Author Response to referee comments on “Coastal ocean acidification and increasing total alkalinity in the NW Mediterranean Sea” by Kapsenberg et al.

Overall author response: We thank the referee for his/her time and the detailed oriented suggestions which have improved the manuscript. For the ease of reviewing our response, we have numbered the Referee Comments from 1 to 17 and refer to these numbers in the Tracked Changes revised document and in our point-by-point response below in blue.

The major revision includes a revised calculation of the deconvolutions according to Garcia-Ibanez et al. (2016), which are now displayed in separate table for the pH and pCO₂ deconvolution (Table 3 and 4). As expected, the revised calculations that closely match those of Garcia-Ibanez produced the same results as our original approach, which made an estimate of the partial derivatives without calculating the sensitivity component first. As such, no substantial changes were needed in the Results or Discussion.

Anonymous Referee #1 Submitted on 27 Feb 2017

The authors did a valuable work to clarify several aspects of their analysis and to improve the readability of the manuscript. Further, they provided detailed and convincing answers to the reviewers’ comments supporting their thoughts. However, a couple of points (point 2 and 4 of their response letter) of the previous review still need to be addressed accurately and are source of concerns before the manuscript can be accepted for publication.

Regarding point 2 of the response letter.

1) L10P196-215: the description of the deconvolution needs further explanation. The answer provided by the authors is not satisfactory.

   To my understanding of this section, the authors computed 4 timeseries of pH by using: the true observations of T and the climatological monthly means of the other three variables; the true observations of S and the climatological monthly means of the other three variables, and so on for DIC and ALK.

   Then, the linear regression analysis is performed on these 4 pH timeseries, and the estimated slopes are reported in Table 3. Therefore, I think that this is not the methodology proposed by Garzia-Ibanes et al., (2016). Indeed, the sensitivity of the pH to the four drivers (i.e. the changes of pH caused by the changes in the drivers ( ) as prescribed in Garzia-Ibanes’ method) is not provided in the manuscript. Is it perhaps computed? Then, the different pH contributions are not computed as the multiplication of times the trend of the variables. Therefore, the equation (1) is not correct with respect to the analysis that is effectively performed, and some of the results and conclusions should be provided in a different way.

   I suggest that the analysis presented in the manuscripts can be maintained, however authors should provide the robustness of the underpinning hypothesis (i.e. the overall trend can be decomposed in such a way) and they should provide the sensitivity of the method to the choice of the temporal means of the variables that are kept constant (i.e. how different would be the results if the averages are computed on yearly or over the whole period?). Revise accordingly this section and the results.

   Our original approach estimated each partial derivative in one step by performing one regression. We have now closely followed the method of Garcia-Ibanez et al. (2016) by solving for each component of each partial derivative using the observed values of one variable and mean values (all samples from 2009-2015) for the remaining three variables.
The new calculation essentially produced the same results. Small numerical differences have been updated throughout the Abstract, Results, and Discussion. The agreement between both analytical methods was expected given that the method of Garcia-Ibanez et al. (2016) was the mathematical underpinning of our original approach.

P13L272-278: provided that the deconvolution is computed as previously described, these comments should be revised since these numbers are not produced by the multiplication of times (i.e. the trends of T, S, alkalinity and DIC reported in table 2 and the sensitivity of pH to the vars).

Since we have updated the analysis, this is no longer relevant.

L271: why do these results indicate that the deconvolution analyses well represent the observed trend?

We now specify that the “deconvolution reproduced influences of temperature sensitivity well”.

Regarding point 4 of the response letter.

2) At P13L282-284 it is said that the trend of atmospheric CO2 represents the “maximum influence of anthropogenic CO2 forcing at Point B” under the assumption that “increase in atmospheric CO2 causes an equal increase in seawater pCO2”. This assumption is quite questionable. The authors should provide some evidences in support of this assumption.

We have removed the word “maximum” as the emphasis is on the fact that the waters at 1 m are likely in equilibrium with the atmosphere on annual time-frames. We have added a reference showing evidence for this.

Then, at P16L345-347, it is argued that the atmospheric pCO2 increase is the remaining part composing the contribution of ΔCT to ΔpCO2, which assumes that the atmospheric ΔpCO2 is the actual contribution and not, as previously hypothesized, the maximum one. As the authors surely understand, the similarity between two numbers does not imply any physical relationship. Therefore, this conclusion seems not supported by the results. Please resolve it.

We have removed the word “maximum” as the emphasis is on the fact that the waters at 1 m are likely in equilibrium with the atmosphere on annual time-frames. We have added a reference showing evidence for this.

Further, at L347-349: which is the causal relationship between the influence of atmospheric pCO2 and the significance of monthly CT trends? The increase of atmospheric pCO2 should have an effect throughout the year (in winter and autumn months too). Therefore, results do not show the influence of atmospheric pCO2 to the significance of monthly CT trends.

L347-349 read, “The influence of atmospheric CO2 can also be observed in the significance of monthly CT trends (eight months out of the year) compared to AT trends (three months out of the year, Fig. 5).”

The point here is that the increase in CT is distributed over a longer period throughout the year than the increase in AT. The added input of atmospheric CO2 potentially pushed monthly CT increase into a statistically significant category. We provide quantitative evidence for this idea using the significant increases shown in Fig. 5. We have clarified this approach with the revised sentence:
“Monthly C\textsubscript{T} trends are positive and statistically significant over more months than A\textsubscript{T} trends (8 vs. 3 months), which are more seasonally restricted (Fig. 5).”

Finally, L354-356: since it has not been demonstrated that the subtraction of delta AT from delta CT gives the contribution of atmospheric pCO\textsubscript{2} (i.e. trends in other processes can have contributed), these sentences appear poorly supported by the results.

Given what is known of ocean chemistry and all other parameters involved in the carbonate system, biology, and oceanography at Point B, we have put all the proper caution and outlined all assumptions surrounding this approach for calculations at 1 m. In addition, the referee has not provided any evidence of alternative explanations that would refute our conclusions. We have already stated the assumptions of this method for data from 1 m depth, and again emphasize that this is a “simple model” when presenting the Discussion on data from 50 m.

Other minor points

3) Abstract
L2P27-28: CT increase could be driven by the same processes that caused the increase in AT not by the increase of AT itself.

*We have edited the sentence to clarify this, “The remaining C\textsubscript{T} increase may have been driven by the same unidentified process that caused an increase in A\textsubscript{T}”.*

4) L2P34-35: the conclusion about rapid warming could be misleading by the fact that the length of the timeseries is very short. As well, also some of the trend values reported in Table 2 appear quite large. I wonder whether the length of the timeseries (only 9 years) could have played any role in overestimating the slopes, since it seems (after a simple visual inspection of Fig. 2) that some timeseries have a maximum in 2012-2013 and values do not increase more after that period. AT and CT have high values in 2012-2013, but these are not independent from one another (i.e. these parameters have shared ion constituents) and the remaining parameters do not show particularly unusual patterns in 2012-2013. In addition, we have discussed how the process influencing AT and CT trends might be wholly independent from the other trends. I would suggest testing the robustness of the trends by using a bootstrap analysis (or any other re-sampling technique) or testing a regime shift analysis to verify whether it is a trend or a regime shift.

I acknowledge that authors specify that trends (i.e. warming, and acidification) referred to the specific 2007-2015 period in several parts of the manuscript, however, a comment about the reliability of trends computed on very short timeseries should be added somewhere in the manuscript (e.g. at L363-365 and in the conclusion).

The data show that rapid warming occurred over the study period, whether or not the study period is considered short or long. It is unclear which specific trends the referee is referring to in the comments that trends “appear quite large”.

Only time will tell how consistent these trends are over time. We are simply describing changes that have occurred over the study period (the longest for the coastal Mediterranean Sea).

5) P8L140-141: avoid to use the “river signature” of the Mediterranean Sea while the Bay of Villefranche is described.

*We have removed this statement from the Methods.*
6) P8L144: provide the position of rivers in Figure 1

We did not include a map of local rivers because: (1) we do not present time-series data from rivers, (2) we do not have data that indicate which are the influential rivers (which could also be larger rivers further away), and (3) we only discuss rivers as a potential influence on the observed trends. For this reason, distance and direction of local rivers nearest to the study sites was already reported in Section 2.1, “Paillon, due 4 km West; Var due 10 km West; and Roya due 26 km East”.

7) P10L190: Should it be called “climatological monthly means”? Even if the word “climatological” is referred to a temporal average over longer periods than the presently considered 9-year period, the use of “monthly means” can be misleading. Provide a definition of how anomalies are computed (i.e., at L190, L212 and L215).

L190: We have revised the text in the Methods (Section 2.2) to read: “To quantify interannual changes in carbonate parameters, the data were detrended for seasonality by subtracting the respective climatological monthly means computed for the period 2009-2015 from the time-series (‘monthly means’ from hereon).”

L212: We have now written: “For these data, missing daily values were linearly interpolated, monthly means were calculated and subtract from the time-series to generate an anomaly time-series.” We do not specify climatological monthly means as this definition is defined previously.

L215: We have clarified: “…linear regressions were performed on changes in At and Ct by month (mean value of observations within one month) from 2009 through 2015...”

8) P12L243: more than 400 samples. Done.

9) P12L244: do the authors mean that the trends of all variables are significant both at 1 and 50 m and only Salinity at 1 m is not significant? The sentence is not very clear. Then, avoid writing all trends estimates (and confidence interval and number of points) since they are already shown in Table 2. Provide the number of points in Table 2 along with the unit of the variable trends.

The referee has correctly interpreted this sentence. We have simplified the reporting of trends in paragraph form. We have now added the N values to Table 2. Unit variables have been moved from the Table 2 legend into the table.

10) Table 2: Which is the meaning of “Total” in the first column? are you meaning the whole Mediterranean Sea?

We assume the referee is referring to Table 1 for this comment. Total does indeed mean the whole Mediterranean Sea. We have added this clarification to the Table 1 legend.

11) P15L311: provide an appropriate symbol for AT and S that indicates that AT and S are monthly means. Then, more importantly, add a new plot to figure 4 reporting the regression between salinity and alkalinity based on the monthly means.

We have revised the alkalinity and salinity variables reported in Equation 2 to identify that these are monthly mean values. This equation still has a wide margin of error and given the importance of interannual variability at this site as well, it is not a focal point of our manuscript.
12) P15L328-329 and Fig. S1: it would be interesting to see some statistical tests on the relationship between diel pH variability and T and Chl variability. Or just do not mention it. The Figure S1 does not show a clear message.

We have analyzed the data with a linear regression but these are not statistically significant. We have removed the figure from the supplemental text and only state that diel pH variation is unrelated to temperature and Chl-a (data not shown).

13) I acknowledge that the authors have chosen to not further investigate the high frequency pH time-series, however, I suggest adding at least the estimate of the diel variability of pH to be compared with the trend estimate (L268) and the annual range (L263). Providing the different scales of variability of pH (daily, seasonal, interannual) would be of great interest for many readers.

We already both reported (Section 3.4) and plotted (Figure 7) diel pH variability for this site. But to put all numbers together, we have added a sentence summarizing pH variations over different timescales in the first paragraph of the Discussion and a short statement in the Abstract.

14) L338-341: the assumption that the increase in AT is due to increases in its carbon constituents deserve a better verification. Since HCO₃⁻ and CO₃²⁻ are computed by SeaCarb, the no-carbonate AT can be easily derived and the regression of no-carbonate AT can be calculated in order to verify the assumption. Otherwise, some of the conclusions that follow (e.g. L350-353) cannot be validated by the results.

Computing the non-carbonate AT does not reveal an increase in AT (see figure below). This is not surprising as what is left is the alkalinity of borate (a function of salinity which changes very little at our study site) and the contribution of silicate and phosphate which are extremely small at an oligotrophic site such as Point B. We believe that this result is trivial and does not warrant a mention in the manuscript.
15) L366-370: which is the rationale of the relationship between the temperature increase and climate indexes? Provide any statistical correlation index.
   Using the same reference, we have clarified that both the AMO and NAO are associated with episodic warming of the Mediterranean Sea.

16) P18L391 and L410-411: provide a short definition of “atmospheric forcing”. Do the authors refer to CO2 exchange, Evaporation minus Precipitation, and warming? This definition should be introduced in the abstract at P2L26.
   We have now specified CO2 forcing in all instances.

17) Plots b, d and e of Figure 7 are never introduced nor commented in the text. Remove them if not needed.
   The content of Figure 7 was discussed throughout Section 3.4, but we have now explicitly added “Fig. 7x” throughout this portion of the text.
Coastal ocean acidification and increasing total alkalinity in the NW Mediterranean Sea

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Abstract. Coastal time-series of ocean carbonate chemistry are critical for understanding how global anthropogenic change manifests in near-shore ecosystems. Yet, they are few and have low temporal resolution. At the time-series station Point B in the NW Mediterranean Sea, seawater was sampled weekly from 2007 through 2015, at 1 and 50 m, and analyzed for total dissolved inorganic carbon ($C_T$) and total alkalinity ($A_T$). Parameters of the carbonate system such as pH (pH$_T$, total hydrogen ion scale) were calculated and a deconvolution analysis was performed to identify drivers of change. The rate of surface ocean acidification was $-0.0028 \pm 0.0003$ units pH$_T$ yr$^{-1}$. This rate is larger than previously identified open-ocean trends due rapid warming that occurred over the study period ($0.072 \pm 0.022$ °C yr$^{-1}$). The total pH$_T$ change over the study period was of similar magnitude as the diel pH$_T$ variability at this site. The acidification trend can be attributed to atmospheric carbon dioxide (CO$_2$) forcing ($59\%$, $2.08 \pm 0.01$ ppm CO$_2$ yr$^{-1}$) and warming ($41\%$). Similar trends were observed at 50 m but rates were generally slower. At 1 m depth, the increase in atmospheric CO$_2$ accounted for approximately 40% of the observed increase in $C_T$ ($2.97 \pm 0.20$ µmol kg$^{-1}$ yr$^{-1}$). The remaining increase in $C_T$ may have been driven by the same unidentified process that caused an increase in $A_T$ ($2.08 \pm 0.19$ µmol kg$^{-1}$ yr$^{-1}$). Based on the analysis of monthly trends, synchronous increases in $C_T$ and $A_T$ were fastest in the spring-summer transition. The driving process of the interannual increase in $A_T$ has a seasonal and shallow component, which may indicate riverine or groundwater influence. 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 multiyear 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.
Keywords – ocean change, ocean acidification, time-series, pH, alkalinity, dissolved inorganic carbon, pCO₂, Mediterranean Sea
1. Introduction

Maintaining time-series of oceanographic data is essential for understanding anthropogenic changes in the ocean (Tanhua et al., 2013). On land, fossil fuel burning, cement production, and land use changes have contributed ~600 Gt carbon to the atmosphere during the period 1750-2015 (Le Quéré et al., 2016). In the recent decade 2006-2015, an estimated 25% of this anthropogenic carbon has been absorbed by the ocean in the form of carbon dioxide (CO$_2$; Le Quéré et al., 2016), and causing global changes to the ocean carbonate system. Absorption of CO$_2$ by seawater produces carbonic acid, which decreases seawater pH, and is of great concern for biological processes and marine ecosystems (Doney et al., 2009; Gattuso and Hansson, 2011; Pörtner et al., 2014). Since the preindustrial era, global mean ocean pH has declined by 0.1 (Rhein et al., 2013). Due to the declining trend of ocean pH with increasing anthropogenic CO$_2$, the process is termed ‘ocean acidification’, but this expression represents a suite of chemical changes, including increases in total dissolved inorganic carbon (C$_T$) and partial pressure of CO$_2$ (pCO$_2$) and decrease in calcium carbonate saturation states (Ω, aragonite and calcite; Dickson, 2010). Rates of ocean acidification differ by ocean region and range from -0.0026 (Irminger Sea, North Atlantic) to -0.0013 (South Pacific) units pH yr$^{-1}$ (Bates et al., 2014). Such time-series remain spatially limited, especially in coastal regions, which provide valuable ecosystem services (Barbier et al., 2011; Costanza et al., 1997) and are under high anthropogenic impact (Halpern et al., 2008). Here, we present the first coastal ocean acidification time-series at high temporal resolution.

Compared to the global ocean, marginal seas serve a critical role in anthropogenic CO$_2$ storage via enhanced CO$_2$ uptake and export to the ocean interior (Lee et al., 2011). As a marginal sea, the Mediterranean Sea has a naturally high capacity to absorb but also buffer anthropogenic CO$_2$ (Álvarez et al., 2014; Palmieri et al., 2015). This is primarily due to the high total alkalinity (A$_T$) of Mediterranean waters and overturning circulation (Lee et al.,...
In the Mediterranean Sea, the salinity-$A_T$ relationship is driven by the addition of river discharge and Black Sea input, which are generally high in $A_T$ (Copin-Montégut, 1993; Schneider et al., 2007). Combined with evaporation, this results in higher $A_T$ and salinity in the Mediterranean Sea compared to the Atlantic Mediterranean source water (Jiang et al., 2014). On average, Mediterranean Sea $A_T$ is 10% higher than in the global ocean (Palmiéri et al., 2015). The surface ocean acidification rate, estimated at $\Delta pH_T$ (total hydrogen ion scale) of -0.08 since 1800, is comparable to that of the global ocean despite a 10% greater anthropogenic carbon inventory (Palmiéri et al., 2015). Due to its important role in carbon sequestration and ecological sensitivity to anthropogenic change with economic consequences (Lacoue-Labarthe et al., 2016), the Mediterranean Sea could provide insight to global trends (Lejeusne et al., 2010).

Over the last few years, numerous studies have estimated ocean acidification rates across the Mediterranean Sea (Table 1). Together, these studies cover various study periods with a range of techniques yielding different results. For example, estimates of change in pH of bottom waters since the preindustrial era range between -0.005 to -0.06 (Palmiéri et al., 2015) and as much as -0.14 for full profile estimates (Touratier and Goyet, 2011). Techniques for estimating ocean acidification in the Mediterranean Sea thus far include: (1) hind-casting, using high-resolution regional circulation models (Palmiéri et al., 2015), the TrOCA approach as applied to cruise-based profile data (Krasakopoulou et al., 2011; Touratier and Goyet, 2011; Touratier et al., 2016) and others (Howes et al., 2015), (2) partially reconstructed time-series (Marcellin Yao et al., 2016), (3) comparative study periods (Luchetta et al., 2010; Meier et al., 2014), and (4) sensor-based observations over a short study period (Flecha et al., 2015). Ocean acidification time-series of consistent sampling over many years are lacking for the Mediterranean Sea (The MerMex Group et al., 2011).
particularly along the coast where river discharge influences the carbonate system (Ingrosso et al., 2016).

Compared to the open ocean, shallow coastal sites exhibit natural variability in carbonate chemistry over annual timeframes (Hofmann et al., 2011; Kapsenberg and Hofmann, 2016; Kapsenberg et al., 2015), complicating the detection and relevance of open ocean acidification in isolation of other processes (Duarte et al., 2013). In the NW Pacific coast, rapid acidification of surface waters (ΔpH -0.058 units yr⁻¹) at Tatoosh Island was documented in the absence of changes in known drivers of local pH variability (e.g., upwelling, eutrophication, and more; Wootton and Pfister, 2012; Wootton et al., 2008).

Further inshore, in the Hood Canal sub-basin of the Puget Sound, only 24–49 % of the estimated pH decline from pre-industrial values could be attributed to anthropogenic CO₂ (Feely et al., 2010). The excess decrease in pH was attributed to increased remineralization (Feely et al., 2010). Acidification rates documented along the North Sea Dutch coastline and inlets were highly variable in space, with some exceeding the expected anthropogenic CO₂ rate by an order of magnitude while others exhibited an increase in pH (Provoost et al., 2010).

Variability in coastal carbonate chemistry stems from both physical (e.g., upwelling, river discharge; Feely et al., 2008; Vargas et al., 2016) and biological processes (e.g., primary production, respiration, net calcification). Within watersheds, coastal carbonate chemistry is affected by eutrophication (Borges and Gypens, 2010; Cai et al., 2011), groundwater supply (Cai et al., 2003), and land use and rain influence on river alkalinity (Raymond and Cole, 2003; Stets et al., 2014). Over longer periods, pH can also be influenced by atmospheric deposition (Omstedt et al., 2015). Through primary production and respiration, coastal ecosystems produce pH fluctuations over hours (e.g., seagrass, kelp) to months (e.g., phytoplankton blooms; Kapsenberg and Hofmann, 2016). Due to existing pH variability in
coastal seas, it is necessary to quantify high-frequency trends in order to interpret the pH changes inferred from lower-frequency sampling.

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

2. Materials and methods

2.1. Site description

A carbonate chemistry time-series was initiated in 2007 and maintained through 2015 in the NW Mediterranean Sea at the entrance of the Bay of Villefranche-sur-Mer, France (Fig. 1): Point B station (43.686° N, 7.316° E, 85 m bottom depth). A second site, Environment Observable Littoral buoy (EOL, 43.682° N, 7.319° E, 80 m bottom depth), was used for pH sensor deployment starting in 2014. These two sites are 435 m apart. The site Point B is an historical sampling point, since 1957, regarding several oceanographic parameters. A full site description and research history has been detailed by De Carlo et al. (2013). Briefly, the Bay is a narrow north-south facing inlet with steep bathymetry and estimated volume of 310 million m$^3$. The surrounding region is predominately composed of limestone with a series of shallow, submarine groundwater karst springs (Gilli, 1995). The North current, a major and structuring counter-clockwise current in the Ligurian Sea, can sometimes flow close to Point B. The Bay can also be, on occasion, influenced by local
countercurrents. Both of these hydrodynamics movements have signatures of river discharge. 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 $\mu$mol kg$^{-1}$ (data from *Agence de l’Eau Rhône-Méditerranée-Corse*, http://sierm.eaurmc.fr), and is lower than seawater $A_T$. The Paillon River, whose plume on occasion reaches into the Bay ([L. Mousseau, pers. obs.]), was sampled on 18 August 2014 and had a $A_T$ of 1585 ± 0.1 $\mu$mol kg$^{-1}$ ($N = 2$, J.-P. Gattuso, unpubl.). Due to low primary productivity, seasonal warming drives the main annual variability in carbonate chemistry at this location (De Carlo et al., 2013).

2.2. Point B data collection, processing, and analysis

To document long-term changes in ocean carbonate chemistry at Point B, seawater was sampled weekly from 9 January 2007 to 22 December 2015. Samples were collected at 1 and 50 m, using a 12-L Niskin bottle at 9:00 local time. Seawater was transferred from the Niskin bottle to 500 mL borosilicate glass bottles and fixed within an hour via addition of saturated mercuric chloride for preservation of carbonate parameters, following recommendations by Dickson et al. (2007). Duplicate samples were collected for each depth. For each sampling event, CTD casts were performed either with a Seabird 25 or Seabird 25+ profiler whose sensors are calibrated at least every two years. Accuracy of conductivity (SBE4 sensor) and temperature (SBE3 sensor) measurements from CTD casts were 0.0003 S m$^{-1}$ and 0.001°C, respectively.

Within six months of collection, bottle samples were analyzed for $C_T$ and $A_T$ via potentiometric titration following methods described by Edmond (1970) and DOE (1994), by *Service National d’Analyse des Paramètres Océaniques du CO$_2$*, at the Université Pierre et Marie Curie in Paris, France. Precision of $C_T$ and $A_T$ was less than 3 $\mu$mol kg$^{-1}$, and the
average accuracy was 2.6 and 3 µmol kg⁻¹, as compared with seawater certified reference
material (CRM) provided by A. Dickson (Scripps Institution of Oceanography). Only
obvious outliers were omitted from the analyses: three CT values at 1 m (> 2300 µmol kg⁻¹),
one AT value at 1 m (> 2900 µmol kg⁻¹), and one AT value at 50 m (< 2500 µmol kg⁻¹). The
CT and AT measurements on replicate bottle samples were averaged for analyses.
Calculations of the carbonate system parameters were performed using the R package
seacarb version 3.1 with CT, AT, in situ temperature and salinity as inputs (Gattuso et al.,
2016). Total concentrations of silicate (SiOH₄⁻) and phosphate (PO₃⁵⁻) were used when
available from Point B (L. Mousseau, unpubl., http://somlit.epoc.u-bordeaux1.fr/fr/).
Detection limits for nutrients were 0.03 µM for SiOH₄⁻ and 0.003 to 0.02 µM for PO₃⁵⁻;
relative precision of these analyses is 5-10 % (Aminot and Kérouel, 2007). Total boron
concentration was calculated from salinity using the global ratio determined by Lee et al.
(2010). The following constants were used: K₁ and K₂ from Lueker et al. (2000), K₂ from
Perez and Fraga (1987), and K₃ from Dickson (1990). Reported measured parameters are
temperature, salinity, AT, and CT, and derived parameters are pH₇ (total hydrogen ion scale),
CT-normalized to 25 °C (pH₇₂₅), pCO₂, and aragonite (Ωₐ) and calcite (Ωₐ) saturation states.
Salinity-normalized changes in AT (nAT) and CT (nCT) were calculated by dividing by in situ
salinity and multiplying by 38. Except for pH₇₂₅, all parameters are reported at in situ
temperatures.
The average uncertainties of the derived carbonate parameters were calculated
according to the Gaussian method (Dickson and Riley, 1978) implemented in the “errors”
function of the R package seacarb 3.1 (Gattuso et al., 2016). The uncertainties are ± 2.7 x 10⁻¹⁰
mol H⁺ (about 0.015 units pH₇), ±15 µatm pCO₂, and ± 0.1 unit of the aragonite and calcite
saturation states.
To quantify interannual changes in carbonate parameters, the data were detrended for seasonality by subtracting the respective climatological monthly means computed for the period 2009-2015 from the time-series (‘monthly means’ from hereon). The resulting residuals were analyzed using a linear regression to compute anomaly trends. This approach follows methods from Bates et al. (2014) to allow for comparisons of trends observed at different time-series stations. All analyses were performed in R (R Core Team, 2016).

### 2.3. Deconvolution of pH$_T$ and pCO$_2$

To identify proportional contributions of various drivers to ocean acidification trends at Point B, deconvolution of time-series pH$_T$ and pCO$_2$ was performed following methods from García-Ibáñez et al. (2016) for observations at 1 and 50 m. The equation is described below for pH$_T$, where changes in pH$_T$ are driven by changes in temperature ($T$), salinity ($S$), $A_T$, and $C_T$ over time ($t$), according to the following model:

$$\frac{dpH_T}{dt} = \frac{dpH_T}{dT} \frac{dT}{dt} + \frac{dpH_T}{dS} \frac{dS}{dt} + \frac{dpH_T}{dA_T} \frac{dA_T}{dt} + \frac{dpH_T}{dC_T} \frac{dC_T}{dt}$$

Here, $\frac{dpH_T}{dvar}$ represents the slope contribution of changing var to the estimated change in pH$_T$, where var is either temperature ($T$), salinity ($S$), $A_T$, or $C_T$. The sensitivity of pH to var $\frac{dpH_T}{dvar}$ was estimated by calculating pH$_T$ using the true observations of var and holding the other three variables constant (mean value of the time-series) and regressing it to var. Sensitivity $\frac{dpH_T}{dvar}$ was then multiplied by the anomaly rate of var (Table 2). The calculation was repeated for pCO$_2$ ($\frac{dpCO_2}{dt}$) in order to compare the rate of increase with that of atmospheric CO$_2$.

As a sub-component of $\frac{dpCO_2}{dC_T}$, the rate of anthropogenic CO$_2$ increase was estimated from atmospheric CO$_2$ concentrations nearest to Point B (Plateau Rosa, Italy,
interpolated, monthly means were calculated and subtracted from the time-series to generate an anomaly time-series. A linear regression was performed on anomalies where the slope represents the rate of anthropogenic CO₂ increase in the atmosphere. Finally, to help identify different processes that might have contributed to the observed trends, linear regressions were performed on changes in $A_T$ and $C_T$ per month (mean value of observations within one month) from 2009 through 2015 and on the salinity-$A_T$ relationship by year.

2.4. SeaFET data collection, processing, and analysis

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

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

3. Results

3.1. Time-series trends

At Point B from January 2007 to December 2015, more than 400 samples were collected for carbonate chemistry at both 1 and 50 m. Anomaly trends detected at 1 m (Fig. 2) were also significant at 50 m (Fig. 3, Table 2), with the exception that salinity increased at 50 m (0.0063 ± 0.0020 units yr\(^{-1}\)). At 1 m, trends were significant for pH\(_T\) (-0.0028 units yr\(^{-1}\)), A\(_T\) (2.08 µmol kg\(^{-1}\) yr\(^{-1}\)), C\(_T\) (2.97 µmol kg\(^{-1}\) yr\(^{-1}\)), pCO\(_2\) (3.53 µatm yr\(^{-1}\)), and Ω\(_a\) (-0.0064 units yr\(^{-1}\)). At the same time, temperature anomaly increased (0.072 ºC yr\(^{-1}\)), but no significant change in the salinity was detected at 1 m. Trends of carbonate chemistry parameters were faster at 1 m compared to 50 m, with the exception of salinity and temperature. The warming rate at 50 m was slightly greater compared to 1 m, mostly due to increasing summer temperatures since 2007.

Strong seasonal cycles of carbonate chemistry parameters were present at Point B at 1 m (Fig. 4). Climatological monthly means (2007-2015) are described briefly and listed in Table S1. Mean temperature range was 11.2 ºC with a maximum at 24.77 ± 1.35 ºC in August and minimum of 13.58 ± 0.41 ºC in February. The range in A\(_T\) was 19 µmol kg\(^{-1}\) from June to September. The C\(_T\) range was 33 µmol kg\(^{-1}\) with a peak in late winter and minimum values in
August and October. Due to summer warming coinciding with the period of peak primary productivity (De Carlo et al. 2013), warming countered the influence of low $C_T$ on pH. As a result, pH$_T$ reached minimum values in summer ($8.02 \pm 0.03$, July and August) and peaked in late winter ($8.14 \pm 0.01$, February and March), for an overall annual pH range of 0.12. The corresponding pCO$_2$ range was 128 µatm from February to August. Seasonal cycles were smaller at 50 m compared to 1 m (Table S1).

3.2. Deconvolution of pH$_T$ and pCO$_2$

Deconvolutions of pH and pCO$_2$ are presented in Table 3 and 4, respectively. The estimated anomaly trends $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ from the deconvolution fall within the error of the observed anomaly trends (Table 2). The contribution of warming to the pH$_T$ anomaly $\zeta$ matched the difference between the trends of pH$_T$ and pH$_{T25C}$ (Table 3), which verifies that the deconvolution reproduced influences of temperature sensitivity well. Overall, these results indicate that the deconvolution analyses represent the observed trends well.

At both depths, the predominant driver of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ was the increase in $C_T$. Increasing $A_T$ countered 66-69% and 60% of the influence of increasing $C_T$ on $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$, respectively. At 1 m, warming accounted for 39% and 37% of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$, respectively. Since warming was slightly greater at 50 m compared to 1 m, warming accounted for a larger proportional influence on $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ at 50 m compared to 1 m. Increasing salinity at 50 m contributed slightly to $\frac{dpH_T}{dt}$ (4%) and $\frac{dpCO_2}{dt}$ (2%). Atmospheric CO$_2$ anomaly at Plateau Rosa increased by $2.08 \pm 0.01$ ppm yr$^{-1}$ ($F_{1,3265} = 4664, P < 0.001, R^2 = 0.93$) during the study period 2007-2015, and represents the anthropogenic CO$_2$ forcing on seawater pH. To estimate the influence of anthropogenic CO$_2$
forcing at Point B, we assume air-sea CO₂ equilibrium (e.g., increase in atmospheric CO₂ causes an equal increase in seawater pCO₂) for the water mass at 1 m. This assumption is based on evidence that Point B is a weak sink for atmospheric CO₂ with near-balanced air-sea CO₂ flux on an annual time-frame (De Carlo et al., 2013). Considering the error associated with deconvolution of pCO₂ at 1 m, atmospheric CO₂ increase can, at most, represent 3.8%-4.3% of the total C_T contribution to pCO₂ trends unaccounted for.

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

3.3. Salinity and A_T relationships

Over an annual observation period at 1 m, salinity was a poor predictor of A_T, with the exception of 2007 (Fig. 6). The R² value for each annual salinity-A_T relationship at 1 m ranged from 0.00 (in 2013) to 0.87 (in 2007) with y-intercepts (A_T0, total alkalinity of the freshwater end-member) ranging between -176 µmol kg⁻¹ (in 2007) and 2586 µmol kg⁻¹ (in 2013). The interannual variability of the salinity-A_T relationship was driven by the variability in A_T observed at salinity < 38.0 that was present from November through July.

Changes in salinity (based on monthly means) at Point B was small and ranged from 37.64 ± 0.26 to 38.21 ± 0.11 from May to September, following freshwater input in winter and spring and evaporation throughout summer and fall (Fig. 4). Highest (> 38.0) and most
stable salinity observations were made in August through October and coincided with the period of maximum $A_T$ (2562 and 2561 ± 9 µmol kg$^{-1}$ in September and October, respectively). Minimum $A_T$ (2543 ± 14 µmol kg$^{-1}$) was observed in June, one month after minimum salinity. To capture this seasonality without the inter-annual variation of $A_T$, the salinity-$A_T$ relationship at 1 m was estimated from climatological monthly means ($c_{A_T}$ and $c_S$, $N=12$) where $c_{A_T}$ units are µmol kg$^{-1}$ and error terms are standard errors ($R^2 = 0.74$):

$$c_{A_T} = 1554.9 (\pm 185.9) + 26.3 (\pm 4.9) \times c_S$$ (2)

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

3.4. High-frequency pH data

To verify the weekly sampling scheme at Point B, a continuous record of high-frequency pH observations was obtained via 11 consecutive SeaFET deployments from June 2014 to April 2016. Deployment periods averaged 58 ± 25 days with 5 ± 2 calibration samples per deployment (Fig. 7). Only 5% of the data was removed during quality control, due to biofouling in one deployment and battery exhaustion in another, yielding 610 days of data. The mean offset between calibration samples and the calibrated SeaFET pH time-series was ± 0.007, indicating a high-quality pH dataset (Fig. 7c). Sensor data corroborated the seasonal pH and temperature cycle observed at Point B (Fig. 7a-b). Event-scale effects (e.g., pH$_T$ change ≥ 0.1 for days to weeks, sensu Kapsenberg and Hofmann 2016) were absent at this site suggesting that weekly sampling was sufficient to describe seasonal and interannual changes in carbonate chemistry at Point B. The magnitude of diel pH$_T$ variability was small (the 2.5$^{th}$ to 97.5$^{th}$ percentiles ranged between 0.01 and 0.05 units pH$_T$, Fig. 7d-e). Diel pH variations increased from winter to spring with the greatest variability in April, May, and...
June (ΔpH$_T$ > 0.035). The magnitude of pH variability was not correlated with temperature or the concentration of chlorophyll-a (data not shown).

4. Discussion

High resolution time-series are necessary to document coastal ocean acidification. At Point B in the NW coastal Mediterranean Sea, near-surface pH$_T$ decreased by 0.0028 ± 0.0003 units yr$^{-1}$ based on weekly measurements from 2007 through 2015. Temperature increased by 0.072 ± 0.022 °C yr$^{-1}$. In addition, $A_T$ increased by 2.08 ± 0.19 µmol kg$^{-1}$ yr$^{-1}$, a change that is unrelated to direct effects of CO$_2$ absorption by seawater. In less than a decade, the total change in pH at Point B (ΔpH$_T$: 0.0252, Table 1) was of the same magnitude as the diel pH variability (ΔpH$_T$: 0.01-0.05) and 1/5th of the magnitude of the seasonal pH cycle (ΔpH$_T$: 0.12) found at this site.

We can identify the drivers for the ocean acidification trends at Point B using the deconvolution of pH and pCO$_2$ and by assuming that the increase in $A_T$ was due to increases in its carbon constituents, bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$) ions. This assumption is based 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 HCO$_3^-$ and CO$_3^{2-}$ would both contribute to $A_T$ and $C_T$ and thereby explain the observed synchronicity of monthly trends in $A_T$ and $C_T$ (Fig. 5). Using the pCO$_2$ deconvolution, we can then sum the contributions to pCO$_2$ from $A_T$ (-3.08 µatm pCO$_2$ yr$^{-1}$) and $C_T$ (5.14 µatm pCO$_2$ yr$^{-1}$) trends to determine the proportional contribution of Δ$C_T$ to ΔpCO$_2$ that is unrelated to changes in $C_T$ brought on by $A_T$. The remaining 2.06 µatm pCO$_2$ yr$^{-1}$ increase due to increasing $C_T$ closely matched the magnitude of atmospheric CO$_2$ increase during the observation period (2.08 ± 0.01 ppm yr$^{-1}$ at Plateau Rosa, Italy). The closeness of these numbers does not imply causation. However, given that surface waters at Point B exhibit a near-zero air-sea CO$_2$ flux over annual cycles (De Carlo et al., 2013), the
Evidence supports the conclusion that the ocean acidification trend at Point B closely follows the rate of atmospheric CO$_2$ increase. The influence of atmospheric CO$_2$ can also be observed in the monthly changes in C$_T$. Monthly C$_T$ trends are positive and statistically significant over more months than A$_T$ trends (8 vs. 3 months), which are more seasonally restricted (Fig. 5).

Applying this simple model to pH$_T$, assuming changes in C$_T$ are due to both increasing A$_T$ (a neutralizing effect) and atmospheric CO$_2$ forcing, the surface ocean acidification trend at Point B can be attributed primarily to atmospheric CO$_2$ forcing (59%) and secondarily to warming (41%).

Using this same approach for observations at 50 m, the C$_T$ contribution to pCO$_2$ trends that was unrelated to A$_T$ change was 1.41 µatm pCO$_2$ yr$^{-1}$, which is 68% of the rate of atmospheric CO$_2$ increase in contrast to 99% at 1 m. Changes in pH$_T$ can then be attributed to atmospheric CO$_2$ forcing (42%), warming (54%), and increasing salinity (3%), which may result from warming. Due to slightly enhanced warming and reduced CO$_2$ penetration observed at 50 m, warming had a greater effect on the ocean acidification trend than atmospheric CO$_2$ forcing at depth compared to the surface.

The acidification rate at Point B (-0.0028 units pH yr$^{-1}$) is larger than those reported for other ocean time-series sites (-0.0026 to -0.0013 units pH yr$^{-1}$, Bates et al., 2014), likely due to differences in warming rates. The observed warming from 2007 through 2015 (0.72 to 0.88 °C decade$^{-1}$) is extremely rapid relative to global trends in the upper 75 m from 1971 to 2010 (0.11 °C decade$^{-1}$, Rhein et al., 2013). The coastal region of Point B has warmed steadily since 1980 and with periods of rapid warming (Parravicini et al., 2015).

Exacerbated warming may be related to the positive phases of the Atlantic Multi-decadal Oscillation (AMO) and North Atlantic Oscillation (NAO), both of which are associated with episodic warming of the Mediterranean Sea (Lejeunse et al., 2010). The AMO has been...
positive since the 1990s\(^1\) and positive NAO phases were prevalent during the second half of our study\(^2\).

Nearest to Point B, the acidification rate at DYFAMED, an open-sea site about 50 km offshore from Point B (Fig. 1), was estimated at \(-0.003 \pm 0.001\) units pH\textsubscript{SW} yr\(^{-1}\) from 1995 to 2011 (Marcellin Yao et al., 2016). At DYFAMED, warming contributed approximately 30% to the acidification rate and the remaining 70% was attributed to anthropogenic CO\(_2\) (Marcellin Yao et al., 2016). The uncertainty is large and makes direct comparison with Point B unreliable but the results are agreeable. However, \(A_T\) at the DYFAMED did not change significantly from 2007 through 2014 \((F_{1,51} 3.204, P = 0.0794, R^2 0.08, \text{data from Coppola et al., 2016})\). This may indicate that the processes driving changes in \(A_T\) at Point B are unique to the coastal environment.

Similar changes in coastal carbonate chemistry were observed elsewhere in the nearshore Mediterranean Sea. In the Northern Adriatic Sea, Luchetta et al. (2010) determined an acidification rate in pH\(_T\) of \(-0.0025\) yr\(^{-1}\) and an increase in \(A_T\) of 2.98 µmol kg\(^{-1}\) yr\(^{-1}\) at depths shallower than 75 m, by comparing cruise data between the winters of 1983 and 2008. Point B and Adriatic Sea observations are independent but reflect changes in seawater chemistry that may be occurring across a wider coastal region. Additional time-series would help resolve the spatial extent of the observed trends. Specifically, the Eastern Mediterranean Sea would offer an important contrast, as pH of eastern waters is expected to be more sensitive to atmospheric CO\(_2\) addition due to their ability to absorb more anthropogenic CO\(_2\) than either the western Mediterranean or Atlantic waters (Álvarez et al., 2014).

While the trends in atmospheric CO\(_2\) forcing and temperature account for the ocean acidification trend, the increase in \(A_T\) and \(C_T\) increase beyond what can be attributed to

\(^1\) http://www.cgd.ucar.edu/cas/catalog/climind/AMO.html
\(^2\) http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/month nao_index.shtml
Changes in atmospheric CO₂ was unexpected. The fastest increases in $A_T$ and $C_T$ occurred from May through July (Fig. 5), when the thermal stratification settles. In the NW Mediterranean, the main processes governing seasonal variability in $A_T$ are evaporation increasing $A_T$ in summer (i.e., June through September at Point B) and, to a lesser extent, phytoplankton uptake of nitrate ($NO_3^-$) and phosphate ($PO_4^{3-}$) increasing $A_T$ from January through March (Cossarini et al., 2015). During the transition of these processes, salinity decreases to a minimum in May, reflecting freshwater input that dilutes $A_T$ to minimum values at the start of summer. 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 waters (Copin-Montégut and Bégovic, 2002).

Notably, monthly trends of $C_T$ at Point B were not statistically significant from November through January for the period 2007-2015. 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. Summer warming leads to pCO₂ off-gassing to the atmosphere (De Carlo et al., 2013), thereby further decreasing $C_T$. The increases in $A_T$ and $C_T$ from 2007 through 2015 were more pronounced at 1 m compared to 50 m. This indicates that the process driving $A_T$ and $C_T$ trends are stronger at the surface and affect carbonate chemistry primarily during the spring-summer transition from May through July.

While the drivers of ocean acidification trends are identified and quantified above, the increase in $A_T$ and increase in $C_T$ beyond what can be attributed to changes in atmospheric CO₂ requires some speculation. Some biogeochemical processes can be ruled out as drivers. For example, changes in benthic processes are very unlikely. Reduced calcium carbonate (CaCO₃) precipitation rates would increase $A_T$ but would increase $C_T$. Even so, the dominant ecosystem in the Bay of Villefranche-sur-Mer is seagrass meadows, which harbor relatively
few calcifying organisms. Dissolution of calcium carbonate sediment would contribute to $A_T$ and $C_T$ increase in the water column. However, as the water was supersaturated with respect to both aragonite and calcite, this could only be mediated by biological processes. Carbonate dissolution following CO$_2$ production via oxic degradation of organic matter releases $A_T$ and $C_T$ in a 1:1 ratio (Moulin et al., 1985). Likewise, anaerobic remineralization produces alkalinity (Cai et al., 2011). In the sediment of the Bay of Villefranche, sulfate reduction coupled with precipitation of sulfide minerals is the dominant anoxic mineralization pathway (Gaillard et al., 1989). An increase in these processes would explain the observed increase in $A_T$ and $C_T$, but as trends were slower at 50 m compared to 1 m, this would suggest the dominance of a process taking place in surface waters.

In the upper water column at Point B, changes in biological processes are unlikely to explain the observed trends in $A_T$ and $C_T$. For example, the concentration of chlorophyll-a, a proxy of primary production, has decreased since 1995, nutrients increased, and phytoplankton blooms have shifted towards earlier dates in the year (Irisson et al., 2012). While a decrease in net primary production could drive $C_T$ trends, the observed increase in NO$_3^-$ and PO$_4^{3-}$ would cause a small decrease in $A_T$ (Wolf-Gladrow et al., 2007). Stimulated community respiration could result from warming waters but enhanced remineralization would cause a decrease in $A_T$ (Wolf-Gladrow et al., 2007).

The lack of salinity change at the surface excludes additional processes as drivers of $A_T$ and $C_T$ increase 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. Increased input of Eastern Mediterranean Sea waters could increase $A_T$, but this is unlikely as this water mass flows much deeper than Point B (Millot and Taupier-Letage, 2005).
Instead, the observed changes in $A_T$ and $C_T$ could be due to increased limestone weathering which would increase the input of $A_T$ from land to the sea via rivers and groundwater. Rivers contribute both $A_T$ and $C_T$ to the Mediterranean Sea (Copin-Montégut, 1993; Tamše et al., 2015). River $A_T$ originates from erosion and is correlated with bedrock composition (e.g., McGrath et al., 2016). Positive trends in river $A_T$ have been documented in North America and occur via a number of processes including: (1) the interplay of rainfall and land-use (Raymond and Cole, 2003), (2) anthropogenic limestone addition (a.k.a., liming) used to enhance agriculture soil pH (Oh and Raymond, 2006; Stets et al., 2014) and freshwater pH (Clair and Hindar, 2005), and (3) potentially indirect effects of anthropogenic CO$_2$ on groundwater CO$_2$-acidification and weathering (Macpherson et al., 2008). Such, and other, processes were hypothesized to have driven $A_T$ changes in the Baltic Sea (Müller et al., 2016). There, an increase in $A_T$ of 3.4 µmol kg$^{-1}$ yr$^{-1}$ was observed from 1995 to 2014 (mean salinity = 7). In contrast to Point B, the increase in Baltic Sea $A_T$ was not noticeable at salinity > 30 (Müller et al., 2016).

Given the above speculations, the simplest plausible mechanisms causing the unexpected $A_T$ and $C_T$ trends would be through increasing $A_T$ of the freshwater end-member of Point B. Local precipitation, however, did not have an influential effect and was not correlated with salinity or $A_T$ (Fig. S1). While submarine groundwater springs can be a significant source of nutrients, $A_T$, and $C_T$ to the ocean (Cai et al., 2003; Slomp and Van Cappellen, 2004), carbonate chemistry contributions of local submarine springs are currently unknown (Gilli, 1995). 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. If river runoff exerts a dominant control on Point B carbonate chemistry, there is a lag effect, as freshwater influence peaked in May but $A_T$ and $C_T$ increased fastest from May through July. Consequently, this hypothesis needs
further investigation. Until the source of $A_T$ increase is properly identified, use of this observation in modeling should be implemented with caution.

5. Conclusion

Predictions of coastal ocean acidification remain challenging due to the complexity of biogeochemical processes occurring at the ocean-land boundary. At the Point B coastal monitoring station in the NW Mediterranean Sea, surface ocean acidification was due to atmospheric CO$_2$ forcing and rapid warming over the observation period 2007-2015. However, additional trends in $A_T$ and $C_T$ were observed and remain unexplained, but these trends could relate to riverine and groundwater input. The influence of a coastal boundary processes influencing seawater $A_T$ and $C_T$ presents a potentially major difference between coastal and offshore changes in ocean chemistry. This study highlights the importance of considering other anthropogenic influences in the greater land-sea region that may contribute to coastal biogeochemical cycles (sensu Duarte et al. 2013) and alter projections of anthropogenic change in near-shore waters.

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

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

Competing interests - The authors declare that they have no conflict of interest.
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Table 1. Previous estimates or documentation of pH change (ΔpH) in the Mediterranean Sea.

Total indicates estimates made for the whole Mediterranean Sea. TrOCA is the ‘Tracer combining Oxygen, inorganic Carbon, and total Alkalinity’ method, NR means ‘not reported’, and PI is ‘pre-industrial era’. *indicates studies where the reported pH change was assumed to be at in situ temperatures.

<table>
<thead>
<tr>
<th>Region</th>
<th>Site</th>
<th>Method</th>
<th>Study period</th>
<th>pH scale</th>
<th>°C</th>
<th>ΔpH yr ± SE</th>
<th>Total ΔpH</th>
<th>Reference</th>
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<td>Point B, 1 m</td>
<td>time-series, anomaly</td>
<td>2007-2015</td>
<td>in situ</td>
<td>0.0024 ± 0.0003</td>
<td>-0.0024</td>
<td>This study.</td>
<td></td>
</tr>
<tr>
<td>NW</td>
<td>Point B, 1 m</td>
<td>time-series, anomaly</td>
<td>2007-2015</td>
<td>total</td>
<td>25</td>
<td>-0.0017 ± 0.0002</td>
<td>-0.0153</td>
<td>This study.</td>
</tr>
<tr>
<td>NW</td>
<td>Point B</td>
<td>model</td>
<td>1967-2003</td>
<td>in situ</td>
<td>0.0014</td>
<td>-0.0014</td>
<td>-0.05</td>
<td>Howes et al. (2015)</td>
</tr>
<tr>
<td>NW</td>
<td>DYFAMED</td>
<td>time-series, observed</td>
<td>1995-2011</td>
<td>seawater</td>
<td>-0.005 ± 0.001</td>
<td>-0.0051</td>
<td>Marcellin Yao et al. (2016)</td>
<td></td>
</tr>
<tr>
<td>NW</td>
<td>DYFAMED</td>
<td>time-series, comparison</td>
<td>1998-2000,</td>
<td>seawater</td>
<td>-</td>
<td>-0.02</td>
<td>Meier et al. (2014)</td>
<td></td>
</tr>
<tr>
<td>NW</td>
<td>Gulf of Lion</td>
<td>TrOCA</td>
<td>PI-2011</td>
<td>in situ*</td>
<td>-</td>
<td>-0.15 to -0.11</td>
<td>-0.15</td>
<td>Touratier et al. (2016)</td>
</tr>
<tr>
<td>East</td>
<td>N Adriatic Sea</td>
<td>cruise comparison</td>
<td>1983, 2008</td>
<td>total</td>
<td>25</td>
<td>-0.0025</td>
<td>-0.063</td>
<td>Luchetta et al. (2010)</td>
</tr>
<tr>
<td>East</td>
<td>Otranto Strait</td>
<td>TrOCA</td>
<td>PI-1995</td>
<td>seawater</td>
<td>-</td>
<td>&lt; -0.1 to -0.05, &lt; 0.014</td>
<td>&lt; 0.014</td>
<td>Krasakopoulou et al. (2011)</td>
</tr>
<tr>
<td>Total</td>
<td>Full profile</td>
<td>TrOCA</td>
<td>PI-2001</td>
<td>in situ*</td>
<td>-</td>
<td>-0.14 to -0.05</td>
<td>-0.14</td>
<td>Touratier and Guyart (2011)</td>
</tr>
<tr>
<td>Total</td>
<td>Bottom waters</td>
<td>model</td>
<td>1800-2001</td>
<td>in situ*</td>
<td>-</td>
<td>-0.06 to -0.005</td>
<td>-0.06</td>
<td>Palmisiri et al. (2015)</td>
</tr>
<tr>
<td>Total</td>
<td>Surface waters</td>
<td>model</td>
<td>1800-2001</td>
<td>in situ*</td>
<td>-</td>
<td>-0.084 ± 0.001</td>
<td>-0.084</td>
<td>Palmisiri et al. (2015)</td>
</tr>
<tr>
<td>Gibraltar</td>
<td>Strait</td>
<td>Espartel sill, pH, pCO₂ sensors</td>
<td>2012-2015</td>
<td>total</td>
<td>25</td>
<td>-0.0044 ± 0.00006</td>
<td>-0.0044</td>
<td>Flecha et al. (2015)</td>
</tr>
</tbody>
</table>

Comment [LK23]: Deleted: 17.34
Table 2. Time-series anomaly regression analyses on seawater carbonate chemistry at Point B for salinity (S), temperature (T), dissolved inorganic carbon (CT), total alkalinity (AT), pH, pCO2, calcite (Ωc) and aragonite (Ωa) saturation state, and salinity-normalized AT (nAT) and CT (nCT), at 1 and 50 m. Slopes represent the change in the variable unit per year. *P* < 0.001 indicates *p*-values far smaller than 0.001.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Variable</th>
<th>Slope ± SE</th>
<th>Intercept ± SE</th>
<th>N</th>
<th>F</th>
<th>df</th>
<th>Slope P</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S</td>
<td>-0.0017 ± 0.0044</td>
<td>3.38 ± 8.82</td>
<td>412</td>
<td>0.147</td>
<td>1,415</td>
<td>0.702 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T (ºC)</td>
<td>0.072 ± 0.022</td>
<td>-145 ± 44</td>
<td>413</td>
<td>10.999</td>
<td>1,411</td>
<td>0.001 0.026</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CT (µmol kg⁻¹)</td>
<td>2.97 ± 0.20</td>
<td>-5965 ± 400</td>
<td>416</td>
<td>221.87</td>
<td>1,414</td>
<td>&lt;0.001 0.349</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AT (µmol kg⁻¹)</td>
<td>2.08 ± 0.19</td>
<td>-4189 ± 379</td>
<td>417</td>
<td>122.429</td>
<td>1,415</td>
<td>&lt;0.001 0.228</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>-0.0028 ± 0.0003</td>
<td>5.72 ± 0.66</td>
<td>412</td>
<td>74.205</td>
<td>1,410</td>
<td>&lt;0.001 0.153</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH25</td>
<td>-0.0017 ± 0.0002</td>
<td>3.46 ± 0.43</td>
<td>412</td>
<td>64.204</td>
<td>1,410</td>
<td>&lt;0.001 0.1354</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pCO2 (µatm)</td>
<td>3.53 ± 0.39</td>
<td>-7105 ± 776</td>
<td>412</td>
<td>83.927</td>
<td>1,410</td>
<td>&lt;0.001 0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ωc</td>
<td>-0.0109 ± 0.0022</td>
<td>22.0 ± 4.5</td>
<td>417</td>
<td>24.08</td>
<td>1,410</td>
<td>&lt;0.001 0.055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ωa</td>
<td>-0.0064 ± 0.0015</td>
<td>12.9 ± 3.1</td>
<td>417</td>
<td>17.33</td>
<td>1,410</td>
<td>&lt;0.001 0.041</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>nAT (µmol kg⁻¹)</td>
<td>2.20 ± 0.28</td>
<td>-4425 ± 360</td>
<td>412</td>
<td>62.34</td>
<td>1,410</td>
<td>&lt;0.001 0.132</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nCT (µmol kg⁻¹)</td>
<td>3.12 ± 0.29</td>
<td>-6275 ± 579</td>
<td>412</td>
<td>117.46</td>
<td>1,410</td>
<td>&lt;0.001 0.223</td>
<td></td>
</tr>
</tbody>
</table>

Comment [LK24]:

Deleted: , ºC

Deleted: , µmol kg⁻¹

Deleted: , µmol kg⁻¹

Deleted: 25 ºC-normalized

Deleted: (µatm)
**Table 3.** Deconvolution of pH$_T$ anomalies ($\frac{\partial \text{pH}_T}{\partial \text{var}}$ units pH yr$^{-1}$) at 1 and 50 m.

Sensitivity of pH$_T$ with respect to variables ($\frac{\partial \text{pH}_T}{\partial \text{var}}$), where the variable var is either temperature (T), salinity (S), total alkalinity ($A_T$), or dissolved inorganic carbon ($C_T$), was multiplied by the anomaly of var ($\frac{\partial \text{var}}{\partial \text{dt}}$, Table 2). SE is standard error and RMSE is root-mean-squared error. Rounding was performed at the end of the calculations, prior to estimating percent contributions.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>var</th>
<th>$\frac{\partial \text{pH}_T}{\partial \text{var}} \pm \text{SE}$</th>
<th>$\frac{\partial \text{pH}_T}{\partial \text{var}} \frac{\partial \text{var}}{\partial \text{dt}} \pm \text{RMSE}$</th>
<th>Contribution (%)</th>
<th>$\frac{\partial \text{pH}_T}{\partial \text{dt}} \pm \text{RMSE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T (ºC)</td>
<td>-0.0153 ± &lt;0.0001</td>
<td>-0.0011 ± 0.0003</td>
<td>41</td>
<td>-0.0027 ± 0.0005</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.0117 ± &lt;0.0001</td>
<td>&lt;0.0001 ± 0.0001</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_T$ (µmol kg$^{-1}$)</td>
<td>0.0015 ± &lt;0.0001</td>
<td>0.0031 ± 0.0003</td>
<td>-115</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_T$ (µmol kg$^{-1}$)</td>
<td>-0.0016 ± &lt;0.0001</td>
<td>-0.0047 ± 0.0003</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>T (ºC)</td>
<td>-0.0154 ± &lt;0.0001</td>
<td>-0.0014 ± 0.0003</td>
<td>54</td>
<td>-0.0026 ± 0.0005</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.0116 ± &lt;0.0001</td>
<td>&lt;0.0001 ± &lt;0.0001</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_T$ (µmol kg$^{-1}$)</td>
<td>0.0015 ± &lt;0.0001</td>
<td>0.0024 ± 0.0002</td>
<td>-92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_T$ (µmol kg$^{-1}$)</td>
<td>-0.0016 ± &lt;0.0001</td>
<td>-0.0035 ± 0.0003</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Deconvolution of pCO$_2$ anomalies (d$^{13}$C, µatm yr$^{-1}$) at 1 and 50 m. Details are the same as in Table 3.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>var</th>
<th>δpH$_T$ δvar ± SE</th>
<th>δpH$_T$ δvar / δvar dt ± RMSE</th>
<th>Contribution (%)</th>
<th>δpH$_T$ δdvar / dt ± RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T (ºC)</td>
<td>16.49 ± 0.05</td>
<td>1.19 ± 0.36</td>
<td>37</td>
<td>3.23 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>10.14 ± &lt;0.01</td>
<td>-0.02 ± 0.05</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_T$ (µmol kg$^{-1}$)</td>
<td>-1.478 ± 0.005</td>
<td>-3.08 ± 0.28</td>
<td>-95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_T$ (µmol kg$^{-1}$)</td>
<td>1.735 ± 0.006</td>
<td>5.14 ± 0.35</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>T (ºC)</td>
<td>15.55 ± 0.03</td>
<td>1.37 ± 0.29</td>
<td>48</td>
<td>2.84 ± 0.49</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>9.355 ± &lt;0.001</td>
<td>0.06 ± 0.02</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_T$ (µmol kg$^{-1}$)</td>
<td>-1.327 ± 0.002</td>
<td>-2.11 ± 0.20</td>
<td>-74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_T$ (µmol kg$^{-1}$)</td>
<td>1.629 ± 0.005</td>
<td>3.52 ± 0.34</td>
<td>124</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Map of study region in the NW Mediterranean Sea (a), along the North current (b) in the Bay of Villefranche-sur-Mer, France (c). Point B station, EOL buoy, and the offshore time-series station DYFAMED are marked. Bathymetric line units are m (c).
Figure 2. Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity, and seawater carbonate chemistry at Point B, 1 m. Regression slopes are drawn ± SE (in grey) and noted with a star for significance at $\alpha = 0.05$. 
Figure 3. Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity, and seawater carbonate chemistry at Point B, 50 m. Regression slopes are drawn ± SE (in grey) and noted with a star for significance at $\alpha = 0.05$. 
Figure 4. Monthly distribution of seawater carbonate chemistry at Point B, 1 m, using a combination of a violin plot showing the relative frequency of the observations (shaded blue area) and a boxplot showing the median, first and third quartiles, as well as outliers (blue).
Figure 5. Monthly trends of total alkalinity (AT, blue) and dissolved inorganic carbon (CT, green) for the period 2007-2015. Errors bars are ± SE of the slope estimate and significance is noted (*) at α=0.05.
Figure 6. Salinity and total alkalinity relationships at Point B for the period 2007-2015, by year, at 1 m. Data points are colored for month.
Figure 7. Time-series pH (a) and temperature (b) from autonomous SeaFET pH sensor deployments at EOL buoy, 2 m. Discrete calibration samples are noted in green, and grey vertical lines bracket deployment periods (a). Calibration sample offsets from processed pH time-series are shown in panel (c). Violin and boxplots (see Fig. 4) show diel pH range by month (d), and an example of this pH variability is shown for May 2015 (e).