seems quite long and difficult to read. Please, rephrase it.

We have revised the end of the abstract.

-Keywords. The two keywords “global ocean change” and “near-shore” seems to me misleading. I would remove “global ocean change” since it is not a topic of the paper, and I would suggest using “coastal area” (as it used in the title) instead of “near shore”.

We have removed “near-shore” and replaced “global ocean change” with “ocean acidification”. To highlight the coastal aspect of our study, we have edited the title to lead with “coastal”: “Coastal ocean acidification and increasing total alkalinity in the NW Mediterranean Sea”.

Conclusion. Few lines about the main findings of the analysis are maybe missing. This would help the paper to convey a clear take home message.

We have expanded the main findings and take home message: “This study exemplifies the importance of understanding changes in coastal carbonate chemistry through the lens of biogeochemical cycling at the land-sea interface. This is the first coastal acidification time-series providing data at high temporal resolution. The data confirm rapid warming in the Mediterranean Sea and demonstrate coastal acidification with a synchronous increase in total alkalinity.”

2) The deconvolution method (section 2.3) and results (section 3.2) should be revised. Authors should provide some details on their calculation method explaining how they deal with the hypotheses of linearity and of constant derivatives in time. These hypotheses hold when dealing with annual values (according to Garcia-Ibanez et al. (2016)), but it seems they do not with the weekly data used in the present analysis. In fact, (as an example) the sum of the pH changes caused by the individual drivers differs of about 30% with respect to anomalies pH trends (21% to observed pH trends). It is said that these differences are negligible (line 774), however no clear explanation is given. A comment on this issue should be provided.

We have now analyzed the regression on the deconvoluted time-series via the anomaly approach as used for generating the time-series trends (e.g., generating a time-series anomaly via subtraction of the respective monthly means). This revision improves the consistency of analyses presented throughout the paper (RC#3) and resolves the inconsistency between the sum of pH changes from the deconvolution compared to the reported trends (which were based on the raw data in the original version of the manuscript).

Using the anomaly approach, for pH, the sum of the pH changes generated by the deconvolution equals the observed change in pH of -0.0028 per year. For pCO₂, the sum of the slopes slightly underestimates the anomaly trend (6% difference) but falls within the range of error. We therefore conclude that the assumptions involved in the approach of Garcia-Ibanez et al. (2016) hold for our dataset. We have updated the methods and results to reflect this change in analysis.

3) The authors state that the timeseries is “detrended for seasonality by subtracting monthly mean . . . resulting anomalies were analysed using a linear regression” (Lines 160-164). To my understanding the analysis is performed according to the approach provided by Bates et al., (2014). Given that, why is the linear regression computed on observations in addition to that one on anomalies? These two trend estimates (one on anomalies and one on observations, Table 2) are slightly different but no explanation or discussion is provided but they are used in different part of the text (i.e. the trends on anomalies are commented throughout the text, while the trends on observations are used in deconvolution analysis). This might be misleading. Author should decide which type of timeseries model they are proposing (i.e. first trend then seasonality or vice versa) and use only one.

We used the same methods as Bates et al. (2014) in order to be able to compare our data and observed trends with those observed elsewhere and presented in Bates et al. (2014). Following Bates et al., 2014, we present both the raw observations and anomaly data. Presentation of the observation data visually shows the strong seasonality of carbonate chemistry parameters at this location and the raw values. We find this visualization useful and have therefore kept both the observed and anomaly data in Figure 2. We however removed analyses performed on the raw observations to avoid confusion (removal of regression lines from raw time-series observations in Fig. 2 and Fig. S1 of the original manuscript, and removal of regression results from statistics presentation in Table 2 and Table S1 of the original manuscript). Since this has simplified the presentation of the results, we have moved the analyses performed on data from 50 m, which were previously in the supplemental data, to the main document.

We have added an explanatory statement (Section 2.2.), which justifies the anomaly approach for comparative purposes with trends published in Bates et al. (2014).

In addition, we have adjusted the deconvolution to display anomaly trends to match the presentation of the time-series results (see RC #2). The deconvolution is also performed on data from 50 m, to maintain consistency with the presentation of time-series at both depths.

4) Line 248-251. Not clear. Do the authors propose a linear model relationship between atmosphere CO₂ trend and seawater CO₂ trend? This should be clarified as well as the assumption of air-sea CO₂ equilibrium. As a consequence, the discussion at line 299-300 seems not well supported by the result. A comment on this issue should be provided since it is claimed that this is one of the most important drivers (see lines 440-442 in discussion).

The contribution of atmospheric CO₂ to the observed trends at Point B is necessary to discuss as it is the main driver of global ocean acidification. The deconvolution of pCO₂ allowed us to compare the rates of atmospheric and seawater CO₂ increase. By assuming a linear model relationship between atmospheric and seawater CO₂ we can estimate the potential maximum contribution of anthropogenic atmospheric CO₂ to the observed trends at Point B.

We have edited the text in Section 3.2 (Deconvolution results) to clarify this and describe the assumption we are making: “To estimate the maximum influence of anthropogenic CO₂ forcing at Point B, we assume air-sea CO₂ equilibrium (e.g., increase in atmospheric CO₂ causes an equal increase in seawater pCO₂). Considering the error associated with deconvolution of pCO₂ at 1 m, atmospheric CO₂ increase can, at most, represent 37-42 % of the total C_T contribution $(\frac{\partial pCO_2}{\partial C_T} \frac{dC_T}{dt})$ to $\frac{dpCO_2}{dt}$.”

5) Section 3.4. EOL time series is very interesting and it could be better exploited. In particular, I would suggest that the search for event-scale effects should be made considering the variability of pH at local scale (and not using a threshold which is valid for open ocean). In fact, plot 6d shows the presence of daily pH variations larger than 0.05. These possible event-scale effects could be investigated. Most importantly, authors could resolve the pH variability at daily, seasonal, events and interannual temporal scales producing an additional interesting result. I would encourage the authors to exploit this time series not only for validating the weekly one.

We agree that the SeaFET time-series offers a unique opportunity to explore pH variability at a local and high-frequency scale, however, extensive discussion on this is outside the scope of this paper. Our data presentation is primarily focused on inter-annual changes and how these observations compare to other coastal and open ocean sites. In this light, we restrict the comparison of the high-frequency pH data to previously published categories in other coastal study regions (e.g., Kapsenberg et al., 2016 as mentioned in the manuscript). For example, under this perspective, at Point B event-scale pH variations defined by day to week(s)-long change in mean pH of ~0.1 are absent. We briefly touch on daily, events, and seasonal pH variation in the Results (Section 3.4). In addition, identifying drivers of the extremely small variation in daily pH variability would require other high-frequency data such as oxygen time-series or wind speed (as done in Kapsenberg et al., 2016). In this light, we have not altered the presentation of the EOL pH time-series.

6) Discussion at lines 338-357. It is not convincing the claimed relationship between Point B and the Northern Adriatic Sea. While the Adriatic Sea has a negative relationship with salinity, Point B has a positive relationship with salinity (eq. 2 at line 274). Therefore, the comparison between the two sites is poorly informative of the behaviour of carbonate system at Point B. I would

suggest reducing this part of the discussion to those elements that help in understanding Point B dynamics.

We have altered this paragraph to only present the results of the Northern Adriatic Sea and removed qualitative comparisons between the sites. Given the similar pH and A_T changes, we now only state: “Point B and Adriatic Sea observations are independent but reflect changes in seawater chemistry that may be occurring across a wider coastal region.”

7) Discussion about the drivers of A_T and C_T trends (lines 376-449). This part, although very interesting, is maybe too long and sometimes not well connected to the results. I would suggest shortening this part, focusing on those drivers that are thought to play the most relevant role.

Since the authors claim that terrestrial input are important, a description of the rivers and underground sources in the region of the Bay of Villefranche-sur-Mer (and their contributions to A_T and C_T) should be added into the introduction and used in the discussion for inferring the changes required to explain the observed trends. Moreover, a budget of the A_T and C_T for the Bay could be estimated, considering the volume of the bay, the exchanges with open sea, and the input terms (from atmosphere and terrestrial sources). This analysis can shed some light on the relative importance of the different boundaries to explain the observed trends, and, eventually, quantifying the missing term.

We have shortened and streamlined the Discussion Section 4.2. on potential drivers of A_T and C_T trends. Due to the lack of data on freshwater contributions to Point B we are unable to create a A_T and C_T budget. There is no river mouth next to Point B (closest rivers are 4, 10, and 25 km away which we have now described in the Methods, see RC#9) and contributions of groundwater are unknown. Likewise, residence time of water in the Bay and exchange with the open sea is not known. Unfortunately, we do not have the data to expand the discussion of A_T and C_T beyond what we have already presented.

Minor points:

8) Lines 107 and 128. Please provide the exact length of the timeseries.

We have added the length of the time-series in both locations.

9) Line 118. A description of the riverine input in the area could be of interest. Have rivers along the coast near the Bay of Villefranche-sur-Mer high A_T (lines 118-119) or low A_T (line 122)?

Line 118-119 (original submission) indicated that A_T for rivers draining into the Mediterranean are generally high (for readers unfamiliar with this region) and line 122 was an example of that. We have moved the following sentence from the Discussion to this section in the methods to help clarify this: “Limestone erosion can be observed in the A_T of rivers nearest to Point B (Paillon, due 4 km West; Var due 10 km West; and Roya due 26 km East). River A_T ranges between 1000 to 2000 $\mu\text{mol kg}^{-1}$ (data from Agence de l’Eau Rhône-Méditerranée-Corse, <http://sierm.eaurmc.fr>), and is lower than seawater A_T .” This sentence was also edited in response to RC#25.

10) Line 215. Not clear what “exception” the authors refer to.

The exception is that salinity and temperature were not changing faster at 1 m compared to 50 m. We have revised the sentence to read “carbonate chemistry parameters” instead of “carbonate chemistry”, which a reader may not include salinity or temperature in.

11) Lines 222-223. Why do the authors report that the T trend on anomalies is not significant for the period 1999-2014? Removing the last year (which has high T) seems a subjective choice that should be clarified. If, for any reason, the year 2015 is considered an outlier and it has to be removed, it should be done for all the variables.

Both referees commented on this (see RC#24) and we have removed the subjective analyses of excluding 2015 temperature (as there are outliers in other parts of the time-series as well).

12) Line 231-234. The sentence is quite long and difficult to read, please rephrase it.

We have edited this text to form two complete sentences.

13) Line 254. Does “which peaked in June” refer to parameters or to their monthly trends? Section 3.3.

We revised the sentence to simplify the statement, which now reads, “The fastest increases in A_T and C_T occurred from May through July.”

14) Lines 262 and 274. It is not clear the message that the authors want to convey. At line 262 it is said that salinity is a poor predictor of A_T , however the section ends with a salinity-alkalinity regression. Please, review this section consistently.

We have edited the text to explain (1) that salinity was a poor predictor of A_T over an annual observation period and (2) why we used monthly means to describe the salinity- A_T relationship. For the latter, we now write: “To capture this seasonality without the inter-annual variation of A_T , the salinity- A_T relationship at Point B was estimated from monthly means...”

15) Lines 294-295. The sentence is long and difficult to read. Please rephrase it. Further, what do the authors mean for “morning sampling”? Is it referred to the sampling procedure of the Point B timeseries? If so, it should be introduced in Material & Method, and motivation explained if important.

We removed this sentence as it does not add important information and this sampling procedure is already described in the Materials and Methods.

16) Line 311-312. This sentence seems inaccurate. Which is the causal factor of C_T increase due to A_T increase?

We have revised this discussion point to clarify that increases in C_T could just be a direct consequence of increasing A_T , which has carbon constituents, and include a discussion on various processes that could give rise to these trends. These edits are part of the revised Discussion (2nd, 3rd, and 4th paragraph of the Discussion). We use this relationship between A_T and C_T to make an assumption that allows us to estimate the role of increasing atmospheric CO_2 on the ocean acidification trend at Point B.

17) Line 313. Which “spatial extent” do the authors mean?

We have removed this sentence for clarity. In the revised Discussion, we simply report other observed trends nearest to Point B (DYFAMED, Adriatic Sea).

18) Lines 336-337. The analysis of the coastal–offshore gradient would deserve some additional investigations, since offshore deep water is supposed to play a role for CT evolution at point B (at lines 323-325).

This may be a misunderstanding as we do not intend to indicate influence of offshore deep water at Point B. We have revised the statement about winter mixing offshore to show that deep water has higher C_T and specify that this is observed at DYFAMED: “For C_T , peak values occur in winter when the water column is fully mixed. For reference, at DYFAMED, mixing occurs down to more than 2000 m depth and C_T is up to 100 $\mu\text{mol kg}^{-1}$ higher in deep (Copin-Montégut and Bégovic, 2002).”

19) Lines 359-369. This part could be moved to introduction.

We have now integrated the text describing coastal ocean acidification trends into the Introduction.

20) Lines 772-776. Table 3 caption reports not only the description of the table but also comments on results. Please remove the unnecessary text.

These statements in Table 3 no longer apply due to the new deconvolution analyses. Nonetheless, we have taken care to remove statements describing results from Table legends.

21) Lines 799-801. Figure 6. Please use the caption to describe the plots without describing the results.

We have removed any potential result statement from the Figure 6 caption.

Anonymous Referee #2, Received and published: 22 November 2016

The article presents, analyses, and discusses the time series of physical parameters and carbonate system properties gathered in a coastal station of the NW Mediterranean Sea and spanning nearly one decade. The analyses on different time scales of ocean acidification, responsible for changes in the marine CO₂ system with effects on the dissolved inorganic carbon (CT), partial pressure of CO₂ (pCO₂), pHT, total alkalinity (AT) and calcium carbonate saturation states is valuable. Actually, sustained observations of inorganic carbon parameters by means of long term time series count on a few sites over the global oceans, and on even fewer in the Mediterranean basin, especially in the coastal area, although such shallow zones can be exposed to intense land sea interactions and to a great complexity of physical and biological processes interacting with ocean acidification. Ocean acidification in coastal zones is remarkably difficult to predict. The present paper can contribute to a better knowledge of the coastal systems vulnerability to ocean acidification, by investigating on the multiple drivers eventually working in this environment. In particular, the analysis of the time series trends (§3.1) appears robust and the decomposition of ocean acidification into the principal drivers is appropriate and informative.

No response needed.

The method applied for the deconvolution of pHT and pCO₂, (proposed in §3.2 and 3.3,) is new for both the Med Sea and coastal regions, and provides useful indications on different processes driving ocean acidification in this site in comparison with open ocean.

No response needed.

The discussion of CT and AT increases as the main drivers of pH decrease (§4.1 and 4.2) is well conducted. The proposed attribution of these two concomitant increases (AT and CT) to terrestrial inputs with changing and increasing AT and CT (riverine water and/or to groundwater springs) seems reasonable. The hypothesis is deeply discussed, although not enough supported by the correlation with low salinity (see major comments). Finally, conclusions well enhance the role of land sea interactions. In conclusion, the publication of this article in OS is worth after a few revisions (reported below).

No response needed.

Major Comments:

22) Discussion on drivers of AT and CT trends (line 402-439). I agree with the suggestion of Referee #1. The description (in terms of carbonate chemistry) of the river and underground sources in the region of the Bay of Villefranche should be added for a more complete discussion.

Unfortunately, these types of data (beyond what we included in the original manuscript) are not available for our study site. We added a statement to the Methods to include the distance of the three nearest rivers in the Bay itself (4, 10, and 25 km) and a statement on the lack of data to pursue hypothesis of A_T and C_T trends: “Signatures of limestone erosion can be observed in A_T of nearby rivers (Var, Paillon, and Roya) but detailed time-series are not available. Likewise, riverine influence at Point B has not been quantified.”

23) Then I'm wondering whether results (§3.3) and discussion (§4.2) might benefit from the recent paper by Fry et al. (2015). In the paper authors calculate “Alk1”, the same as normalized AT, to remove the contribution of evaporation and precipitation, and calculate “Alk2” (accounting for river AT) to remove the riverine input. This was done because Friis et al. (2003) found that misleading results are produced if normalized alkalinity is used in ocean regions receiving river outflows. . . . It seems to me that you have all the necessary data (Alk_m = measured alkalinity, salinity and Alk_r =river alkalinity) requested to calculate Alk2. Following the subtraction of these major processes that affects alkalinity at Point B, I would expect: salinity- AT relationship (through the 9 years of time series) improves the positive AT anomaly disappears (or at least decreases).

The approach of Fry et al. 2015 would reveal insight to the A_T trends at Point B, however, we do not have the necessary data to do this (see RC#22). The river A_T mentioned in the Methods (see RC#9) is based on data that is collected once or twice a year and do not cover the full range of our study period. We agree with both referees that the alkalinity trends could be investigated with the trends in freshwater sources, as is the most likely driver suggested by us as well, but we just do not have the time-series data to do this for this region.

Minor comments:

24) Lines 222-224. Temperature anomaly increased but this significance was lost with the exclusion of the year 2015. . . . The sentence is not clear to me. Do you mean that excluding the year 2015 (it was exceptionally warm and SST raised to the highest values during summer) there was no increase in temperature anomaly? and therefore the temperature increase cannot be the

driver of observed changes in the carbonate system properties ? In any case please rephrase the sentence.

While 2015 was an exceptionally warm year, outliers (e.g., warm events) were also present at the beginning of the time-series. Since we did not take a systematic approach to removing outliers, we have removed this secondary analysis and statements from the paper (RC#11). In addition, we have expanded the discussion on the warming trend that occurred over the study period. Following the revised deconvolution analysis (RC#2), temperature is a significant driver of pH trends.

25) Lines 320-322. During the transition of these processes, salinity decreases to a minimum in May, reflecting the freshwater input that dilutes AT to minimum values. . . Fresh water is able to dilute AT to minimum values if discharging rivers have lower AT than seawater but this might be not true in case of rivers draining carbonatic watershed (later, line 416, authors report that outflowing rivers into the Bay of Villefranche have high AT). This can be misleading, please modify.

We have clarified that, locally, rivers nearest to Point B have an A_T that is lower than seawater A_T . In light of RC#9, we have clarified our definition of 'high' A_T in the following excerpt from the Methods: "Both of these hydrodynamics movements have signatures of river discharge, which for the Mediterranean Sea in general are high in A_T (Copin-Montégut, 1993; Schneider et al., 2007). Limestone erosion can be observed in the A_T of rivers nearest to Point B (Paillon, due 4 km West; Var due 10 km West; and Roya due 26 km East). River A_T ranges between 1000 to 2000 $\mu\text{mol kg}^{-1}$ (data from Agence de l'Eau Rhône-Méditerranée-Corse, <http://sierm.eaurmc.fr>), and is slightly lower than seawater A_T ."

26) Line 325-326. Following winter CT declines due to a combination of phytoplankton bloom carbon uptake and freshwater dilution. . . Again I would be more cautious as freshwater dilutes if it contains lower CT . . .

As the A_T of local rivers is $\sim 1000\text{-}2000 \mu\text{mol kg}^{-1}$, C_T in river water is not likely to be greater than that of seawater. We have added the assumption that river C_T is lower than seawater C_T to this sentence. "Following winter, C_T declines due to a combination of phytoplankton bloom carbon uptake and freshwater dilution (assuming river $C_T < \text{seawater } C_T$), until the onset of summer stratification."

27) Lines 351-357. The correlates between Point B and N Adriatic Sea suggest a common driver of changes in ocean carbonate chemistry at these two sites (possibly linked via shared watersheds of the Alps) Mediterranean Sea. Could you explain and present more clearly this hypothesis?

In response to RC#6, we have removed the qualitative statements comparing Point B with the Northern Adriatic Sea. Instead, we suggest that the two independent studies might indicate a process that is present around a greater coastal region of the Mediterranean Sea.

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1 **Coastal ocean acidification and increasing total alkalinity in the NW Mediterranean Sea**

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17 **Abstract.** Coastal time-series of ocean carbonate chemistry are critical for understanding how
18 global anthropogenic change manifests in near-shore ecosystems. Yet, they are few and have low
19 temporal resolution. At the time-series station Point B in the NW Mediterranean Sea, seawater
20 was sampled weekly from 2007 through 2015, at 1 and 50 m, and analyzed for total dissolved
21 inorganic carbon (C_T) and total alkalinity (A_T). Parameters of the carbonate system such as pH
22 (pH_T , total hydrogen ion scale) were calculated and a deconvolution analysis was performed to
23 identify drivers of change. The rate of surface ocean acidification in pH_T was -0.0028 ± 0.0003
24 yr^{-1} . This rate is larger than previously identified open-ocean trends due rapid warming that
25 occurred over the study period (0.072 ± 0.022 °C yr^{-1}). The acidification trend can be attributed
26 to atmospheric carbon dioxide (CO_2) forcing (61 %, 2.08 ± 0.01 ppm CO_2 yr^{-1}) and warming (39
27 %). Similar trends were observed at 50 m but were generally slower with only 80 % penetration
28 of anthropogenic CO_2 relative to the surface. At 1 m depth, atmospheric forcing accounted for
29 approximately 40 % of the observed C_T increase (2.97 ± 0.20 $\mu mol\ kg^{-1}\ yr^{-1}$). The remaining C_T
30 increase could be driven by the synchronous increase in A_T (2.08 ± 0.19 $\mu mol\ kg^{-1}\ yr^{-1}$). Based
31 on the analysis of monthly trends, concomitant increases in C_T and A_T were fastest in the spring-
32 summer transition. The driving process of the interannual increase in A_T remains to be identified,
33 but it has a seasonal and shallow component, which may indicate riverine or groundwater
34 influence. This study exemplifies the importance of understanding changes in coastal carbonate
35 chemistry through the lens of biogeochemical cycling at the land-sea interface. This is the first
36 coastal acidification time-series providing multiyear data at high temporal resolution. The data
37 confirm rapid warming in the Mediterranean Sea and demonstrate coastal acidification with a
38 synchronous increase in total alkalinity.

Comment [LK1]: RC#1

Deleted: Monitoring global ocean change is necessary in coastal zones due to their physical and biological complexity. Here, we document changes in coastal carbonate chemistry at the coastal time-series station Point Bin the NW Mediterranean Sea from 2007 through 2015 at 1 and 50 m. The rate of surface ocean acidification (-0.0028 ± 0.0003 units $pH_T\ yr^{-1}$) was faster-than-expected based on atmospheric carbon dioxide forcing alone. Changes in carbonate chemistry were predominantly driven by an increase in total dissolved inorganic carbon (C_T , $+2.97 \pm 0.20$ $\mu mol\ kg^{-1}\ yr^{-1}$), > 50 % of which was buffered by a synchronous increase in total alkalinity (A_T , $+2.08 \pm 0.19$ $\mu mol\ kg^{-1}\ yr^{-1}$). The increase in A_T was unrelated to salinity and its cause remains to be identified. Interestingly, concurrent increases in A_T and C_T were most rapid from May to July. Changes at 50 m were slower compared to 1 m. It seems therefore likely that changes in coastal A_T cycling via a shallow coastal process gave rise to these observations.

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63 **Keywords** – ocean change, ocean acidification, time-series, pH, alkalinity, dissolved inorganic

64 carbon, pCO₂, Mediterranean Sea

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66 **1. Introduction**

67 Maintaining time-series of oceanographic data is essential for understanding
68 anthropogenic changes in the ocean (Tanhua et al., 2013). On land, fossil fuel burning, cement
69 production and land use changes have contributed ~600 Gt carbon to the atmosphere during the
70 period 1750-2015 (Le Quéré et al., 2016). In the recent decade 2006-2015, an estimated 25 % of
71 this anthropogenic carbon has been absorbed by the ocean in the form of carbon dioxide (CO₂;
72 (Le Quéré et al., 2016)), and causing global changes to the ocean carbonate system. Absorption
73 of CO₂ by seawater produces carbonic acid, which decreases seawater pH, and is of great
74 concern for biological processes and marine ecosystems (Doney et al., 2009; Gattuso and
75 Hansson, 2011; Pörtner et al., 2014). Since the preindustrial era, global mean ocean pH has
76 declined by 0.1 (Rhein et al., 2013). Due to the declining trend of ocean pH with increasing
77 anthropogenic CO₂, the process is termed ‘ocean acidification’, but this expression represents a
78 suite of chemical changes, including increases in total dissolved inorganic carbon (C_T) and
79 partial pressure of CO₂ (pCO₂) and decrease in calcium carbonate saturation states (Ω, aragonite
80 and calcite; (Dickson, 2010)). Rates of ocean acidification differ by ocean region and range from
81 -0.0026 (Irmingier Sea, North Atlantic) to -0.0013 (South Pacific) units pH yr⁻¹ (Bates et al.,
82 2014). Such time-series remain spatially limited, especially in coastal regions, which provide
83 valuable ecosystem services (Barbier et al., 2011; Costanza et al., 1997) and are under high
84 anthropogenic impact (Halpern et al., 2008). Here, we present the first coastal ocean acidification
85 time-series at high temporal resolution.

86 Compared to the global ocean, marginal seas serve a critical role in anthropogenic CO₂
87 storage via enhanced CO₂ uptake and export to the ocean interior (Lee et al., 2011). As a
88 marginal sea, the Mediterranean Sea has a naturally high capacity to absorb but also buffer

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97 anthropogenic CO₂ (Álvarez et al., 2014; Palmiéri et al., 2015). This is primarily due to the high
98 total alkalinity (A_T) of Mediterranean waters and overturning circulation (Lee et al., 2011;
99 Palmiéri et al., 2015; Schneider et al., 2010). In the Mediterranean Sea, the salinity- A_T
100 relationship is driven by the addition of river discharge and Black Sea input, which are generally
101 both high in A_T (Copin-Montégut, 1993; Schneider et al., 2007). Combined with evaporation,
102 this results in higher A_T and salinity in the Mediterranean Sea compared to the Atlantic
103 Mediterranean source water (Jiang et al., 2014). On average, Mediterranean Sea A_T is 10 %
104 higher than in the global ocean (Palmiéri et al., 2015). The surface ocean acidification rate,
105 estimated at $\Delta p\text{H}_T$ (total hydrogen ion scale) of -0.08 since 1800, is comparable to that of the
106 global ocean despite a 10 % greater anthropogenic carbon inventory (Palmiéri et al., 2015). Due
107 to its important role in carbon sequestration and ecological sensitivity to anthropogenic change
108 with economic consequences (Lacoue-Labarthe et al., 2016), the Mediterranean Sea could
109 provide insight to global trends (Lejeusne et al., 2010).

110 Over the last few years, numerous studies have estimated ocean acidification rates across
111 the Mediterranean Sea (Table 1). Together, these studies cover various study periods with a
112 range of techniques yielding different results. For example, estimates of change in pH of bottom
113 waters since the preindustrial era range between -0.005 to -0.06 (Palmiéri et al., 2015) and as
114 much as -0.14 for full profile estimates (Touratier and Goyet, 2011). Techniques for estimating
115 ocean acidification in the Mediterranean Sea thus far include: (1) hind-casting, using high-
116 resolution regional circulation models (Palmiéri et al., 2015), the TrOCA approach as applied to
117 cruise-based profile data (Krasakopoulou et al., 2011; Touratier and Goyet, 2011; Touratier et
118 al., 2016) and others (Howes et al., 2015), (2) partially reconstructed time-series (Marcellin Yao
119 et al., 2016), (3) comparative study periods (Luchetta et al., 2010; Meier et al., 2014), and (4)

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123 sensor-based observations over a short study period (Flecha et al., 2015). Ocean acidification
124 time-series of consistent sampling over many years are lacking for the Mediterranean Sea (Group
125 et al., 2011), especially along the coast where river discharge influences the carbonate system
126 (Ingrosso et al., 2016).

Comment [LK2]: 'The MerMex Group, 2011'

127 Compared to the open ocean, shallow coastal sites exhibit natural variability in carbonate
128 chemistry over annual timeframes (Hofmann et al., 2011; Kapsenberg and Hofmann, 2016;
129 Kapsenberg et al., 2015), complicating the detection and relevance of open ocean acidification in
130 isolation of other processes (Duarte et al., 2013). In the NW Pacific coast, rapid acidification of
131 surface waters (ΔpH_T -0.058 units yr^{-1}) at Tatoosh Island was documented in the absence of
132 changes in known drivers of local pH variability (e.g., upwelling, eutrophication, and more;
133 (Wootton and Pfister, 2012; Wootton et al., 2008)). Further inshore, in the Hood Canal sub-basin
134 of the Puget Sound, only 24-49 % of the estimated pH decline from pre-industrial values could
135 be attributed to anthropogenic CO_2 (Feely et al., 2010). The excess decrease in pH was attributed
136 to increased remineralization (Feely et al., 2010). Acidification rates documented along the
137 North Sea Dutch coastline and inlets were highly variable in space, with some exceeding the
138 expected anthropogenic CO_2 rate by an order of magnitude while others exhibited an increase in
139 pH (Provoost et al., 2010).

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140 Variability in coastal carbonate chemistry stems from both physical (e.g., upwelling, river
141 discharge; (Feely et al., 2008; Vargas et al., 2016)) and biological processes (e.g., primary
142 production, respiration, net calcification). Within watersheds, coastal carbonate chemistry is
143 affected by eutrophication (Borges and Gypens, 2010; Cai et al., 2011), groundwater supply (Cai
144 et al., 2003), and land use and rain influence on river alkalinity (Raymond and Cole, 2003; Stets
145 et al., 2014). Over longer periods, pH can also be influenced by atmospheric deposition (Omstedt

146 et al., 2015). Through primary production and respiration, coastal ecosystems produce pH
147 fluctuations over hours (e.g., seagrass, kelp) to months (e.g., phytoplankton blooms; (Kapsenberg
148 and Hofmann, 2016)). Due to existing pH variability in coastal seas, it is necessary to quantify
149 high-frequency trends in order to interpret the pH changes inferred from lower-frequency
150 sampling.

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151 In this study, we present the first complete time-series data quantifying the present-day
152 ocean acidification rate for a coastal site in the Mediterranean Sea, based on weekly
153 measurements of A_T and C_T sampled from 2007 through 2015. For a subset of this time-series,
154 pH variability was documented using a SeaFET™ Ocean pH Sensor in order to assess hourly pH
155 variability. For comparison and consistency with other ocean acidification time-series around the
156 world, we report rates of change based on anomalies (Bates et al., 2014) and identify drivers of
157 change.

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159 2. Materials and methods

161 2.1. Site description

162 A carbonate chemistry time-series was initiated in 2007 and maintained through 2015 in
163 the NW Mediterranean Sea at the entrance of the Bay of Villefranche-sur-Mer, France (Fig. 1):
164 Point B station (43.686° N, 7.316° E, 85 m bottom depth). A second site, Environment
165 Observable Littoral buoy (EOL, 43.682° N, 7.319° E, 80 m bottom depth), was used for pH
166 sensor deployment starting in 2014. These two sites are 435 m apart. The site Point B is an
167 historical sampling point, since 1957, regarding several oceanographic parameters. A full site
168 description and research history has been detailed by De Carlo et al. (2013). Briefly, the Bay is a

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175 narrow north-south facing inlet with steep bathymetry and estimated volume of 310 million m³.
176 The surrounding region is predominately composed of limestone with a series of shallow,
177 submarine groundwater karst springs (Gilli, 1995). The North current, a major and structuring
178 counter-clockwise current in the Ligurian Sea, can sometimes flow close to Point B. The Bay can
179 also be, on occasion, influenced by local countercurrents. Both of these hydrodynamics
180 movements have signatures of river discharge, which for the Mediterranean Sea in general are
181 high in A_T (Copin-Montégut, 1993; Schneider et al., 2007). Limestone erosion can be observed
182 in the A_T of rivers nearest to Point B (Paillon, due 4 km West; Var due 10 km West; and Roya
183 due 26 km East). River A_T ranges between 1000 to 2000 $\mu\text{mol kg}^{-1}$ (data from *Agence de l'Eau*
184 *Rhône-Méditerranée-Corse*, <http://sierm.eaurmc.fr>), and is lower than seawater A_T . The Paillon
185 River, whose plume on occasion reaches into the Bay (L. Mousseau, pers. obs.), was sampled on
186 18 August 2014 and had a A_T of $1585 \pm 0.1 \mu\text{mol kg}^{-1}$ ($N = 2$, J.-P. Gattuso, unpubl.). Due to low
187 primary productivity, seasonal warming drives the main annual variability in carbonate
188 chemistry at this location (De Carlo et al., 2013).

189

190 2.2. Point B data collection, processing, and analysis

191 To document long-term changes in ocean carbonate chemistry at Point B, seawater was
192 sampled weekly from 9 January 2007 to 22 December 2015. Samples were collected at 1 and 50
193 m, using a 12-L Niskin bottle at 9:00 local time. Seawater was transferred from the Niskin bottle
194 to 500 mL borosilicate glass bottles and fixed within an hour via addition of saturated mercuric
195 chloride for preservation of carbonate parameters, following recommendations by Dickson et al.
196 (2007). Duplicate samples were collected for each depth. For each sampling event, CTD casts
197 were performed either with a Seabird 25 or Seabird 25+ profiler whose sensors are calibrated at

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201 least every two years. Accuracy of conductivity (SBE4 sensor) and temperature (SBE3 sensor)
202 measurements from CTD casts were 0.0003 S m^{-1} and 0.001°C , respectively.

203 Within six months of collection, bottle samples were analyzed for C_T and A_T via
204 potentiometric titration following methods described by Edmond (1970) and DOE (1994), by
205 *Service National d'Analyse des Paramètres Océaniques du CO₂*, at the Université Pierre et Marie
206 Curie in Paris, France. Precision of C_T and A_T was less than $3 \mu\text{mol kg}^{-1}$, and the average
207 accuracy was 2.6 and $3 \mu\text{mol kg}^{-1}$, as compared with seawater certified reference material
208 (CRM) provided by A. Dickson (Scripps Institution of Oceanography). Only obvious outliers
209 were omitted from the analyses: three C_T values at 1 m ($> 2300 \mu\text{mol kg}^{-1}$), one A_T value at 1 m
210 ($> 2900 \mu\text{mol kg}^{-1}$), and one A_T value at 50 m ($< 2500 \mu\text{mol kg}^{-1}$). The C_T and A_T measurements
211 on replicate bottle samples were averaged for analyses.

212 Calculations of the carbonate system parameters were performed using the R package
213 seacarb version 3.1 with C_T , A_T , *in situ* temperature and salinity as inputs (Gattuso et al., 2016).

214 Total concentrations of silicate (SiOH_4) and phosphate (PO_4^{3-}) were used when available from
215 Point B (L. Mousseau, unpubl., <http://somlit.epoc.u-bordeaux1.fr/fr/>). Detection limits for
216 nutrients were $0.03 \mu\text{M}$ for SiOH_4 and 0.003 to $0.02 \mu\text{M}$ for PO_4^{3-} ; relative precision of these
217 analyses is 5-10 % (Aminot and K  rouel, 2007). Total boron concentration was calculated from
218 salinity using the global ratio determined by Lee et al. (2010). The following constants were
219 used: K_1 and K_2 from Lueker et al. (2000), K_f from Perez and Fraga (1987), and K_s from Dickson
220 (1990). Reported measured parameters are temperature, salinity, A_T , and C_T , and derived
221 parameters are pH_T (total hydrogen ion scale), pH_T normalized to 25°C (pH_{T25}), pCO_2 , and
222 aragonite (Ω_a) and calcite (Ω_c) saturation states. Salinity-normalized changes in A_T (nA_T) and C_T

Comment [LK9]: Updated based on updates within SOMLIT data analyses

223 (nC_T) were calculated by dividing by *in situ* salinity and multiplying by 38. Except for pH_{T25} , all
224 parameters are reported at *in situ* temperatures.

225 The average uncertainties of the derived carbonate parameters were calculated according
226 to the Gaussian method (Dickson and Riley, 1978) implemented in the “errors” function of the R
227 package seacarb 3.1 (Gattuso et al., 2016). The uncertainties are $\pm 2.7 \times 10^{-10}$ mol H^+ (about
228 0.015 units pH_T), $\pm 15 \mu\text{atm } pCO_2$, and ± 0.1 unit of the aragonite and calcite saturation states.

229 To quantify interannual changes in carbonate parameters, the data were detrended for
230 seasonality by subtracting monthly means from the time-series. The resulting anomalies were
231 analyzed using a linear regression. [This approach follows methods from Bates et al. \(2014\) to](#)
232 [allow for comparisons of trends observed at different time-series stations.](#) All analyses were
233 performed in R (Team, 2016).

Comment [LK10]: “R Core Team 2016”

235 2.3. Deconvolution of pH_T and pCO_2

236 To identify proportional contributions of various drivers to ocean acidification trends at
237 Point B, deconvolution of time-series pH_T and pCO_2 was performed following methods from
238 García-Ibáñez et al. (2016) for observations at 1 and 50 m. The equation is described below for
239 pH_T , where changes in pH_T are driven by changes in temperature (T), salinity (S), A_T , and C_T ,
240 over time (t), according to the following model:

$$241 \quad \frac{dpH_T}{dt} = \frac{\partial pH_T}{\partial T} \frac{dT}{dt} + \frac{\partial pH_T}{\partial S} \frac{dS}{dt} + \frac{\partial pH_T}{\partial A_T} \frac{dA_T}{dt} + \frac{\partial pH_T}{\partial C_T} \frac{dC_T}{dt} \quad (1)$$

242 Here, $\frac{\partial pH_T}{\partial var} \frac{dvar}{dt}$ represents the slope contribution of changing *var* to the estimated change
243 in pH_T , where *var* is either T , S , A_T , or C_T . The rate of pH change due to *var* ($\frac{\partial pH_T}{\partial var} \frac{dvar}{dt}$) was
244 estimated by calculating pH_T using the true observations of *var* but monthly mean values of the
245 other three variables, and regressing [the anomaly](#) (following subtraction of respective monthly

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246 [means](#)) to time. The calculation was repeated for $p\text{CO}_2$ ($\frac{dp\text{CO}_2}{dt}$) in order to compare the rate of
247 increase with that of atmospheric CO_2 .

248 As a sub-component of $\frac{\partial p\text{CO}_2}{\partial C_T} \frac{dC_T}{dt}$, the rate of anthropogenic CO_2 increase was estimated
249 from atmospheric CO_2 concentrations nearest to Point B (Plateau Rosa, Italy, courtesy of the
250 World Data Center for Greenhouse Gases, <http://ds.data.jma.go.jp/gmd/wdcgg/>). For these data,
251 missing daily values were linearly interpolated. A linear regression was performed [on anomalies](#)
252 where the slope represents the rate of [anthropogenic](#) CO_2 increase in the atmosphere. Finally, to
253 help identify different processes that might have contributed to the observed trends, linear
254 regressions were performed on change in A_T and C_T by month and on the salinity- A_T relationship
255 by year.

256

257 **2.4. SeaFET data collection, processing, and analysis**

258 To capture pH variability at higher-than-weekly sampling frequencies, a SeaFET™
259 Ocean pH sensor (Satlantic) was deployed on the EOL buoy (435 m from the Point B sampling
260 site) starting in June 2014, at 2 m depth. Autonomous sampling was hourly and deployment
261 periods ranged between 1 and 3 months. Field calibration samples for pH were collected weekly,
262 using a Niskin bottle next to SeaFET within 15 min of measurement. This sampling scheme was
263 sufficient for this site as there is no large high-frequency pH variability. Unlike Point B
264 sampling, SeaFET calibration samples were processed for pH using the spectrophotometric
265 method (Dickson et al., 2007) with purified m-cresol purple (purchased from the Byrne lab,
266 University of South Florida). *In situ* temperature, salinity, and A_T measured at Point B, within 30
267 min of the SeaFET sampling, were used to calculate *in situ* pH_T of the calibration samples.
268 SeaFET voltage was converted to pH_T using the respective calibration samples for each

269 deployment period, following the methods and code described in Bresnahan et al. (2014) but
270 adapted for use in R.

271 The estimated standard uncertainty in SeaFET pH_T is ± 0.01 and was calculated as the
272 square root of the sum of each error squared. The sources of errors are: measurement error of
273 spectrophotometric pH (± 0.004 , $N = 68$ mean SD of 5 replicate measurements per calibration
274 sample for samples collected between 16 July 2014 and 3 May 2016), spatio-temporal mismatch
275 sampling at EOL (± 0.007 , mean offset of pH_T of the calibration samples from calibrated time-
276 series), and variability in purified m-cresol dye batch accuracy as compared to Tris buffer CRM
277 pH (± 0.006 , mean offset of pH_T of the spectrophotometric measurement of Tris buffer from the
278 CRM value).

279

280 3. Results

281

282 3.1. Time-series trends

283 At Point B from January 2007 to December 2015, >400 samples were collected for
284 carbonate chemistry at both 1 and 50 m. Anomaly trends detected at 1 m (Fig. 2) were also
285 significant at 50 m (Fig. 3, Table 2), with the exception that salinity increased at 50 m ($0.0063 \pm$
286 $0.0020 \text{ units yr}^{-1}$, $P = 0.002$). At 1 m, trends were significant for pH_T ($-0.0028 \pm 0.0003 \text{ units yr}^{-1}$,
287 $N = 412$), A_T ($2.08 \pm 0.19 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$, $N = 417$), C_T ($2.97 \pm 0.20 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$, $N = 416$),
288 pCO_2 ($3.53 \pm 0.39 \mu\text{atm yr}^{-1}$, $N = 412$), and Ω_a ($-0.0064 \pm 0.0015 \text{ units yr}^{-1}$, $N = 412$). At the
289 same time, temperature anomaly increased ($0.072 \pm 0.022 \text{ }^\circ\text{C yr}^{-1}$, $N = 413$) and no significant
290 change in the salinity was detected at 1 m ($P = 0.702$, $N = 417$). Trends of carbonate chemistry
291 parameters were faster at 1 m compared to 50 m, with the exception of salinity and temperature,

Comment [LK12]: This section now includes results from 50 m data, which were previously in a supplemental file.

Deleted: Analyses for 50 m are available (Table S1, Fig. S1) but here, we focus on results from 1 m unless explicitly specified otherwise (Fig. 2, Table 2). For time-series anomalies a

Deleted: carbonate chemistry anomalies

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Deleted: , but this significance was lost with the exclusion of the year 2015 (analysis not shown; changes in other carbonate chemistry parameters remained significant). N

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303 The warming rate at 50 m was slightly greater compared to 1 m, mostly due to increasing
304 summer temperatures since 2007.

305 Strong seasonal cycles of carbonate chemistry parameters were present at Point B at 1 m
306 (Fig. 4). Calculated monthly means (2007-2015) are described briefly and listed in Table S1.

307 Mean temperature range was 11.2 °C with a maximum at 24.77 ± 1.35 °C in August and
308 minimum of 13.58 ± 0.41 °C in February. The range in A_T was $19 \mu\text{mol kg}^{-1}$ from June to
309 September. The C_T range was $33 \mu\text{mol kg}^{-1}$ with a peak in late winter and minimum values in

310 August and October. Due to summer warming coinciding with the period of peak primary
311 productivity (De Carlo et al. 2013), warming countered the influence of low C_T on pH. As a
312 result, pH reached minimum values in summer (8.02 ± 0.03 , July and August) and peaked in late
313 winter (8.14 ± 0.01 , February and March), for an overall annual pH range of 0.12. The
314 corresponding $p\text{CO}_2$ range was $128 \mu\text{atm}$ from February to August. Seasonal cycles were smaller
315 at 50 m compared to 1 m (Table S1).

317 3.2. Deconvolution of pH_T and pCO_2

318 Deconvolutions of pH and pCO_2 are presented in Table 3. For both depths, the sum of the
319 slopes ($\frac{d\text{pH}_T}{dt} - \frac{d\text{pCO}_2}{dt}$) match the trends of pH_T (-0.0028 yr^{-1} for 1 m and -0.0026 yr^{-1} for 50 m) and
320 fall within the error of pCO_2 trends. The contribution of warming (e.g., -0.0011 units $\text{pH}_T \text{ yr}^{-1}$ at
321 1 m) matched the difference between the trends of pH_T and pH_{T25C} (Table 2). These results
322 indicate that the deconvolution analyses represent the observed trends well.

323 At 1 m, warming accounted for 39 and 37 % of $\frac{d\text{pH}_T}{dt}$ and $\frac{d\text{pCO}_2}{dt}$, respectively ($P = 0.001$).

324 Since warming was slightly greater at 50 m compared to 1 m, warming accounted for a larger

325 proportional influence on $\frac{d\text{pH}_T}{dt}$ and $\frac{d\text{pCO}_2}{dt}$ at 50 m compared to 1 m. At both depths, the

Comment [LK15]: RC#12

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Deleted: and minimum pH in summer (8.02 ± 0.03 , July and August)

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Comment [LK16]: RC#2 Now includes results for 50 m also.

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Deleted: and salinity had contributing (approx. 35% and 5% respectively) but non-significant effects. The 2007-2015 observation period is likely not long enough to detect significance of the relatively large temperature contribution to .

340 predominant driver of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ was the increase in C_T . Increasing A_T countered the
 341 influence of increasing C_T on $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ by 64 and 60 %, respectively at 1 m and by 65 and
 342 58 %, respectively at 50 m. Increasing salinity at 50 m contributed to both $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$.
 343 Atmospheric CO₂ anomaly at Plateau Rosa increased by 2.08 ± 0.01 ppm yr⁻¹ ($F_{1,3285} =$
 344 4664 , $P < 0.001$, $R^2 = 0.93$) during the study period 2007-2015, and represents the anthropogenic
 345 CO₂ forcing on seawater pH. To estimate the maximum influence of anthropogenic CO₂ forcing
 346 at Point B, we assume air-sea CO₂ equilibrium (e.g., increase in atmospheric CO₂ causes an
 347 equal increase in seawater pCO₂). Considering the error associated with deconvolution of pCO₂
 348 at 1 m, atmospheric CO₂ increase can, at most, represent 37-42 % of the total C_T contribution
 349 ($\frac{\partial pCO_2}{\partial C_T} \frac{dC_T}{dt}$ to $\frac{dpCO_2}{dt}$). This leaves 58-63 % of the total C_T contribution to pCO₂ trends unaccounted
 350 for.

351 As A_T is not influenced by addition of anthropogenic CO₂ to seawater but still increased,
 352 the next question was whether or not the changes in A_T and C_T were process-linked. At 1 m,
 353 regressions of annual monthly trends of A_T and C_T revealed similar seasonal cycles for both
 354 parameters (Fig. 5, Table S2). The fastest increases in A_T and C_T occurred from May through
 355 July. The smallest (non-significant) changes occurred in January. The synchronicity between
 356 monthly trends of A_T and C_T was also observed at 50 m, but the rates were slower (analysis not
 357 shown).

359 3.3. Salinity and A_T relationships

360 Over an annual observation period at 1 m, salinity was a poor predictor of A_T , with the
 361 exception of 2007 (Fig. 6). The R^2 value for each annual salinity- A_T relationship at 1 m ranged

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Comment [LK17]: = 100 * [%contribution of A_T] / [%contribution C_T] for both pH and pCO₂ deconv.

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Deleted: 2.02 ± 0.03 ppm yr⁻¹ ($F_{1,3285} = 5852.43$, $P < 0.001$, $R^2 = 0.64$), with an anomaly rate of

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Comment [LK18]: = $2.08 / (5.26 + 0.36)$
 = $2.08 / (5.26 - 0.36)$

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Deleted: Significant increases in A_T occurred from May to July. Significant increases in C_T occurred from February-August and in November. Results of regression analyses on monthly changes are listed in Table S3.

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Deleted: Given the coastal locale and the increase in A_T , it is interesting to look at the interannual variability of the relationship between salinity and A_T (Fig. 5), with the exception of 2007,

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382 from 0.00 (in 2013) to 0.87 (in 2007) with y-intercepts (A_{T0} , total alkalinity of the freshwater
383 end-member) ranging between $-176 \mu\text{mol kg}^{-1}$ (in 2007) and $2586 \mu\text{mol kg}^{-1}$ (in 2013). The
384 interannual variability of the salinity- A_T relationship was driven by the variability in A_T observed
385 at salinity < 38.0 that was present from November through July.

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386 Changes in salinity (based on monthly means) at Point B was small and ranged from
387 37.64 ± 0.26 to 38.21 ± 0.11 from May to September, following freshwater input in winter and
388 spring and evaporation throughout summer and fall (Fig. 4). Highest (> 38.0) and most stable
389 salinity observations were made in August through October and coincided with the period of
390 maximum A_T (2562 and $2561 \pm 9 \mu\text{mol kg}^{-1}$ in September and October, respectively). Minimum
391 A_T ($2543 \pm 14 \mu\text{mol kg}^{-1}$) was observed in June, one month after minimum salinity. To capture
392 this seasonality without the inter-annual variation of A_T , the salinity- A_T relationship at 1 m was
393 estimated from monthly means ($R^2 = 0.74$) where A_T units are $\mu\text{mol kg}^{-1}$ and error terms are
394 standard errors:

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$$A_T = 1554.9(\pm 185.9) + 26.3(\pm 4.9) \times S \quad (2)$$

396 At 50 m, monthly salinity and A_T were less correlated over an annual cycle (analysis not shown).
397 Salinity remained stable at 38.0 from January through September while A_T declined by $13 \mu\text{mol}$
398 kg^{-1} . In general, seasonal changes were dampened at 50 m compared to 1 m.

400 3.4. High-frequency pH data

401 To verify the weekly sampling scheme at Point B, a continuous record of high-frequency
402 pH observations was obtained via 11 consecutive SeaFET deployments from June 2014 to April
403 2016. Deployment periods averaged 58 ± 25 days with 5 ± 2 calibration samples per deployment
404 (Fig. 7). Only 5 % of the data was removed during quality control, due to biofouling in one

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415 deployment and battery exhaustion in another, yielding 610 days of data. The mean offset
416 between calibration samples and the calibrated SeaFET pH time-series was ± 0.007 , indicating a
417 high-quality pH dataset (Fig. 7c). Sensor data corroborated the seasonal pH and temperature
418 cycle observed at Point B. Event-scale effects (e.g., pH_T change ≥ 0.1 for days to weeks, *sensu*
419 (Kapsenberg and Hofmann 2016)) were absent at this site suggesting that weekly sampling was
420 sufficient to describe seasonal and interannual changes in carbonate chemistry at Point B. The
421 magnitude of diel pH_T variability was small (the 2.5th to 97.5th percentiles ranged between 0.01
422 and 0.05 units pH_T) and unrelated to seasonal warming or the concentration of chlorophyll-a
423 (Fig. S1).

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425 4. Discussion

426 High resolution time-series are necessary to document coastal ocean acidification. At
427 Point B in the NW coastal Mediterranean Sea, near-surface pH_T decreased by 0.0028 ± 0.0003
428 units yr^{-1} and temperature increased by 0.072 ± 0.022 $^{\circ}\text{C yr}^{-1}$ from 2007 through 2015 based on
429 weekly measurements. In addition, A_T increased by 2.08 ± 0.19 $\mu\text{mol kg}^{-1} \text{yr}^{-1}$, a change that is
430 unrelated to direct effects of CO_2 absorption by seawater.

Comment [LK22]: Discussion on potential drivers of A_T has been shortened. As such, sub-headings were removed.

Deleted: 4.1. Observed changes in carbonate chemistry .

431 We can identify the drivers for the ocean acidification trends at Point B using the
432 deconvolution of pH and pCO_2 and by assuming that the increase in A_T was due to increases in
433 its carbon constituents, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. This assumption is based
434 on the fact that (1) HCO_3^- and CO_3^{2-} ions together make up 96 % of A_T at Point B, (2) increases in
435 HCO_3^- and CO_3^{2-} would both contribute to A_T and C_T and thereby explain the observed
436 synchronicity of monthly trends in A_T and C_T (Fig. 5). Using the pCO_2 deconvolution, we can
437 then sum the contributions to pCO_2 from A_T (-3.17 $\mu\text{atm pCO}_2 \text{yr}^{-1}$) and C_T (5.26 $\mu\text{atm pCO}_2 \text{yr}^{-1}$).

Comment [LK23]: RC#16

443 ¹⁾ trends to determine the proportional contribution of ΔC_T to ΔpCO_2 that is unrelated to changes
444 in C_T brought on by A_T . The remaining $2.09 \mu atm pCO_2 yr^{-1}$ due to increasing C_T matches the
445 magnitude of atmospheric CO_2 increase during the observation period ($2.08 \pm 0.01 ppm yr^{-1}$ at
446 Plateau Rosa, Italy). The influence of atmospheric CO_2 can also be observed in the significance
447 of monthly C_T trends (eight months out of the year) compared to A_T trends (three months out of
448 the year, Fig. 5).

449 Applying this simple model to pH_T , assuming changes in C_T ($2.97 \pm 0.20 \mu mol kg^{-1} yr^{-1}$)
450 are due to both increasing A_T (a neutralizing effect) and atmospheric forcing, the observed ocean
451 acidification trend at Point B can be attributed primarily to atmospheric CO_2 forcing (61 %) and
452 secondarily to warming (39 %).

453 Using this same approach for observations at 50 m, the C_T contribution to pCO_2 trends
454 that was unrelated to A_T change was $1.69 \mu atm pCO_2 yr^{-1}$, which is 80 % of the rate of
455 atmospheric CO_2 increase in contrast to 100 % at 1 m. Changes in pH_T can be attributed to
456 warming (50 %), atmospheric CO_2 forcing (46 %), and increasing salinity (4 %, which may
457 result from warming). Due to slightly enhanced warming and reduced CO_2 penetration observed
458 at 50 m, warming has a greater effect on the ocean acidification trend than atmospheric forcing at
459 depth compared to the surface.

460 The acidification rate at Point B is larger than those reported for other ocean time-series
461 sites (-0.0026 to -0.0013 units $pH yr^{-1}$, (Bates et al., 2014)), likely due to differences in warming
462 rates. The observed warming from 2007 through 2015 (0.72 to $0.88 \pm 0.2 \text{ } ^\circ C decade^{-1}$) is
463 extremely rapid relative to global trends in the upper 75 m from 1971 to 2010 ($0.11 \text{ } ^\circ C decade^{-1}$,
464 (Rhein et al., 2013)). The coastal region of Point B has warmed steadily since 1980 and with
465 periods of rapid warming (Parravicini et al., 2015). Exacerbated warming may be driven by

466 positive indices of the Atlantic Multi-decadal Oscillation (AMO) and North Atlantic Oscillation
467 (NAO) (Lejeune et al., 2010). The AMO has been positive since the 1990s¹ and positive NAO
468 phases were prevalent during the second half of our study².

469 Nearest to Point B, the acidification rate at DYFAMED, an open-sea site about 50 km
470 offshore from Point B (Fig. 1), was estimated at -0.003 ± 0.001 units pH yr⁻¹ from 1995 to 2011
471 (Marcellin Yao et al., 2016). At DYFAMED, warming contributed approximately 30 % to the
472 acidification rate and the remaining 70 % was attributed to anthropogenic CO₂ (Marcellin Yao et
473 al., 2016). The uncertainty is large and makes direct comparison with Point B unreliable but the
474 results are agreeable. However, A_T at the DYFAMED did not change significantly from 2007
475 through 2014 ($F_{1,51} 3.204$, $P = 0.0794$, $R^2 0.08$, data from (Coppola et al., 2016)). This may
476 indicate that the processes driving changes in A_T at Point B are unique to the coastal
477 environment.

478 Similar changes in coastal carbonate chemistry were observed elsewhere in the near-
479 shore Mediterranean Sea. In the Northern Adriatic Sea, Luchetta et al. (2010) determined an
480 acidification rate in pH_T of -0.0025 yr⁻¹ and an increase in A_T of $2.98 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ at depths
481 shallower than 75 m, by comparing cruise data between the winters of 1983 and 2008. Point B
482 and Adriatic Sea observations are independent but reflect changes in seawater chemistry that
483 may be occurring across a wider coastal region. Additional time-series would help resolve the
484 spatial extent of the observed trends. Specifically, the Eastern Mediterranean Sea would offer an
485 important contrast, as pH of eastern waters is expected to be more sensitive to atmospheric CO₂
486 addition due to their ability to absorb more anthropogenic CO₂ than either the western
487 Mediterranean or Atlantic waters (Álvarez et al., 2014).

¹ <http://www.cgd.ucar.edu/cas/catalog/climind/AMO.html>

² http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/month_ao_index.shtml

Deleted: To estimate if the observed trends from Point B were also occurring offshore, we turn to time-series station DYFAMED, approx. 50 km from Point B (Fig. 1).

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Comment [LK24]: RC1: Lines 336-337. The analysis of the coastal-offshore gradient would deserve some addition investigations, since offshore deep water is supposed to play a role for CT evolution at point B (at lines 323-325)

Deleted: in addition to being shallow dissipate offshore

Deleted: Another coastal area of the Mediterranean Sea, in the North Adriatic Sea, exhibited similar changes in carbonate chemistry as those observed at Point B. B

Deleted: As coastal sites, Point B and the Gulf of Trieste in the N Adriatic Sea show a strong positive A_{T0} (i.e., freshwater end-member alkalinity) in surface waters (Cantoni et al., 2012; Inghoso et al., 2016). In contrast to Point B, the N Adriatic Sea exhibits a negative salinity- A_T relationship and faster A_T increase (Luchetta et al., 2010), suggesting that rivers may play a stronger role in A_T trends there compared to Point B. Rivers are significant sources of C_T to the Gulf of Trieste, making up 3-16 % of C_T in 2007 (Tamše et al., 2015). The authors note that 2007 was a year of record low river discharge. Notably, this is the only year at Point B for which A_{T0} was negative and salinity- A_T relationship was highly correlated, indicating that 2007 was a year of low freshwater input

... [1]

Comment [LK25]: RC#6, #27

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517 ~~While the trends in atmospheric CO₂ forcing and temperature account for the ocean~~
518 ~~acidification trend, the increase in A_T and C_T increase beyond what can be attributed to~~
519 ~~atmospheric forcing was unexpected.~~ The fastest increases in A_T and C_T occur from May through
520 July (Fig. 5), when the thermal stratification settles. In the NW Mediterranean, the main
521 processes governing seasonal variability in A_T are evaporation increasing A_T in summer (i.e.,
522 June through September at Point B) and, to a lesser extent, phytoplankton uptake of nitrate
523 (NO₃⁻) and phosphate (PO₄³⁻) increasing A_T from January through March (Cossarini et al., 2015).
524 During the transition of these processes, salinity decreases to a minimum in May, reflecting
525 freshwater input that dilutes A_T to minimum values at the start of summer. For C_T, peak values
526 occur in winter when the water column is fully mixed. For reference, at DYFAMED, mixing
527 occurs down to more than 2000 m depth and C_T is up to 100 μmol kg⁻¹ higher in deep waters
528 (Copin-Montégut and Bégovic, 2002). Notably, ~~monthly trends of C_T at Point B were not~~
529 ~~statistically significant from~~ November through January for the period 2007-2015. Following
530 winter, C_T declines due to a combination of phytoplankton bloom carbon uptake and freshwater
531 dilution (assuming river C_T < seawater C_T), until the onset of summer stratification. Summer
532 warming leads to pCO₂ off-gassing to the atmosphere (De Carlo et al., 2013), thereby further
533 decreasing C_T. The increases in A_T and C_T from 2007 through 2015 were more pronounced at 1
534 m compared to 50 m. This ~~indicates that the process driving A_T and C_T trends are stronger at the~~
535 ~~surface and affect carbonate chemistry primarily during the spring-summer transition from May~~
536 ~~through July.~~
537 While the drivers of ocean acidification trends are identified and quantified above, the
538 ~~increase in A_T and increase in C_T beyond what can be attributed to atmospheric forcing requires~~
539 ~~some speculation. Some biogeochemical processes can be ruled out as drivers. For example,~~

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Deleted: We assess the spatial extent of these trends and discuss potential drivers.

Deleted: is often described in pH_T, at Point B, pH is largely a product of underlying changes in

551 changes in benthic processes are very unlikely. Reduced calcium carbonate (CaCO_3)
552 precipitation rates would increase A_T but would increase C_T . Even so, the dominant ecosystem in
553 the Bay of Villefranche-sur-Mer is seagrass meadows, which harbor relatively few calcifying
554 organisms. Dissolution of calcium carbonate sediment would contribute to A_T and C_T increase in
555 the water column. However, as the water was supersaturated with respect to both aragonite and
556 calcite, this could only be mediated by biological processes. Carbonate dissolution following
557 CO_2 production via oxic degradation of organic matter releases A_T and C_T in a 1:1 ratio (Moulin
558 et al., 1985). Likewise, anaerobic remineralization produces alkalinity (Cai et al., 2011). In the
559 sediment of the Bay of Villefranche, sulfate reduction coupled with precipitation of sulfide
560 minerals is the dominant anoxic mineralization pathway (Gaillard et al., 1989). An increase in
561 these processes would explain the observed increase in A_T and C_T , but as trends were slower at
562 50 m compared to 1 m, this would suggest the dominance of a process taking place in surface
563 waters.

564 In the upper water column at Point B, changes in biological processes are unlikely to
565 explain the observed trends in A_T and C_T . For example, the concentration of chlorophyll-a, a
566 proxy of primary production, has decreased since 1995, nutrients increased, and phytoplankton
567 blooms have shifted towards earlier dates in the year (Irisson et al., 2012). While a decrease in
568 net primary production could drive C_T trends, the observed increase in NO_3^- and PO_4^{3-} would
569 cause a small decrease in A_T (Wolf-Gladrow et al., 2007). Stimulated community respiration
570 could result from warming waters but enhanced remineralization would cause a decrease in A_T
571 (Wolf-Gladrow et al., 2007).

572 The lack of salinity change at the surface excludes additional processes as drivers of A_T
573 and C_T increase at Point B. For example, increased summertime evaporation (concentration

Deleted: The lack of salinity change excludes additional processes as drivers of change at Point B. For example, increased summertime evaporation (concentration effect) and reduced freshwater input (decreased dilution effect) would both be expected to cause an increase in salinity, which was not observed and so these are not suspected drivers. - [3]

Deleted: increased remineralization rates could contribute to C_T particularly in summer when the water is warmer, hence promoting respiration, and highly stratified and isolated from C_T -rich bottom waters. However, this would require either (1) a change in substrate (local or regional) for remineralization but no clear trend in particulate organic carbon was observable in the study period (L. Mousseau, unpubl.)

Deleted: (Wolf-Gladrow et al., 2007), or (2) a change in net community metabolism, but warming trends up through 2014 were not significant. Lastly, Both of these processes could influence the increasing rate of C_T in summer but would not account for the increase in A_T .

594 effect) and reduced freshwater input (decreased dilution effect) would both be expected to cause
595 an increase in salinity, which was not observed. Increased input of Eastern Mediterranean Sea
596 waters could increase A_T , but this is unlikely as this water mass flows much deeper than Point B
597 (Millot and Taupier-Letage, 2005).

598 The observed changes in A_T and C_T could be due to increased limestone weathering
599 which would increase the input of A_T from land to the sea via rivers and groundwater. Rivers
600 contribute both A_T and C_T to the Mediterranean Sea (Copin-Montégut, 1993; Tamše et al., 2015).
601 River A_T originates from erosion and is correlated with bedrock composition (e.g., (McGrath et
602 al., 2016)). Positive trends in river A_T have been documented in North America and occur via a
603 number of processes including: (1) the interplay of rainfall and land-use (Raymond and Cole,
604 2003), (2) anthropogenic limestone addition (a.k.a., liming) used to enhance agriculture soil pH
605 (Oh and Raymond, 2006; Stets et al., 2014) and freshwater pH (Clair and Hindar, 2005), and (3)
606 potentially indirect effects of anthropogenic CO_2 on groundwater CO_2 -acidification and
607 weathering (Macpherson et al., 2008). Such, and other, processes were hypothesized to have
608 driven A_T changes in the Baltic Sea (Müller et al., 2016). There, an increase in A_T of $3.4 \mu\text{mol kg}^{-1}$
609 yr^{-1} was observed from 1995 to 2014 (mean salinity = 7). In contrast to Point B, the increase in
610 Baltic Sea A_T was not noticeable at salinity > 30 (Müller et al., 2016).

611 Given the above speculations, the simplest plausible mechanisms causing the unexpected
612 A_T and C_T trends would be through increasing A_T of the freshwater end-member of Point B.
613 Local precipitation, however, did not have an influential effect and was not correlated with
614 salinity or A_T (Fig. S2). While submarine groundwater springs can be a significant source of
615 nutrients, A_T , and C_T to the ocean (Cai et al., 2003; Slomp and Van Cappellen, 2004), carbonate
616 chemistry contributions of local submarine springs are currently unknown (Gilli, 1995).

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Deleted: The observed changes in A_T and C_T could be achieved via augmented limestone weathering increasing A_T input from land to the sea via rivers and submarine groundwater springs.

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Deleted: The inter-annual variability in salinity- A_T relationships at Point B does suggest influence of freshwater discharge (via a slight salinity and A_T dilution in May and June), as has been observed in the N Adriatic Sea (Cantoni et al., 2012; Turk et al., 2010). For the Mediterranean Sea, rivers are a significant source of both A_T and C_T (Copin-Montégut, 1993). The annual variability in salinity- A_T relationships at Point B does suggest influence of river discharge, as has been observed elsewhere in the Mediterranean Sea (Cantoni et al., 2012; Turk et al., 2010). Signatures of limestone erosion can be observed in the A_T of local rivers near Point B (Var, Paillon, and Roya) and range between 1000 to 2000 $\mu\text{mol kg}^{-1}$ (data from *Agence de l'Eau Rhône-Méditerranée-Corse*, <http://sierm.eaurmc.fr>). Even a rainwater outfall at the entrance of Port de la Darse harbor, inside the Bay of Villefranche-sur-Mer, had an A_T of $607 \pm 5 \mu\text{mol kg}^{-1}$ ($N = 2$) following a precipitation event. However,

Deleted: suggesting that rain runoff is not a driving factor of Point B carbonate chemistry

Deleted: have been identified along the Point B coastline (Gilli, 1995), but their carbonate chemistry contributions

647 Signatures of limestone erosion can be observed in A_T of nearby rivers (Var, Paillon, and Roya)
648 but detailed time-series are not available. Likewise, riverine influence at Point B has not been
649 quantified. If river runoff exerts a dominant control on Point B carbonate chemistry, there is a lag
650 effect, as freshwater influence peaked in May but A_T and C_T increased fastest from May through
651 July. Consequently, this hypothesis needs further investigation. Until the source of A_T increase is
652 properly identified, use of this observation in modeling should be implemented with caution.

653

654 5. Conclusion

655 Predictions of coastal ocean acidification remain challenging due the complexity of

656 biogeochemical processes occurring at the ocean-land boundary. At the Point B coastal
657 monitoring station in the NW Mediterranean Sea, surface ocean acidification was due to
658 atmospheric CO_2 forcing and rapid warming over the observation period 2007-2015. However,
659 additional trends in A_T and C_T were observed which remain unexplained but could relate to
660 riverine and groundwater input. The influence of a coastal boundary processes influencing
661 seawater A_T and C_T presents a potentially major difference between coastal and offshore changes
662 in ocean chemistry. This study highlights the importance of considering other anthropogenic
663 influences in the greater land-sea region that may contribute to coastal biogeochemical cycles
664 (*sensu* Duarte et al. (2013)) and alter projections of anthropogenic change in near-shore waters.

665

666 **Data availability** – Time-series data from Point B are available at Pangaea® (doi:
667 10.1594/PANGAEA.727120)

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Comment [LK29]: RC#7, 22, 23

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... [4]

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Deleted: We postulate that the enhanced acidification trend could stem from changes in freshwater inputs from land which are also the source of interannual variability in A_T at this site.

Deleted: (1)

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Deleted: and experimental design in global ocean change biology.

686 **Author contribution** – JPG initiated the study, LM supervised data collection, SA performed
687 SeaFET deployments and calibration, JPG and LK designed and JPG conducted statistical
688 analyses, and LK prepared the manuscript with contributions from all authors.

689

690 **Competing interests** - The authors declare that they have no conflict of interest.

691

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981 **Table 1.** Previous estimates or documentation of pH change (ΔpH) in the Mediterranean Sea.

982 TrOCA is the ‘Tracer combining Oxygen, inorganic Carbon, and total Alkalinity’ method,

983 NR means ‘not reported’, and PI is ‘pre-industrial era’. *indicates studies where the reported

984 pH change was assumed to be at *in situ* temperatures.

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Region	Site	Method	Study period	pH scale	°C	$\Delta\text{pH yr}^{-1} \pm \text{SE}$	Total ΔpH	Reference
NW	Point B, 1 m	time-series, anomaly	2007-2015	total	<i>in situ</i>	-0.0028 ± 0.0003	-0.0252	This study
NW	Point B, 1 m	time-series, anomaly	2007-2015	total	25	-0.0017 ± 0.0002	-0.0153	This study
NW	Point B	model	1967-2003	total	<i>in situ</i>	-0.0014	-0.05	Howes et al. (2015)
NW	DYFAMED	time-series, observed	1995-2011	seawater	17.34	-0.003 ± 0.001	-0.051	Marcellin Yao et al. (2016)
NW	DYFAMED	time-series comparison	1998-2000, 2003-2005	seawater	<i>in situ</i> *	-	-0.02	Meier et al. (2014)
NW	Gulf of Lion	TrOCA	PI-2011	NR	<i>in situ</i> *	-	-0.15 to -0.11	Touratier et al. (2016)
East	N Adriatic Sea	cruise comparison	1983, 2008	total	25	-0.0025	-0.063	Luchetta et al. (2010)
East	Otranto Strait	TrOCA	PI-1995	seawater	25	-	< -0.1 to -0.05, ± 0.014	Krasakopoulou et al. (2011)
Total	Full profile	TrOCA	PI-2001	NR	<i>in situ</i> *	-	-0.14 to -0.05	Touratier and Goyet (2011)
Total	Bottom waters	model	1800-2001	total	<i>in situ</i> *	-	-0.06 to -0.005	Palmiéri et al. (2015)
Total	Surface waters	model	1800-2001	total	<i>in situ</i> *	-	-0.084 \pm 0.001	Palmiéri et al. (2015)
Gibraltar Strait	Espartel sill	pH, pCO ₂ sensors	2012-2015	total	25	-0.0044 ± 0.00006	-	Flecha et al. (2015)

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992 **Table 2.** Time-series anomaly regression analyses on seawater carbonate chemistry at Point B
 993 for salinity (S), temperature (T, °C), dissolved inorganic carbon (C_T , $\mu\text{mol kg}^{-1}$), total alkalinity
 994 (A_T , $\mu\text{mol kg}^{-1}$), pH_T , 25 °C-normalized pH_T (pH_{T25}), pCO_2 (μatm) calcite (Ω_c) and aragonite
 995 (Ω_a) saturation state, and salinity-normalized A_T (nA_T) and C_T (nC_T), at 1 and 50 m. Slopes
 996 represent the change in the variable unit per year. $P \ll 0.001$ indicates p -values far smaller than
 997 0.001.

Comment [LK30]: RC#3
 Deleted: (observed values and anomalies)

Depth (m)	Variable	Slope \pm SE	Intercept \pm SE	F	df	Slope P	R ²
1	S	-0.0017 \pm 0.0044	3.38 \pm 8.82	0.147	1,415	0.702	0
	T	0.072 \pm 0.022	-145 \pm 44	10.999	1,411	0.001	0.026
	C_T	2.97 \pm 0.20	-5965 \pm 400	221.87	1,414	$\ll 0.001$	0.349
	A_T	2.08 \pm 0.19	-4189 \pm 379	122.429	1,415	$\ll 0.001$	0.228
	pH_T	-0.0028 \pm 0.0003	5.72 \pm 0.66	74.205	1,410	$\ll 0.001$	0.153
	pH_{T25}	-0.0017 \pm 0.0002	3.46 \pm 0.43	64.204	1,410	$\ll 0.001$	0.1354
	pCO_2	3.53 \pm 0.39	-7105 \pm 776	83.927	1,410	$\ll 0.001$	0.17
	Ω_c	-0.0109 \pm 0.0022	22.0 \pm 4.5	24.08	1,410	$\ll 0.001$	0.055
	Ω_a	-0.0064 \pm 0.0015	12.9 \pm 3.1	17.33	1,410	$\ll 0.001$	0.041
	nA_T	2.20 \pm 0.28	-4425 \pm 560	62.34	1,410	$\ll 0.001$	0.132
	nC_T	3.12 \pm 0.29	-6275 \pm 579	117.486	1,410	$\ll 0.001$	0.223
	50	S	0.0063 \pm 0.0020	-12.8 \pm 4.1	9.858	1,410	0.002
T		0.088 \pm 0.019	-177 \pm 38	21.927	1,406	$\ll 0.001$	0.0512
C_T		2.16 \pm 0.21	-4344 \pm 418	108.105	1,409	$\ll 0.001$	0.2091
A_T		1.59 \pm 0.15	-3192 \pm 309	106.947	1,410	$\ll 0.001$	0.2069
pH_T		-0.0026 \pm 0.0002	5.28 \pm 0.50	112.111	1,405	$\ll 0.001$	0.2168
pH_{T25}		-0.0013 \pm 0.0003	2.55 \pm 0.54	21.863	1,405	$\ll 0.001$	0.0512
pCO_2		2.79 \pm 0.25	-5603 \pm 501	125.1	1,405	$\ll 0.001$	0.236
Ω_c		-0.0070 \pm 0.0027	14.0 \pm 5.4	6.648	1,405	0.01	0.0162
Ω_a		-0.0038 \pm 0.0019	7.6 \pm 3.7	4.155	1,405	0.042	0.0102
nA_T		1.15 \pm 0.13	-2309 \pm 254	82.309	1,405	$\ll 0.001$	0.1689
nC_T		1.82 \pm 0.19	-3661 \pm 376	94.98	1,405	$\ll 0.001$	0.19

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1001 **Table 3.** Estimated contribution of temperature (T), salinity (S), total alkalinity (A_T), and
 1002 dissolved inorganic carbon (C_T) to $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ at 1 and 50 m. Slopes represent the change in
 1003 the variable unit per year. P of $\ll 0.001$ indicates a p -value far smaller than 0.001. Sum of %
 1004 contributions for 50 m do not equal 100 % due to rounding.

Depth (m)	Contributing Variable	Slope \pm SE	% contribution	Slope P
1	T	-0.0011 ± 0.0003	39	0.001
	S	0.0000 ± 0.0001	0	0.61
	A_T	0.0030 ± 0.0003	-107	$\ll 0.001$
	C_T	-0.0047 ± 0.0003	168	$\ll 0.001$
	$\frac{dpH_T}{dt}$ sum	-0.0028	100	
	T	1.22 ± 0.37	37	0.001
	S	-0.001 ± 0.042	0	0.974
	A_T	-3.17 ± 0.28	-96	$\ll 0.001$
	C_T	5.26 ± 0.36	159	$\ll 0.001$
	$\frac{dpCO_2}{dt}$ sum	3.30	100	
50	T	-0.0013 ± 0.0003	50	$\ll 0.001$
	S	-0.0001 ± 0.000	4	0.005
	A_T	0.0023 ± 0.0002	-88	$\ll 0.001$
	C_T	-0.0035 ± 0.0003	135	$\ll 0.001$
	$\frac{dpH_T}{dt}$ sum	-0.0026	101	
	T	1.29 ± 0.28	42	$\ll 0.001$
	S	0.065 ± 0.020	2	0.001
	A_T	-2.35 ± 0.22	-77	$\ll 0.001$
	C_T	4.04 ± 0.41	132	$\ll 0.001$
	$\frac{dpCO_2}{dt}$ sum	3.05	99	

Comment [LK32]: RC#20 -Table 3 was updated with anomaly regressions and now also includes results for 50 m.

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Deleted: pH_T and pCO₂ anomalies at 1 m

Deleted: The sum of the slopes () is slightly inflated compared to the observed trends reported in Table 2 (-0.0037 vs. -0.0031 yr⁻¹ for pH_T, and 4.26 vs. 3.78 μatm yr⁻¹ for pCO₂). These differences are negligible relative to the error associated with the slope estimates.

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1005

1014 **Figure 1.** Map of study region in the NW Mediterranean Sea (a), along the North current (b) in
1015 the Bay of Villefranche-sur-Mer, France (c). Point B station, EOL buoy, and the offshore time-
1016 series station DYFAMED are marked. Bathymetric line units are m (c).

1017
1018 **Figure 2.** Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity, and
1019 seawater carbonate chemistry at Point B, 1 m. Regression slopes are drawn \pm SE (in grey) and
1020 noted with a star for significance at $\alpha = 0.05$.

1021
1022 Figure 3. Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity, and
1023 seawater carbonate chemistry at Point B, 50 m. Regression slopes are drawn \pm SE (in grey) and
1024 noted with a star for significance at $\alpha = 0.05$.

1025
1026 **Figure 4.** Monthly distribution of seawater carbonate chemistry at Point B, 1 m, using a
1027 combination of a violin plot showing the relative frequency of the observations (shaded blue
1028 area) and a boxplot showing the median, first and third quartiles, as well as outliers (blue).**Figure**
1029 5. Monthly trends of total alkalinity (A_T , blue) and dissolved inorganic carbon (C_T , green) for the
1030 period 2007-2015. Errors bars are \pm SE of the slope estimate and significance is noted (*)
1031 at $\alpha=0.05$.

1032
1033 **Figure 6.** Salinity and total alkalinity relationships by year for the period 2007-2015, at Point B,
1034 1 m. Data points are colored for month.

1035

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1042 **Figure 7.** Time-series pH (a) and temperature (b) from autonomous SeaFET pH sensor
1043 deployments at EOL buoy, 2 m. Discrete calibration samples are noted in green, and grey
1044 vertical lines bracket deployment periods (a). Calibration sample offsets from processed pH
1045 time-series are shown in panel (c). Violin and boxplots (see Fig. 4) show diel pH range by month
1046 (d), and an example of this pH variability is shown for May 2015 (e).

Comment [LK33]: RC#21

Deleted: Mean offset of c

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Deleted: was $\text{pH}_T \pm 0.007$

Deleted: was small and peaked in April and May (d) and exhibits a clear, small, diel cycle (e, representative example from May 2015)

As coastal sites, Point B and the Gulf of Trieste in the N Adriatic Sea show a strong positive A_{T0} (i.e., freshwater end-member alkalinity) in surface waters (Cantoni et al., 2012; Ingrosso et al., 2016). In contrast to Point B, the N Adriatic Sea exhibits a negative salinity- A_T relationship and faster A_T increase (Luchetta et al., 2010), suggesting that rivers may play a stronger role in A_T trends there compared to Point B. Rivers are significant sources of C_T to the Gulf of Trieste, making up 3-16 % of C_T in 2007 (Tamše et al., 2015). The authors note that 2007 was a year of record low river discharge. Notably, this is the only year at Point B for which A_{T0} was negative and salinity- A_T relationship was highly correlated, indicating that 2007 was a year of low freshwater input

The correlates between Point B and N Adriatic Sea suggest a common driver of changes in ocean carbonate chemistry at these two sites (possibly linked via shared watersheds of the Alps), and these

4.2. Potential drivers of changes in carbonate chemistry

The lack of salinity change excludes additional processes as drivers of change at Point B. For example, increased summertime evaporation (concentration effect) and reduced freshwater input (decreased dilution effect) would both be expected to cause an increase in salinity, which was not observed and so these are not suspected drivers.

Sediment dissolution is unlikely to contribute to the observed increase as both aragonite and calcite were supersaturated throughout the study period; conditions that are not conducive to large rates of dissolution. An overall reduction in calcium carbonate (CaCO_3) precipitation rates

is unlikely, as the dominant ecosystem in the Bay of Villefranche-sur-Mer is seagrass meadows, which harbor relatively few calcifying organisms and there has been no obvious changes in the abundance of calcifiers (J.-P. Gattuso, pers. obs.). All the same, the sheer volume of the bay would likely dilute any signature of changes in calcification or dissolution of sediment or organisms. For the Mediterranean Sea, in general, the influence of biogenic CaCO_3 on A_T is small compared to the influence of river and Black Sea A_T (Copin-Montégut, 1993). Increased input from the east Mediterranean Sea waters could increase A_T , but this is questionable (Millot and Taupier-Letage, 2005), because here eastern waters are higher in A_T , salinity and pH are also greater and C_T is a little lower compared to the western waters (Álvarez et al., 2014; Touratier and Goyet, 2011).

For C_T , there are a few additional drivers to discuss.

This contrast clouds the perspective that changes in A_T of freshwater sources can influence A_T at Point B, and a more in depth study will be necessary to address this.

Given the discussion above, the simplest plausible mechanisms causing changes in carbonate chemistry at Point B would be through (1) increasing anthropogenic atmospheric CO_2 , and (2) increasing A_T of freshwater sources (i.e., rivers, groundwater). Freshwater has a shallow and coastal influence and is also dominant in the N Adriatic Sea, which exhibits similar trends as those observed at Point B.

1 **Data Supplement**

3
 4 **Table S1.** Monthly means \pm SD (*N*) for carbonate chemistry parameters at Point B, at 1 and 50 m
 5 for the period 2007-2015, for salinity (*S*), temperature (*T*), dissolved inorganic carbon (*C_T*), total
 6 alkalinity (*A_T*), pH (pH_T, total hydrogen ion scale), pCO₂, and aragonite saturation state (Ω_a).

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Month	<i>S</i>	<i>T</i> (°C)	<i>C_T</i> ($\mu\text{mol kg}^{-1}$)	<i>A_T</i> ($\mu\text{mol kg}^{-1}$)	pH _T	pCO ₂ (μatm)	Ω_a
1 m							
Jan	37.89 \pm 0.42 (38)	14.38 \pm 0.76 (36)	2251 \pm 8 (38)	2551 \pm 10 (38)	8.13 \pm 0.01 (36)	346 \pm 10 (36)	3.19 \pm 0.09 (36)
Feb	37.95 \pm 0.23 (32)	13.58 \pm 0.41 (32)	2259 \pm 11 (32)	2555 \pm 8 (32)	8.14 \pm 0.01 (32)	343 \pm 10 (32)	3.14 \pm 0.06 (32)
Mar	37.86 \pm 0.25 (35)	13.67 \pm 0.49 (35)	2259 \pm 10 (35)	2555 \pm 8 (35)	8.14 \pm 0.01 (35)	344 \pm 10 (35)	3.14 \pm 0.06 (35)
Apr	37.76 \pm 0.24 (34)	15.04 \pm 1.08 (34)	2254 \pm 11 (34)	2553 \pm 9 (34)	8.12 \pm 0.02 (34)	357 \pm 16 (34)	3.19 \pm 0.08 (34)
May	37.64 \pm 0.26 (37)	18.08 \pm 1.31 (37)	2241 \pm 20 (37)	2547 \pm 17 (37)	8.09 \pm 0.02 (37)	390 \pm 21 (37)	3.31 \pm 0.09 (37)
Jun	37.74 \pm 0.17 (37)	21.29 \pm 1.77 (37)	2233 \pm 18 (37)	2543 \pm 14 (37)	8.05 \pm 0.02 (37)	436 \pm 29 (37)	3.41 \pm 0.11 (37)
Jul	37.93 \pm 0.17 (40)	24.06 \pm 1.55 (40)	2227 \pm 14 (40)	2549 \pm 13 (40)	8.02 \pm 0.03 (40)	469 \pm 33 (40)	3.57 \pm 0.10 (40)
Aug	38.08 \pm 0.12 (30)	24.77 \pm 1.35 (30)	2226 \pm 14 (30)	2555 \pm 10 (30)	8.02 \pm 0.03 (30)	471 \pm 37 (30)	3.65 \pm 0.10 (30)
Sep	38.21 \pm 0.11 (32)	23.48 \pm 1.23 (31)	2229 \pm 10 (31)	2562 \pm 9 (32)	8.04 \pm 0.03 (30)	443 \pm 33 (30)	3.66 \pm 0.09 (30)
Oct	38.19 \pm 0.10 (33)	20.82 \pm 1.09 (33)	2226 \pm 10 (33)	2561 \pm 9 (33)	8.08 \pm 0.02 (33)	394 \pm 18 (33)	3.63 \pm 0.08 (33)
Nov	37.99 \pm 0.27 (37)	18.20 \pm 0.99 (36)	2230 \pm 13 (37)	2555 \pm 12 (37)	8.11 \pm 0.01 (36)	366 \pm 14 (36)	3.48 \pm 0.07 (36)
Dec	37.97 \pm 0.25 (32)	16.14 \pm 1.12 (32)	2241 \pm 12 (32)	2555 \pm 12 (32)	8.13 \pm 0.02 (32)	352 \pm 16 (32)	3.35 \pm 0.06 (32)
50 m							
Jan	38.02 \pm 0.11 (37)	14.49 \pm 0.71 (35)	2253 \pm 9 (37)	2554 \pm 6 (37)	8.13 \pm 0.01 (35)	347 \pm 10 (35)	3.18 \pm 0.07 (35)
Feb	38.03 \pm 0.10 (32)	13.71 \pm 0.43 (32)	2259 \pm 11 (32)	2556 \pm 7 (32)	8.13 \pm 0.01 (32)	343 \pm 9 (32)	3.12 \pm 0.06 (32)
Mar	38.01 \pm 0.12 (35)	13.59 \pm 0.39 (35)	2260 \pm 9 (35)	2554 \pm 8 (35)	8.13 \pm 0.01 (35)	346 \pm 9 (35)	3.09 \pm 0.05 (35)
Apr	37.98 \pm 0.10 (34)	14.06 \pm 0.57 (34)	2258 \pm 11 (34)	2553 \pm 8 (34)	8.12 \pm 0.01 (34)	351 \pm 11 (34)	3.10 \pm 0.08 (34)
May	37.99 \pm 0.11 (37)	15.01 \pm 0.85 (37)	2253 \pm 16 (37)	2551 \pm 10 (37)	8.12 \pm 0.02 (37)	360 \pm 16 (37)	3.15 \pm 0.10 (37)
Jun	38.00 \pm 0.09 (37)	15.06 \pm 0.59 (37)	2249 \pm 16 (37)	2548 \pm 11 (37)	8.12 \pm 0.01 (37)	358 \pm 12 (37)	3.16 \pm 0.08 (37)
Jul	38.01 \pm 0.07 (39)	15.43 \pm 1.12 (39)	2246 \pm 14 (39)	2546 \pm 9 (39)	8.11 \pm 0.02 (39)	363 \pm 21 (39)	3.16 \pm 0.10 (39)
Aug	37.99 \pm 0.07 (28)	15.27 \pm 0.66 (28)	2240 \pm 10 (28)	2543 \pm 8 (28)	8.12 \pm 0.01 (28)	353 \pm 12 (28)	3.20 \pm 0.07 (28)
Sep	38.00 \pm 0.11 (32)	16.20 \pm 1.69 (31)	2237 \pm 13 (31)	2547 \pm 11 (32)	8.12 \pm 0.02 (30)	357 \pm 22 (30)	3.29 \pm 0.17 (30)
Oct	38.11 \pm 0.13 (33)	18.49 \pm 1.83 (33)	2233 \pm 12 (33)	2554 \pm 12 (33)	8.10 \pm 0.02 (33)	377 \pm 21 (33)	3.43 \pm 0.15 (33)
Nov	38.09 \pm 0.11 (36)	17.95 \pm 1.19 (35)	2234 \pm 14 (36)	2557 \pm 9 (36)	8.11 \pm 0.02 (35)	366 \pm 15 (35)	3.43 \pm 0.12 (35)
Dec	38.04 \pm 0.16 (32)	16.20 \pm 1.10 (32)	2241 \pm 11 (32)	2556 \pm 9 (32)	8.12 \pm 0.02 (32)	352 \pm 14 (32)	3.33 \pm 0.08 (32)

7

- 11 **Table S2**, Regression analyses on monthly trends of A_T and C_T ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$) for the period
 12 2007-2015, at 1 m. Slope is change yr^{-1} .

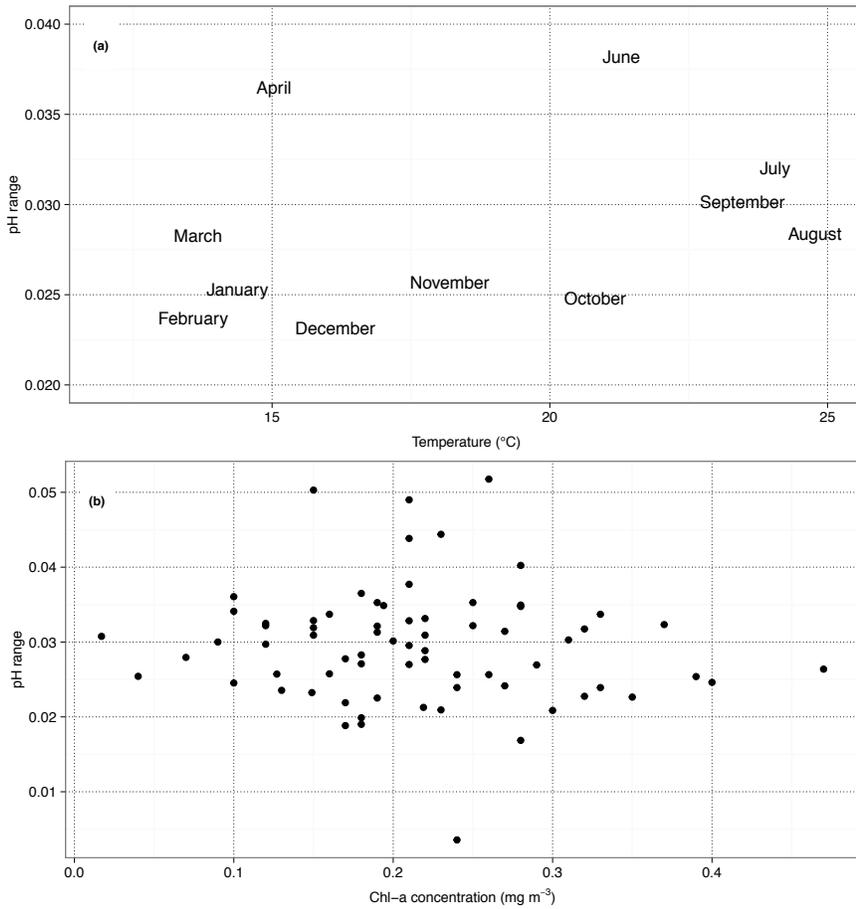
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<i>Parameter</i>	<i>Month</i>	<i>Slope</i> \pm <i>SE</i>	<i>Intercept</i> \pm <i>SE</i>	<i>F</i> _{1,7}	<i>Slope P</i>	<i>R</i> ²
A_T	Jan	-1.33 \pm 0.83	5225 \pm 1677	0.2666	0.155	0.267
	Feb	1.09 \pm 0.93	366 \pm 1874	0.1632	0.281	0.163
	Mar	1.48 \pm 0.81	-418 \pm 1628	0.3227	0.111	0.323
	Apr	1.77 \pm 0.84	-1010 \pm 1688	0.3886	0.073	0.389
	May	4.00 \pm 1.58	-5498 \pm 3183	0.4771	0.039	0.477
	Jun	4.53 \pm 0.90	-6566 \pm 1802	0.785	0.001	0.785
	Jul	3.36 \pm 1.03	-4201 \pm 2080	0.6007	0.014	0.601
	Aug	2.01 \pm 1.07	-1490 \pm 2152	0.3355	0.102	0.336
	Sep	1.81 \pm 0.86	-1075 \pm 1723	0.3886	0.073	0.389
	Oct	1.39 \pm 0.94	-225 \pm 1884	0.238	0.183	0.238
	Nov	1.89 \pm 1.23	-1254 \pm 2465	0.2542	0.166	0.254
	Dec	2.00 \pm 1.29	-1470 \pm 2596	0.2556	0.165	0.256
C_T	Jan	-0.14 \pm 0.46	2536 \pm 922	0.0135	0.766	0.014
	Feb	2.64 \pm 0.90	-3052 \pm 1806	0.5526	0.022	0.553
	Mar	2.32 \pm 0.77	-2411 \pm 1550	0.5644	0.02	0.564
	Apr	2.93 \pm 0.84	-3637 \pm 1697	0.6324	0.01	0.632
	May	5.06 \pm 1.82	-7936 \pm 3663	0.5244	0.027	0.524
	Jun	5.72 \pm 1.26	-9260 \pm 2540	0.7452	0.003	0.745
	Jul	4.27 \pm 0.91	-6369 \pm 1838	0.7575	0.002	0.758
	Aug	3.37 \pm 1.17	-4541 \pm 2357	0.5407	0.024	0.541
	Sep	1.80 \pm 1.05	-1383 \pm 2117	0.2935	0.132	0.294
	Oct	2.84 \pm 0.65	-3480 \pm 1312	0.73	0.003	0.73
	Nov	2.57 \pm 1.34	-2932 \pm 2693	0.3442	0.097	0.344
	Dec	1.70 \pm 1.25	-1175 \pm 2506	0.2098	0.215	0.21

13

18 **Figure S1.** Relationship between monthly mean temperature (a) and Chlorophyll-a (b) and diel
19 pH_T range at EOL, 2 m. Chl-a was measured weekly at Point B using a fluorimetric method
20 (http://rade.obs-vlfr.fr/Protocole_Chlab.htm)

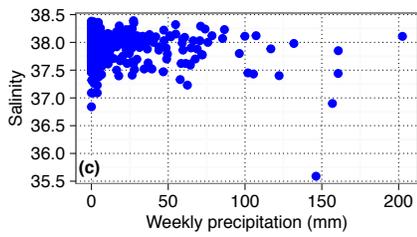
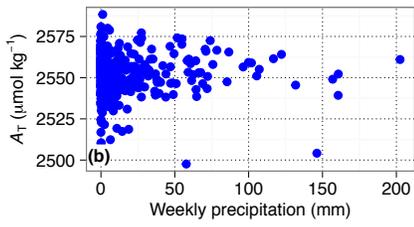
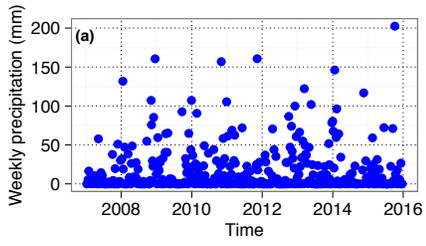
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28 **Figure S2.** Precipitation at Nice airport (weekly cumulative precipitation from Tuesday to
29 Monday) during the period 2007-2015 (a) and its relationship to A_T (b) and salinity (c), at Point
30 B at 1 m.

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Table S1. Time-series anomaly regression analyses on seawater carbonate chemistry, at Point B, 50 m, for salinity (S), temperature (T, °C), dissolved inorganic carbon (C_T , $\mu\text{mol kg}^{-1}$), total alkalinity (A_T , $\mu\text{mol kg}^{-1}$), pH_T , 25 °C-normalized pH_T (pH_{T25}), calcite (Ω_c) and aragonite (Ω_a) saturation state, and salinity-normalized A_T (nA_T) and C_T (nC_T). Slope is change yr^{-1} . $P \ll 0.001$ indicate p-values far smaller than 0.001.

<i>Variable</i>	<i>Slope ± SE</i>	<i>Intercept ± SE</i>	<i>F</i>	<i>df</i>	<i>Slope P</i>	<i>R²</i>
S	0.0063 ± 0.0020	-12.8 ± 4.1	9.858	1, 410	0.002	0.0235
T	0.088 ± 0.019	-177 ± 38	21.927	1, 406	<<0.001	0.0512
C_T	2.16 ± 0.21	-4344 ± 418	108.105	1, 409	<<0.001	0.2091
A_T	1.59 ± 0.15	-3192 ± 309	106.947	1, 410	<<0.001	0.2069
pH_T	-0.0026 ± 0.0002	5.28 ± 0.50	112.111	1, 405	<<0.001	0.2168
pH_{T25}	-0.0013 ± 0.0003	2.55 ± 0.54	21.863	1, 405	<<0.001	0.0512
pCO_2	2.79 ± 0.25	-5603 ± 501	125.1	1, 405	<<0.001	0.236
Ω_c	-0.0070 ± 0.0027	14.0 ± 5.4	6.648	1, 405	0.01	0.0162
Ω_a	-0.0038 ± 0.0019	7.6 ± 3.7	4.155	1, 405	0.042	0.0102
nA_T	1.15 ± 0.13	-2309 ± 254	82.309	1, 405	<<0.001	0.1689
nC_T	1.82 ± 0.19	-3661 ± 376	94.98	1, 405	<<0.001	0.19

Figure S1. Time-series observations (a-g) and anomalies (h-n) of seawater carbonate chemistry at Point B, 50 m. Significant regression slopes are drawn \pm SE (in grey) and noted with a star for significance at $\alpha=0.05$.

