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 CO_2*). 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 pCO_2, 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 CO$_2$ *to the observed trends at Point B is necessary to discuss as it is the main driver of global ocean acidification. The deconvolution of pCO*$_2$ *allowed us to compare the rates of atmospheric and seawater CO*$_2$ *increase. By assuming a linear model relationship between atmospheric and seawater CO*$_2$ *we can estimate the potential maximum contribution of anthropogenic atmospheric CO*$_2$ *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 CO$_2$ *forcing at Point B, we assume air-sea CO*$_2$ *equilibrium (e.g., increase in atmospheric CO*$_2$ *causes an equal increase in seawater pCO*$_2$*). Considering the error associated with deconvolution of pCO*$_2$ *at 1 m, atmospheric CO*$_2$ *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 AT and CT 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 AT and CT) 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 AT and CT 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 AT (lines 118-119) or low AT (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 AT, 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 CT increase due to AT 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 addition 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 µmol* 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 no necessary 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 (Alkm= measured alkalinity, salinity and Alkr=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 µmol 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 ~1000-2000 umol 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 < 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.

References:

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Copin-Montégut, C.: Alkalinity and carbon budgets in the Mediterranean Sea, Global Biogeochem. Cycles, 7, 915-925, 10.1029/93GB01826, 1993.

Kapsenberg, L., and Hofmann, G. E.: Ocean pH time-series and drivers of variability along the northern Channel Islands, California, USA, Limnol. Oceanogr., 61, 953-968, 10.1002/lno.10264, 2016.

Schneider, A., Wallace, D. W. R., and Körtzinger, A.: Alkalinity of the Mediterranean Sea, Geophys. Res. Lett., 34, L15608, 10.1029/2006GL028842, 2007.