# 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 pCO<sub>2</sub> 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  $\Delta$ CT to  $\Delta$ pCO2, which assumes that the atmospheric  $\Delta$ pCO2 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.

The matching of these rates, Henry's Law, and the trends of surface samples all provide strong evidence at the study site and at annual time-frames, surface water is in CO<sub>2</sub> equilibrium with the atmosphere. This was shown previously using the first four years of this time-series (De Carlo et al. 2013). We have not changed our conclusion but we have now added the De Carlo et al. (2013) reference and included a statement indicating that the closeness of the rates does not imply causation.

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 CO<sub>2</sub> 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  $C_T$  trends are positive and statistically significant over more months than  $A_T$  trends (8 vs. 3 months), which are more seasonally restricted (Fig. 5)."

Finally, L354-356: since it has not been demonstrated that the subtraction of delta AT from delta CT gives the contribution of atmospheric pCO2 (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  $C_T$  increase may have been driven by the same unidentified process that caused an increase in  $A_T$ ".

**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 patters 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  $A_T$  and  $C_T$  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 pHT 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  $A_T$  does not reveal an increase in  $A_T$  (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 CO<sub>2</sub> 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.

- 1 Coastal ocean acidification and increasing total alkalinity in the NW Mediterranean Sea
- 2
- 3 Lydia Kapsenberg<sup>1</sup>, Samir Alliouane<sup>1</sup>, Frédéric Gazeau<sup>1</sup>, Laure Mousseau<sup>1</sup>, and Jean-Pierre
- 4 Gattuso<sup>1,2,§</sup>
- 5
- 6 <sup>1</sup>Sorbonne Universités, Université Pierre et Marie Curie-Paris 6, CNRS-INSU, Laboratoire
- 7 d'Océanographie de Villefranche, 06230, Villefranche-sur-Mer, France
- 8 <sup>2</sup>Institute for Sustainable Development and International Relations, Sciences Po, 27 rue Saint

- 9 Guillaume, F-75007 Paris, France
- 10
- 11 <sup>§</sup>Corresponding author
- 12 E-mail: gattuso@obs-vlfr.fr
- 13 Phone: +33 4 93 76 38 59

14	Abstract. Coastal time-series of ocean carbonate chemistry are critical for understanding	
15	how global anthropogenic change manifests in near-shore ecosystems. Yet, they are few and	
16	have low temporal resolution. At the time-series station Point B in the NW Mediterranean	
17	Sea, seawater was sampled weekly from 2007 through 2015, at 1 and 50 m, and analyzed for	
18	total dissolved inorganic carbon ( $C_T$ ) and total alkalinity ( $A_T$ ). Parameters of the carbonate	
19	system such as $pH(pH_T, total hydrogen ion scale)$ were calculated and a deconvolution	
20	analysis was performed to identify drivers of change. The rate of surface ocean acidification	
21	was $-0.0028 \pm 0.0003$ units pH <sub>T</sub> yr <sup>-1</sup> . This rate is larger than previously identified open-ocean	
22	trends due rapid warming that occurred over the study period ( $0.072 \pm 0.022 \text{ °C yr}^{-1}$ ). The	
23	total $pH_{\underline{T}}$ change over the study period was of similar magnitude as the diel $pH_{\underline{T}}$ variability at	
24	this site. The acidification trend can be attributed to atmospheric carbon dioxide (CO <sub>2</sub> )	
25	forcing (59 %, 2.08 $\pm$ 0.01 ppm CO <sub>2</sub> yr <sup>-1</sup> ) and warming (41 %). Similar trends were observed	~
26	at 50 m but rates were generally slower. At 1 m depth, the increase in atmospheric CO2	
27	accounted for approximately 40 % of the observed increase in $C_T$ (2.97 ± 0.20 µmol kg <sup>-1</sup> yr <sup>-1</sup>	
28	<sup>1</sup> ). The remaining increase in $C_{\rm T}$ may have been driven by the same unidentified process that	~
29	<u>caused an increase in <math>A_{\rm T}</math> (2.08 ± 0.19 µmol kg<sup>-1</sup> yr<sup>-1</sup>). Based on the analysis of monthly</u>	
30	trends, synchronous increases in $C_{\rm T}$ and $A_{\rm T}$ were fastest in the spring-summer transition. The	
31	driving process of the interannual increase in $A_{T}$ has a seasonal and shallow component,	
32	which may indicate riverine or groundwater influence. This study exemplifies the importance	
33	of understanding changes in coastal carbonate chemistry through the lens of biogeochemical	
34	cycling at the land-sea interface. This is the first coastal acidification time-series providing	
35	multiyear data at high temporal resolution. The data confirm rapid warming in the	
36	Mediterranean Sea and demonstrate coastal acidification with a synchronous increase in total	
37	alkalinity.	

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51 Keywords – ocean change, ocean acidification, time-series, pH, alkalinity, dissolved

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52 inorganic carbon, pCO<sub>2</sub>, Mediterranean Sea

#### 53 1. Introduction

54 Maintaining time-series of oceanographic data is essential for understanding anthropogenic changes in the ocean (Tanhua et al., 2013). On land, fossil fuel burning, 55 cement production, and land use changes have contributed ~600 Gt carbon to the atmosphere 56 57 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 58 carbon dioxide (CO2; Le Quéré et al., 2016), and causing global changes to the ocean 59 60 carbonate system. Absorption of CO2 by seawater produces carbonic acid, which decreases seawater pH, and is of great concern for biological processes and marine ecosystems (Doney 61 62 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 63 ocean pH with increasing anthropogenic CO2, the process is termed 'ocean acidification', but 64 this expression represents a suite of chemical changes, including increases in total dissolved 65 66 inorganic carbon  $(C_T)$  and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and decrease in calcium carbonate saturation states ( $\Omega$ , aragonite and calcite; Dickson, 2010). Rates of ocean acidification differ 67 by ocean region and range from -0.0026 (Irminger Sea, North Atlantic) to -0.0013 (South 68 Pacific) units pH yr<sup>-1</sup> (Bates et al., 2014). Such time-series remain spatially limited, especially 69 70 in coastal regions, which provide valuable ecosystem services (Barbier et al., 2011; Costanza 71 et al., 1997) and are under high anthropogenic impact (Halpern et al., 2008). Here, we present 72 the first coastal ocean acidification time-series at high temporal resolution. 73 Compared to the global ocean, marginal seas serve a critical role in anthropogenic CO<sub>2</sub> storage via enhanced CO<sub>2</sub> uptake and export to the ocean interior (Lee et al., 2011). As a 74 75 marginal sea, the Mediterranean Sea has a naturally high capacity to absorb but also buffer

76 anthropogenic CO<sub>2</sub> (Álvarez et al., 2014; Palmiéri et al., 2015). This is primarily due to the

high total alkalinity  $(A_T)$  of Mediterranean waters and overturning circulation (Lee et al.,

78	2011; Palmiéri et al., 2015; Schneider et al., 2010). In the Mediterranean Sea, the salinity- $A_{\rm T}$	
79	relationship is driven by the addition of river discharge and Black Sea input, which are	
80	generally, high in A <sub>T</sub> (Copin-Montégut, 1993; Schneider et al., 2007). Combined with	
81	evaporation, this results in higher $A_{\rm T}$ and salinity in the Mediterranean Sea compared to the	
82	Atlantic Mediterranean source water (Jiang et al., 2014). On average, Mediterranean Sea $A_{\rm T}$	
83	is 10 % higher than in the global ocean (Palmiéri et al., 2015). The surface ocean	
84	acidification rate, estimated at $\Delta pH_T$ (total hydrogen ion scale) of -0.08 since 1800, is	
85	comparable to that of the global ocean despite a 10 % greater anthropogenic carbon inventory	
86	(Palmiéri et al., 2015). Due to its important role in carbon sequestration and ecological	
87	sensitivity to anthropogenic change with economic consequences (Lacoue-Labarthe et al.,	
88	2016), the Mediterranean Sea could provide insight to global trends (Lejeusne et al., 2010).	
89	Over the last few years, numerous studies have estimated ocean acidification rates	
90	across the Mediterranean Sea (Table 1). Together, these studies cover various study periods	
91	with a range of techniques yielding different results. For example, estimates of change in pH	
92	of bottom waters since the preindustrial era range between -0.005 to -0.06 (Palmiéri et al.,	
93	2015) and as much as -0.14 for full profile estimates (Touratier and Goyet, 2011). Techniques	
94	for estimating ocean acidification in the Mediterranean Sea thus far include: (1) hind-casting,	
95	using high-resolution regional circulation models (Palmiéri et al., 2015), the TrOCA	
96	approach as applied to cruise-based profile data (Krasakopoulou et al., 2011; Touratier and	
97	Goyet, 2011; Touratier et al., 2016) and others (Howes et al., 2015), (2) partially	
98	reconstructed time-series (Marcellin Yao et al., 2016), (3) comparative study periods	
99	(Luchetta et al., 2010; Meier et al., 2014), and (4) sensor-based observations over a short	
100	study period (Flecha et al., 2015). Ocean acidification time-series of consistent sampling over	
101	many years are lacking for the Mediterranean Sea (The MerMex Group et al., 2011),	

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104 et al., 2016).

105 Compared to the open ocean, shallow coastal sites exhibit natural variability in 106 carbonate chemistry over annual timeframes (Hofmann et al., 2011; Kapsenberg and 107 Hofmann, 2016; Kapsenberg et al., 2015), complicating the detection and relevance of open 108 ocean acidification in isolation of other processes (Duarte et al., 2013). In the NW Pacific coast, rapid acidification of surface waters ( $\Delta p H_T$  -0.058 units yr<sup>-1</sup>) at Tatoosh Island was 109 110 documented in the absence of changes in known drivers of local pH variability (e.g., 111 upwelling, eutrophication, and more; Wootton and Pfister, 2012; Wootton et al., 2008). 112 Further inshore, in the Hood Canal sub-basin of the Puget Sound, only 24-49 % of the 113 estimated pH decline from pre-industrial values could be attributed to anthropogenic CO2 114 (Feely et al., 2010). The excess decrease in pH was attributed to increased remineralization 115 (Feely et al., 2010). Acidification rates documented along the North Sea Dutch coastline and 116 inlets were highly variable in space, with some exceeding the expected anthropogenic CO2 117 rate by an order of magnitude while others exhibited an increase in pH (Provoost et al., 118 2010). 119 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 120 121 production, respiration, net calcification). Within watersheds, coastal carbonate chemistry is 122 affected by eutrophication (Borges and Gypens, 2010; Cai et al., 2011), groundwater supply 123 (Cai et al., 2003), and land use and rain influence on river alkalinity (Raymond and Cole, 124 2003; Stets et al., 2014). Over longer periods, pH can also be influenced by atmospheric 125 deposition (Omstedt et al., 2015). Through primary production and respiration, coastal 126 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 127

- 129 coastal seas, it is necessary to quantify high-frequency trends in order to interpret the pH 130 changes inferred from lower-frequency sampling. 131 In this study, we present the first complete time-series data quantifying the present-132 day ocean acidification rate for a coastal site in the Mediterranean Sea, based on weekly 133 measurements of A<sub>T</sub> and C<sub>T</sub> sampled from 2007 through 2015. For a subset of this timeseries, pH variability was documented using a SeaFET<sup>™</sup> Ocean pH Sensor in order to assess 134 135 hourly pH variability. For comparison and consistency with other ocean acidification time-136 series around the world, we report rates of change based on anomalies (Bates et al., 2014) and 137 identify drivers of change. 138 139 2. Materials and methods 140 141 2.1. Site description 142 A carbonate chemistry time-series was initiated in 2007 and maintained through 2015 143 in the NW Mediterranean Sea at the entrance of the Bay of Villefranche-sur-Mer, France 144 (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 145 146 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 147
- 148 parameters. A full site description and research history has been detailed by De Carlo et al.
- 149 (2013). Briefly, the Bay is a narrow north-south facing inlet with steep bathymetry and
- 150 estimated volume of 310 million m<sup>3</sup>. The surrounding region is predominately composed of
- 151 limestone with a series of shallow, submarine groundwater karst springs (Gilli, 1995). The
- 152 North current, a major and structuring counter-clockwise current in the Ligurian Sea, can
- 153 sometimes flow close to Point B. The Bay can also be, on occasion, influenced by local

- 154 countercurrents. Both of these hydrodynamics movements have signatures of river discharge.
- Limestone erosion can be observed in the A<sub>T</sub> of rivers nearest to Point B (Paillon, due 4 km
- 156 West; Var due 10 km West; and Roya due 26 km East). River A<sub>T</sub> ranges between 1000 to
- 157 2000 µmol kg<sup>-1</sup> (data from Agence de l'Eau Rhône-Méditerranée-Corse,
- 158 http://sierm.eaurmc.fr), and is lower than seawater A<sub>T</sub>. The Paillon River, whose plume on
- 159 occasion reaches into the Bay (L. Mousseau, pers. obs.), was sampled on 18 August 2014 and
- had a  $A_{\rm T}$  of 1585 ± 0.1 µmol kg<sup>-1</sup> (N = 2, J.-P. Gattuso, unpubl.). Due to low primary
- 161 productivity, seasonal warming drives the main annual variability in carbonate chemistry at
- 162 this location (De Carlo et al., 2013).
- 163

#### 164 2.2. Point B data collection, processing, and analysis

165 To document long-term changes in ocean carbonate chemistry at Point B, seawater 166 was sampled weekly from 9 January 2007 to 22 December 2015. Samples were collected at 1 167 and 50 m, using a 12-L Niskin bottle at 9:00 local time. Seawater was transferred from the 168 Niskin bottle to 500 mL borosilicate glass bottles and fixed within an hour via addition of 169 saturated mercuric chloride for preservation of carbonate parameters, following 170 recommendations by Dickson et al. (2007). Duplicate samples were collected for each depth. 171 For each sampling event, CTD casts were performed either with a Seabird 25 or Seabird 25+ 172 profiler whose sensors are calibrated at least every two years. Accuracy of conductivity 173 (SBE4 sensor) and temperature (SBE3 sensor) measurements from CTD casts were 0.0003 S m<sup>-1</sup> and 0.001°C, respectively. 174 175 Within six months of collection, bottle samples were analyzed for  $C_{\rm T}$  and  $A_{\rm T}$  via potentiometric titration following methods described by Edmond (1970) and DOE (1994), by 176

- 177 Service National d'Analyse des Paramètres Océaniques du CO<sub>2</sub>, at the Université Pierre et
- 178 Marie Curie in Paris, France. Precision of  $C_{\rm T}$  and  $A_{\rm T}$  was less than 3 µmol kg<sup>-1</sup>, and the

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181	average accuracy was 2.6 and 3 $\mu$ mol kg <sup>-1</sup> , as compared with seawater certified reference
182	material (CRM) provided by A. Dickson (Scripps Institution of Oceanography). Only
183	obvious outliers were omitted from the analyses: three $C_{\rm T}$ values at 1 m (> 2300 $\mu$ mol kg <sup>-1</sup> ),
184	one $A_{\rm T}$ value at 1 m (> 2900 $\mu$ mol kg <sup>-1</sup> ), and one $A_{\rm T}$ value at 50 m (< 2500 $\mu$ mol kg <sup>-1</sup> ). The
185	$C_{\rm T}$ and $A_{\rm T}$ measurements on replicate bottle samples were averaged for analyses.
186	Calculations of the carbonate system parameters were performed using the R package
187	seacarb version 3.1 with $C_T$ , $A_T$ , <i>in situ</i> temperature and salinity as inputs (Gattuso et al.,
188	2016). Total concentrations of silicate (SiOH <sub>4</sub> ) and phosphate ( $PO_4^{3-}$ ) were used when
189	available from Point B (L. Mousseau, unpubl., http://somlit.epoc.u-bordeaux1.fr/fr/).
190	Detection limits for nutrients were 0.03 $\mu$ M for SiOH <sub>4</sub> and 0.003 to 0.02 $\mu$ M for PO <sub>4</sub> <sup>3-</sup> ;
191	relative precision of these analyses is 5-10 % (Aminot and Kérouel, 2007). Total boron
192	concentration was calculated from salinity using the global ratio determined by Lee et al.
193	(2010). The following constants were used: $K_1$ and $K_2$ from Lucker et al. (2000), $K_f$ from
194	Perez and Fraga (1987), and $K_s$ from Dickson (1990). Reported measured parameters are
195	temperature, salinity, $A_T$ , and $C_T$ , and derived parameters are pH <sub>T</sub> (total hydrogen ion scale),
196	$pH_T$ normalized to 25 °C (pH_{T25}), pCO_2, and aragonite ( $\Omega_a)$ and calcite ( $\Omega_c)$ saturation states.
197	Salinity-normalized changes in $A_T$ (n $A_T$ ) and $C_T$ (n $C_T$ ) were calculated by dividing by <i>in situ</i>
198	salinity and multiplying by 38. Except for $pH_{T25}$ , all parameters are reported at <i>in situ</i>
199	temperatures.
200	The average uncertainties of the derived carbonate parameters were calculated
201	according to the Gaussian method (Dickson and Riley, 1978) implemented in the "errors"
202	function of the R package seacarb 3.1 (Gattuso et al., 2016). The uncertainties are $\pm$ 2.7 x 10 <sup>-</sup>
203	$^{10}$ mol H $^{+}$ (about 0.015 units pH $_{T}), \pm 15$ µatm pCO $_{2},$ and $\pm$ 0.1 unit of the aragonite and calcite

saturation states.

205	To quantify interannual changes in carbonate parameters, the data were detrended for		Comment [LK5]: <mark>#7</mark>
206	seasonality by subtracting the respective climatological monthly means, computed for the		Deleted: s
207	period 2009-2015 from the time-series ('monthly means' from hereon). The resulting		
208	residuals, were analyzed using a linear regression to compute anomaly trends. This approach	1	Deleted: anomalies
209	follows methods from Bates et al. (2014) to allow for comparisons of trends observed at		
210	different time-series stations. All analyses were performed in R (R Core Team, 2016).		
211			
212	2.3. Deconvolution of pH <sub>T</sub> and pCO <sub>2</sub>		Comment [LK6]: <mark>#1</mark>
213	To identify proportional contributions of various drivers to ocean acidification trends		
214	at Point B, deconvolution of time-series $pH_T$ and $pCO_2$ was performed following methods		
215	from García-Ibáñez et al. (2016) for observations at 1 and 50 m. The equation is described		
216	below for $pH_T$ , where changes in $pH_T$ are driven by changes in temperature ( <i>T</i> ), salinity ( <i>S</i> ),		
217	$A_{\rm T}$ , and $C_{\rm T}$ , over time (t), according to the following model:		
218	$\frac{dpH_T}{dt} = \frac{\partial pH_T}{\partial T}\frac{dT}{dt} + \frac{\partial pH_T}{\partial S}\frac{dS}{dt} + \frac{\partial pH_T}{\partial A_T}\frac{dA_T}{dt} + \frac{\partial pH_T}{\partial C_T}\frac{dC_T}{dt} $ (1)		
219	Here, $\frac{\partial p H_T}{\partial var} \frac{dvar}{dt}$ represents the slope contribution of changing <i>var</i> to the estimated		
220	change in pH <sub>T</sub> ( $\frac{dpH_T}{dt}$ ), where var is either temperature (T), salinity (S), $A_T$ , or $C_T$ . The		
221	<u>sensitivity of pH</u> to var $\left(\frac{\partial pH_T}{\partial nar}\right)$ was estimated by calculating pH <sub>T</sub> using the true observations	1	Deleted: rate of
222	of var and holding the other three variables constant (mean value of the time-series) and		Deleted: change due Deleted: $\frac{dvar}{dt}$
			Deleted: but
223	regressing it to var. Sensitivity $\left(\frac{\partial pH_T}{\partial r}\right)$ was then multiplied by the anomaly rate of var (Table		Deleted: monthly mean values
		<u> </u>	Deleted: of the other three variables
224	<u>2).</u> The calculation was repeated for pCO <sub>2</sub> $\left(\frac{dpCO_2}{dt}\right)$ in order to compare the rate of increase		Deleted: , and regressing the anomaly (following subtraction of respective monthly means) to time
225	with that of atmospheric CO <sub>2</sub> .		
226	As a sub-component of $\frac{\partial p C O_2}{\partial C_T} \frac{d C_T}{dt}$ , the rate of anthropogenic CO <sub>2</sub> increase was		
227	estimated from atmospheric CO <sub>2</sub> concentrations nearest to Point B (Plateau Rosa, Italy,		

- 238 courtesy of the World Data Center for Greenhouse Gases,
- 239 http://ds.data.jma.go.jp/gmd/wdcgg/). For these data, missing daily values were linearly
- 240 interpolated, monthly means were calculated and subtracted from the time-series to generate
- 241 <u>an anomaly time-series</u>. A linear regression was performed on anomalies where the slope
- 242 represents the rate of anthropogenic CO<sub>2</sub> increase in the atmosphere. Finally, to help identify
- 243 different processes that might have contributed to the observed trends, linear regressions were
- performed on changes in  $A_{\rm T}$  and  $C_{\rm T}$  per month (mean value of observations within one

245 month) from 2009 through 2015 and on the salinity- $A_{\rm T}$  relationship by year.

246

#### 247 2.4. SeaFET data collection, processing, and analysis

248 To capture pH variability at higher-than-weekly sampling frequencies, a SeaFET™ 249 Ocean pH sensor (Satlantic) was deployed on the EOL buoy (435 m from the Point B 250 sampling site) starting in June 2014, at 2 m depth. Autonomous sampling was hourly and 251 deployment periods ranged between 1 and 3 months. Field calibration samples for pH were 252 collected weekly, using a Niskin bottle next to SeaFET within 15 min of measurement. This 253 sampling scheme was sufficient for this site as there is no large high-frequency pH 254 variability. Unlike Point B sampling, SeaFET calibration samples were processed for pH 255 using the spectrophotometric method (Dickson et al., 2007) with purified m-cresol purple 256 (purchased from the Byrne lab, University of South Florida). In situ temperature, salinity, and 257 AT measured at Point B, within 30 min of the SeaFET sampling, were used to calculate in situ 258 pH<sub>T</sub> of the calibration samples. SeaFET voltage was converted to pH<sub>T</sub> using the respective 259 calibration samples for each deployment period, following the methods and code described in 260 Bresnahan et al. (2014) but adapted for use in R.

261 The estimated standard uncertainty in SeaFET  $pH_T$  is  $\pm 0.01$  and was calculated as the 262 square root of the sum of each error squared. The sources of errors are: measurement error of

Comment [LK7]: <mark>#7</mark>
Comment [LK8]: <mark>#7</mark>

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- 264 spectrophotometric pH ( $\pm$  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
- 266 mismatch sampling at EOL ( $\pm$  0.007, mean offset of pH<sub>T</sub> of the calibration samples from
- 267 calibrated time-series), and variability in purified m-cresol dye batch accuracy as compared
- 268 to Tris buffer CRM pH ( $\pm$  0.006, mean offset of pH<sub>T</sub> of the spectrophotometric measurement
- 269 of Tris buffer from the CRM value).
- 270
- 271 3. Results
- 272

#### 273 3.1. Time-series trends

274 At Point B from January 2007 to December 2015, more than 400 samples were 275 collected for carbonate chemistry at both 1 and 50 m. Anomaly trends detected at 1 m (Fig. 2) 276 were also significant at 50 m (Fig. 3, Table 2), with the exception that salinity increased at 50 277 m (0.0063  $\pm$  0.0020 units yr<sup>-1</sup>). At 1 m, trends were significant for pH<sub>T</sub> (-0.0028 units yr<sup>-1</sup>),  $A_{\rm T}$  (2.08 µmol kg<sup>-1</sup> yr<sup>-1</sup>),  $C_{\rm T}$  (2.97 µmol kg<sup>-1</sup> yr<sup>-1</sup>), pCO<sub>2</sub> (3.53 µatm yr<sup>-1</sup>), and  $\Omega_{\rm a}$  (-0.0064 278 279 units yr<sup>-1</sup>). At the same time, temperature anomaly increased (0.072 °C yr<sup>-1</sup>), but no 280significant 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 281 282 temperature. The warming rate at 50 m was slightly greater compared to 1 m, mostly due to 283 increasing summer temperatures since 2007. 284 Strong seasonal cycles of carbonate chemistry parameters were present at Point B at 1 285 m (Fig. 4). <u>Climatological</u> monthly means (2007-2015) are described briefly and listed in Table S1. Mean temperature range was 11.2 °C with a maximum at 24.77  $\pm$  1.35 °C in August 286 287 and minimum of  $13.58 \pm 0.41$  °C in February. The range in  $A_{\rm T}$  was 19 µmol kg<sup>-1</sup> from June to September. The  $C_{\rm T}$  range was 33 µmol kg<sup>-1</sup> with a peak in late winter and minimum values in 288

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<b>Deleted:</b> , $P = 0.002$
<b>Deleted:</b> ± 0.0003
<b>Deleted:</b> , $N = 412$
<b>Deleted:</b> ± 0.19
<b>Deleted:</b> , $N = 417$
<b>Deleted:</b> $\pm 0.20$
<b>Deleted:</b> , $N = 416$
<b>Deleted:</b> ± 0.39
<b>Deleted:</b> , $N = 412$
<b>Deleted:</b> $\pm 0.0015$
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<b>Deleted:</b> ± 0.022
<b>Deleted:</b> , $N = 413$
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<b>Deleted:</b> $(P = 0.702, N = 417)$
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306	August and October. Due to summer warming coinciding with the period of peak primary	
307	productivity (De Carlo et al. 2013), warming countered the influence of low $C_T$ on pH. As a	
308	result, $pH_{\underline{T}}$ reached minimum values in summer (8.02 ± 0.03, July and August) and peaked in	
309	late winter (8.14 $\pm$ 0.01, February and March), for an overall annual pH range of 0.12. The	
310	corresponding pCO2 range was 128 µatm from February to August. Seasonal cycles were	
311	smaller at 50 m compared to 1 m (Table S1).	
312		
313	3.2 Deconvolution of pHz and pCO	 Comment II K101: #1
515		
314	Deconvolutions of pH and $pCO_2$ are presented in Table 3 and 4, respectively. The	
315	estimated anomaly trends $\left(\frac{dpH_T}{dt}, \frac{dpCO_2}{dt}\right)$ from the deconvolution fall within the error of the	 Deleted: sum of the slopes
316	observed anomaly trends (Table 2). The contribution of warming to the pH <sub>T</sub> anomaly ( $\zeta$	 Deleted: e.g.,
317	0.0011 units $yr^{-1}$ , at 1 m) matched the difference between the trends of pH <sub>T</sub> and pH <sub>T25C</sub> (Table	 Deleted: pH <sub>T</sub>
318	2), which verifies that the deconvolution reproduced influences of temperature sensitivity	
319	well. Overall, these results indicate that the deconvolution analyses represent the observed	 Deleted: T
320	trends well.	
321	At both depths, the predominant driver of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ was the increase in $C_T$ .	 <b>Deleted:</b> At 1 m, warming accounted for 39 and 37 % of $dpH_T = dpCO_2$ are strictly ( $D = 0.001$ ). Since a matrix
322	Increasing $A_T$ countered 66-69 and 60 % of the influence of increasing $C_T$ on $\frac{dpH_T}{dp}$ and $\frac{dpCO_2}{dp}$	$\frac{dt}{dt}$ and $\frac{dt}{dt}$ , respectively ( $P = 0.001$ ). 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
	$\frac{dt}{dt} = \frac{dt}{dt}$	$\frac{dpCO_2}{dt}$ at 50 m compared to 1 m.
323	respectively. At 1 m, warming accounted for $\frac{41}{2}$ and 37 % of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ , respectively.	Comment [LK11]: = 100* [%contribution of At]/[%contribution Ct]
324	Since warming was slightly greater at 50 m compared to 1 m, warming accounted for a larger	for both pH and pCO2 deconv. Deleted: by 64 and 60 %,
325	proportional influence on $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ at 50 m compared to 1 m. Increasing salinity at 50	Deleted: at 1 m and by 65 and 58 %, respectively at 50 m Deleted: 40
	ut ut	
326	m contributed slightly to $\frac{dpH_T}{\sqrt{dt}}$ (4 %) and $\frac{dpCO_2}{dt}$ (2 %).	 Deleted: both
327	Atmospheric CO <sub>2</sub> anomaly at Plateau Rosa increased by $2.08 \pm 0.01$ ppm yr <sup>-1</sup> ( $F_{1,3285}$	
328	= 4664, $P \ll 0.001$ , $R^2 0.93$ ) during the study period 2007-2015, and represents the	
329	anthropogenic CO <sub>2</sub> forcing on seawater pH. To estimate the influence of anthropogenic CO <sub>2</sub>	 Deleted: maximum

- 344 forcing at Point B, we assume air-sea CO<sub>2</sub> equilibrium (e.g., increase in atmospheric CO<sub>2</sub>
- causes an equal increase in seawater pCO<sub>2</sub>) for the water mass at 1 m. This assumption is
- based on evidence that Point B is a weak sink for atmospheric CO<sub>2</sub> with near-balanced air-sea
- 347 <u>CO<sub>2</sub> flux on an annual time-frame (De Carlo et al., 2013).</u> Considering the error associated
- 348 with deconvolution of pCO<sub>2</sub> at 1 m, atmospheric CO<sub>2</sub> increase can, at most, represent 38-43
- 349 % of the total  $C_{\rm T}$  contribution  $\left(\frac{\partial p C O_2}{\partial C_T} \frac{d C_T}{dt}\right)$  to  $\frac{d p C O_2}{dt}$ . This leaves 57-62 % of the total  $C_{\rm T}$
- 350 contribution to  $pCO_2$  trends unaccounted for.
- 351 As  $A_{\rm T}$  is not influenced by addition of anthropogenic CO<sub>2</sub> to seawater but still
- 352 increased, the next question was whether or not the changes in  $A_{\rm T}$  and  $C_{\rm T}$  were process-
- 353 linked. At 1 m, regressions of annual monthly trends of  $A_{\rm T}$  and  $C_{\rm T}$  revealed similar seasonal
- 354 cycles for both parameters (Fig. 5, Table S2). The fastest increases in  $A_{\rm T}$  and  $C_{\rm T}$  occurred
- 355 from May through July. The smallest (non-significant) changes occurred in January. The
- 356 synchronicity between monthly trends of  $A_{\rm T}$  and  $C_{\rm T}$  was also observed at 50 m, but the rates 357 were slower (analysis not shown).
- 358

#### 359 **3.3. Salinity and** *A*<sub>T</sub> **relationships**

360	Over an annual observation period at 1 m, salinity was a poor predictor of $A_{\rm T}$ , with the
361	exception of 2007 (Fig. 6). The $R^2$ value for each annual salinity- $A_T$ relationship at 1 m
362	ranged from 0.00 (in 2013) to 0.87 (in 2007) with y-intercepts ( $A_{T0}$ , total alkalinity of the
363	freshwater end-member) ranging between -176 $\mu mol~kg^{-1}$ (in 2007) and 2586 $\mu mol~kg^{-1}$ (in
364	2013). The interannual variability of the salinity- $A_T$ relationship was driven by the variability
365	in $A_{\rm T}$ observed at salinity < 38.0 that was present from November through July.
366	Changes in salinity (based on monthly means) at Point B was small and ranged from
367	$37.64\pm0.26$ to $38.21\pm0.11$ from May to September, following freshwater input in winter

and spring and evaporation throughout summer and fall (Fig. 4). Highest (> 38.0) and most

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-	<b>Comment [LK14]:</b> =2.08/(5.14 + 0.35) =2.08/(5.14 - 0.35)
T	Deleted: 8
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373	stable salinity observations were made in August through October and coincided with the	
374	period of maximum $A_{\rm T}$ (2562 and 2561 ± 9 µmol kg <sup>-1</sup> in September and October,	
375	respectively). Minimum $A_{\rm T}$ (2543 ± 14 µmol kg <sup>-1</sup> ) was observed in June, one month after	
376	minimum salinity. To capture this seasonality without the inter-annual variation of A <sub>T</sub> , the	
377	salinity- $A_{\rm T}$ relationship at 1 m was estimated from <u>climatological</u> monthly means ( $c_{\rm A_{\rm T}}$ and	
378	$c_{N} = 12$ where $c_{A_{T}}$ units are $\mu$ mol kg <sup>-1</sup> and error terms are standard errors ( $R^{2} = 0.74$ ):	Comment [LK15]: <b>#11</b>
379	$cA_{\rm T} = 1554.9(\pm 185.9) + 26.3(\pm 4.9) \times cS$ (2)	<b>Deleted:</b> $R^2 = 0.74$
380	At 50 m, monthly salinity and $A_T$ were less correlated over an annual cycle (analysis not	
381	shown). Salinity remained stable at 38.0 from January through September while $A_{\rm T}$ declined	
382	by 13 $\mu mol~kg^{\text{-1}}.$ In general, seasonal changes were dampened at 50 m compared to 1 m.	
383		
384	3.4. High-frequency pH data	
385	To verify the weekly sampling scheme at Point B, a continuous record of high-	
386	frequency pH observations was obtained via11 consecutive SeaFET deployments from June	
387	2014 to April 2016. Deployment periods averaged $58 \pm 25$ days with $5 \pm 2$ calibration	
388	samples per deployment (Fig. 7). Only 5 % of the data was removed during quality control,	
389	due to biofouling in one deployment and battery exhaustion in another, yielding 610 days of	
390	data. The mean offset between calibration samples and the calibrated SeaFET pH time-series	
391	was $\pm$ 0.007, indicating a high-quality pH dataset (Fig. 7c). Sensor data corroborated the	
392	seasonal pH and temperature cycle observed at Point B (Fig. 7a-b). Event-scale effects (e.g.,	Comment [LK16]: #17
393	$pH_T$ change $\geq 0.1$ for days to weeks, <i>sensu</i> Kapsenberg and Hofmann 2016) were absent at	
394	this site suggesting that weekly sampling was sufficient to describe seasonal and interannual	
395	changes in carbonate chemistry at Point B. The magnitude of diel $\ensuremath{pH_T}$ variability was small	
396	(the 2.5 <sup>th</sup> to 97.5 <sup>th</sup> percentiles ranged between 0.01 and 0.05 units pH <sub>T</sub> , Fig. 7d-e). Diel pH	Comment [LK17]: #17
397	variations increased from winter to spring with the greatest variability in April, May, and	
1		

399	June ( $\Delta pH_{\underline{T}} > 0.035$ ). The magnitude of pH variability was not correlated with temperature or		Deleted: and
400	the concentration of chlorophyll-a (data not shown)		Deleted: unrelated to seasonal warming
100	and concentration of entorphysical (data not one only).		Deleted: Fig. S1
401			
402	4. Discussion		
403	High resolution time-series are necessary to document coastal ocean acidification. At		
404	Point B in the NW coastal Mediterranean Sea, near-surface $pH_{\rm T}$ decreased by 0.0028 $\pm$		
405	0.0003 units yr <sup>-1</sup> , based on weekly measurements from 2007 through 2015. Temperature		Deleted: and
100			Deleted: t
406	increased by $0.0/2 \pm 0.022$ °C yr , in addition, $A_{\rm T}$ increased by $2.08 \pm 0.19$ µmol kg yr , a	******	<b>Deleted:</b> from 2007 through 2015 based on weekly measurements
407	change that is unrelated to direct effects of CO <sub>2</sub> absorption by seawater. In less than a decade,		
408	the total change in pH at Point B ( $\Delta pH_T$ : 0.0252, Table 1) was of the same magnitude as the		Comment [LK19]: #12
409	diel pH variability ( $\Delta pH_{\underline{T}}$ : 0.01-0.05) and 1/5 <sup>th</sup> of the magnitude of the seasonal pH cycle		
410	( $\Delta pH_{\underline{T}}$ : 0.12) found at this site.		
411	We can identify the drivers for the ocean acidification trends at Point B using the		
412	deconvolution of pH and pCO <sub>2</sub> and by assuming that the increase in $A_T$ was due to increases		
413	in its carbon constituents, bicarbonate ( $HCO_3^-$ ) and carbonate ( $CO_3^{2-}$ ) ions. This assumption is		
414	based on the fact that (1) $HCO_3^-$ and $CO_3^{2-}$ ions together make up 96 % of $A_T$ at Point B, (2)		
415	increases in HCO <sub>3</sub> <sup>-</sup> and CO <sub>3</sub> <sup>2-</sup> would both contribute to $A_{\rm T}$ and $C_{\rm T}$ and thereby explain the		
416	observed synchronicity of monthly trends in $A_T$ and $C_T$ (Fig. 5). Using the pCO <sub>2</sub>		
417	deconvolution, we can then sum the contributions to pCO <sub>2</sub> from $A_T$ (-3.08 µatm pCO <sub>2</sub> yr <sup>-1</sup> )		Deleted: 17
418	and $C_{\rm T}$ (5.14 µatm pCO <sub>2</sub> yr <sup>-1</sup> ) trends to determine the proportional contribution of $\Delta C_{\rm T}$ to		Deleted: 26
419	$\Delta pCO_2$ that is unrelated to changes in $C_T$ brought on by $A_T$ . This remaining 2.06 µatm pCO <sub>2</sub>		Deleted: e
420	yr <sup>-1</sup> increase due to increasing $C_{\rm T}$ closely matched the magnitude of atmospheric CO <sub>2</sub>		Deleted: s
421	increase during the observation period ( $2.08 \pm 0.01$ ppm yr <sup>-1</sup> at Plateau Rosa, Italy). The		Comment [LK20]: <mark>#2</mark>
422	closeness of these numbers does not imply causation. However, given that surface waters at		
423	Point B exhibit a near-zero air-sea CO <sub>2</sub> flux over annual cycles (De Carlo et al., 2013), the		

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436	evidence supports the conclusion that the ocean acidification trend at Point B closely follows		
437	the rate of atmospheric CO <sub>2</sub> increase. The influence of atmospheric CO <sub>2</sub> can also be observed		
438	in the monthly changes in $C_{T}$ . Monthly $C_{T}$ trends are positive and statistically significant over		Deleted: significance of
			Deleted: trends
439	more months than, $A_{\rm T}$ trends (8 vs. 3 months), which are more seasonally restricted (Fig. 5),		Deleted: (eight months out of the year) compared to
140	Any lying this simple model to $\mathbf{n}\mathbf{I}\mathbf{I}$ , assuming shares on $C$ and the tablet		Deleted:
440	Apprying uns simple model to prir, assuming changes in C <sub>T</sub> are due to both		<b>Deleted:</b> (three months out of the year, Fig. 5).
441	increasing $A_{\rm T}$ (a neutralizing effect) and atmospheric CO <sub>2</sub> forcing, the surface ocean		<b>Deleted:</b> $(2.97 \pm 0.20 \ \mu mol \ kg^{-1} \ yr^{-1})$
	······································		Deleted: observed
442	acidification trend at Point B can be attributed primarily to atmospheric CO <sub>2</sub> forcing (59 %)		Deleted: 61
443	and secondarily to warming ( <u>41</u> %).		Deleted: 39
444	Using this same approach for observations at 50 m, the $C_{\rm T}$ contribution to pCO <sub>2</sub>		
445	trends that was unrelated to $A_{\rm T}$ change was 1.41 µatm pCO <sub>2</sub> yr <sup>-1</sup> , which is 68 % of the rate of		Deleted: 69
		· · · · · · · · · · · · · · · · · · ·	Deleted: 80
446	atmospheric CO <sub>2</sub> increase in contrast to $92$ % at 1 m. Changes in pH <sub>T</sub> can then be attributed		Deleted: 100
447	to atmospheric CO <sub>2</sub> forcing ( $\frac{42}{9}$ ), warming (54 %), and increasing salinity (3 %, which		Comment [LK21]: =(-0.0035+0.0024)/-0.0026
	T		Deleted: warming (50 %),
448	may result from warming). Due to slightly enhanced warming and reduced CO <sub>2</sub> penetration		Deleted: 46
440	absorved at 50 m moments had a greater affect on the assess and iffection trand then	ľ,	Deleted: 4
449	observed at 50 m, warming nag, a greater effect on the ocean actumcation trend than		Deleted: s
450	atmospheric $\underline{CO_2}$ forcing at depth compared to the surface.		
451	The acidification rate at Point B (-0.0028 units $pH_T yr^{-1}$ ) is larger than those reported		
452	for other ocean time-series sites (-0.0026 to -0.0013 units pH yr <sup>-1</sup> , Bates et al., 2014), likely		Deleted: pH
453	due to differences in warming rates. The observed warming from 2007 through 2015 (0.72 to		
454	$0.88 \pm 0.2$ °C decade <sup>-1</sup> ) is extremely rapid relative to global trends in the upper 75 m from		
455	1971 to 2010 (0.11 °C decade <sup>-1</sup> , Rhein et al., 2013). The coastal region of Point B has		
456	warmed steadily since 1980 and with periods of rapid warming (Parravicini et al., 2015).		
457	Exacerbated warming may be <u>related to the positive phases of the</u> Atlantic Multi-decadal		Deleted: driven by
150	Oscillation (AMO) and North Atlantic Oscillation (NAO) both of which are accepted with		Deleted: positive indices of the
438	Oscillation (AMO) and North Atlanuc Oscillation (NAO), poth of which are associated with		Comment [LK22]: <b>#15</b>
459	episodic warming of the Mediterranean Sea (Lejeusne et al., 2010). The AMO has been		

positive since the 1990s<sup>1</sup> and positive NAO phases were prevalent during the second half of
our study<sup>2</sup>.

Nearest to Point B, the acidification rate at DYFAMED, an open-sea site about 50 km 481 offshore from Point B (Fig. 1), was estimated at  $-0.003 \pm 0.001$  units pH<sub>SW</sub> yr<sup>-1</sup> from 1995 to 482 483 2011 (Marcellin Yao et al., 2016). At DYFAMED, warming contributed approximately 30 % 484 to the acidification rate and the remaining 70 % was attributed to anthropogenic CO<sub>2</sub> 485 (Marcellin Yao et al., 2016). The uncertainty is large and makes direct comparison with Point 486 B unreliable but the results are agreeable. However, A<sub>T</sub> at the DYFAMED did not change 487 significantly from 2007 through 2014 ( $F_{1,51}$  3.204, P = 0.0794,  $R^2$  0.08, data from Coppola et 488 al., 2016). This may indicate that the processes driving changes in  $A_T$  at Point B are unique to

489 the coastal environment.

490 Similar changes in coastal carbonate chemistry were observed elsewhere in the near-491 shore Mediterranean Sea. In the Northern Adriatic Sea, Luchetta et al. (2010) determined an acidification rate in pH<sub>T</sub> of -0.0025 yr<sup>-1</sup> and an increase in  $A_T$  of 2.98 µmol kg<sup>-1</sup> yr<sup>-1</sup> at depths 492 493 shallower than 75 m, by comparing cruise data between the winters of 1983 and 2008. Point 494 B and Adriatic Sea observations are independent but reflect changes in seawater chemistry 495 that may be occurring across a wider coastal region. Additional time-series would help 496 resolve the spatial extent of the observed trends. Specifically, the Eastern Mediterranean Sea 497 would offer an important contrast, as pH of eastern waters is expected to be more sensitive to atmospheric CO<sub>2</sub> addition due to their ability to absorb more anthropogenic CO<sub>2</sub> than either 498 499 the western Mediterranean or Atlantic waters (Álvarez et al., 2014). 500 While the trends in atmospheric CO<sub>2</sub> forcing and temperature account for the ocean 501 acidification trend, the increase in AT and CT increase beyond what can be attributed to

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

<sup>&</sup>lt;sup>2</sup> http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/month\_nao\_index.shtml

502	changes in atmospheric $CO_2$ was unexpected. The fastest increases in $A_T$ and $C_T$ occurred	Deleted: forcing
503	from May through July (Fig. 5), when the thermal stratification settles. In the NW	
504	Mediterranean, the main processes governing seasonal variability in $A_{\rm T}$ are evaporation	
505	increasing $A_{\rm T}$ in summer (i.e., June through September at Point B) and, to a lesser extent,	
506	phytoplankton uptake of nitrate (NO <sub>3</sub> <sup>-</sup> ) and phosphate (PO <sub>4</sub> <sup>3-</sup> ) increasing $A_T$ from January	
507	through March (Cossarini et al., 2015). During the transition of these processes, salinity	
508	decreases to a minimum in May, reflecting freshwater input that dilutes $A_{\rm T}$ to minimum	
509	values at the start of summer. For $C_{\rm T}$ , peak values occur in winter when the water column is	
510	fully mixed. For reference, at DYFAMED, mixing occurs down to more than 2000 m depth	
511	and $C_{\rm T}$ is up to 100 µmol kg <sup>-1</sup> higher in deep waters (Copin-Montégut and Bégovic, 2002).	
512	Notably, monthly trends of C <sub>T</sub> at Point B were not statistically significant from November	
513	through January for the period 2007-2015. Following winter, $C_{\rm T}$ declines due to a	
514	combination of phytoplankton bloom carbon uptake and freshwater dilution (assuming river	
515	$C_{\rm T}$ < seawater $C_{\rm T}$ ), until the onset of summer stratification. Summer warming leads to pCO <sub>2</sub>	
516	off-gassing to the atmosphere (De Carlo et al., 2013), thereby further decreasing $C_{\rm T}$ . The	
517	increases in $A_{\rm T}$ and $C_{\rm T}$ from 2007 through 2015 were more pronounced at 1 m compared to	
518	50 m. This indicates that the process driving $A_{\rm T}$ and $C_{\rm T}$ trends are stronger at the surface and	
519	affect carbonate chemistry primarily during the spring-summer transition from May through	
520	July.	
521	While the drivers of ocean acidification trends are identified and quantified above, the	
522	increase in $A_{\rm T}$ and increase in $C_{\rm T}$ beyond what can be attributed to changes in atmospheric	
523	<u>CO<sub>2</sub> requires some speculation. Some biogeochemical processes can be ruled out as drivers.</u>	Deleted: forcing
524	For example, changes in benthic processes are very unlikely. Reduced calcium carbonate	
525	(CaCO <sub>3</sub> ) precipitation rates would increase $A_T$ but would increase $C_T$ . Even so, the dominant	
526	ecosystem in the Bay of Villefranche-sur-Mer is seagrass meadows, which harbor relatively	

529	few calcifying organisms. Dissolution of calcium carbonate sediment would contribute to $A_{\rm T}$
530	and $C_{\rm T}$ increase in the water column. However, as the water was supersaturated with respect
531	to both aragonite and calcite, this could only be mediated by biological processes. Carbonate
532	dissolution following CO <sub>2</sub> production via oxic degradation of organic matter releases $A_{\rm T}$ and
533	$C_{\rm T}$ in a 1:1 ratio (Moulin et al., 1985). Likewise, anaerobic remineralization produces
534	alkalinity (Cai et al., 2011). In the sediment of the Bay of Villefranche, sulfate reduction
535	coupled with precipitation of sulfide minerals is the dominant anoxic mineralization pathway
536	(Gaillard et al., 1989). An increase in these processes would explain the observed increase in
537	$A_{\rm T}$ and $C_{\rm T}$ , but as trends were slower at 50 m compared to 1 m, this would suggest the
538	dominance of a process taking place in surface waters.
539	In the upper water column at Point B, changes in biological processes are unlikely to
540	explain the observed trends in $A_T$ and $C_T$ . For example, the concentration of chlorophyll-a, a
541	proxy of primary production, has decreased since 1995, nutrients increased, and
542	phytoplankton blooms have shifted towards earlier dates in the year (Irisson et al., 2012).
543	While a decrease in net primary production could drive $C_{\rm T}$ trends, the observed increase in
544	$NO_3^-$ and $PO_4^{3-}$ would cause a small decrease in $A_T$ (Wolf-Gladrow et al., 2007). Stimulated
545	community respiration could result from warming waters but enhanced remineralization
546	would cause a decrease in $A_{\rm T}$ (Wolf-Gladrow et al., 2007).
547	The lack of salinity change at the surface excludes additional processes as drivers of
548	$A_{\rm T}$ and $C_{\rm T}$ increase at Point B. For example, increased summertime evaporation
549	(concentration effect) and reduced freshwater input (decreased dilution effect) would both be
550	expected to cause an increase in salinity, which was not observed. Increased input of Eastern
551	Mediterranean Sea waters could increase $A_{T_i}$ but this is unlikely as this water mass flows

552 much deeper than Point B (Millot and Taupier-Letage, 2005).

553	Instead, the observed changes in $A_{\rm T}$ and $C_{\rm T}$ could be due to increased limestone	Deleted: T
554	weathering which would increase the input of $A_T$ from land to the sea via rivers and	
555	groundwater. Rivers contribute both $A_T$ and $C_T$ to the Mediterranean Sea (Copin-Montégut,	
556	1993; Tamše et al., 2015). River $A_T$ originates from erosion and is correlated with bedrock	
557	composition (e.g., McGrath et al., 2016). Positive trends in river $A_{\rm T}$ have been documented in	
558	North America and occur via a number of processes including: (1) the interplay of rainfall	
559	and land-use (Raymond and Cole, 2003), (2) anthropogenic limestone addition (a.k.a.,	
560	liming) used to enhance agriculture soil pH (Oh and Raymond, 2006; Stets et al., 2014) and	
561	freshwater pH (Clair and Hindar, 2005), and (3) potentially indirect effects of anthropogenic	
562	$\mathrm{CO}_2$ on groundwater $\mathrm{CO}_2$ -acidification and weathering (Macpherson et al., 2008). Such, and	
563	other, processes were hypothesized to have driven $A_{\rm T}$ changes in the Baltic Sea (Müller et al.,	
564	2016). There, an increase in $A_T$ of 3.4 $\mu$ mol kg <sup>-1</sup> yr <sup>-1</sup> was observed from 1995 to 2014 (mean	
565	salinity = 7). In contrast to Point B, the increase in Baltic Sea $A_{\rm T}$ was not noticeable at	
566	salinity > 30 (Müller et al., 2016).	
567	Given the above speculations, the simplest plausible mechanisms causing the	
568	unexpected $A_{\rm T}$ and $C_{\rm T}$ trends would be through increasing $A_{\rm T}$ of the freshwater end-member	
569	of Point B. Local precipitation, however, did not have an influential effect and was not	
570	correlated with salinity or $A_T$ (Fig. S1). While submarine groundwater springs can be a	Deleted: 2
571	significant source of nutrients, $A_{T}$ , and $C_{T}$ to the ocean (Cai et al., 2003; Slomp and Van	
572	Cappellen, 2004), carbonate chemistry contributions of local submarine springs are currently	
573	unknown (Gilli, 1995). Signatures of limestone erosion can be observed in $A_{\rm T}$ of nearby	
574	rivers (Var, Paillon, and Roya) but detailed time-series are not available. Likewise, riverine	
575	influence at Point B has not been quantified. If river runoff exerts a dominant control on	
576	Point B carbonate chemistry, there is a lag effect, as freshwater influence peaked in May but	
577	$A_{\rm T}$ and $C_{\rm T}$ increased fastest from May through July. Consequently, this hypothesis needs	

- 580 further investigation. Until the source of  $A_{\rm T}$  increase is properly identified, use of this
- 581 observation in modeling should be implemented with caution.
- 582

#### 583 **5.** Conclusion

584	Predictions of coastal ocean acidification remain challenging due the complexity of	
585	biogeochemical processes occurring at the ocean-land boundary. At the Point B coastal	
586	monitoring station in the NW Mediterranean Sea, surface ocean acidification was due to	
587	atmospheric CO <sub>2</sub> forcing and rapid warming over the observation period 2007-2015.	
588	However, additional trends in $A_{\rm T}$ and $C_{\rm T}$ were observed and remain unexplained, but these	[]
589	trends could relate to riverine and groundwater input. The influence of a coastal boundary	
590	processes influencing seawater $A_{\rm T}$ and $C_{\rm T}$ presents a potentially major difference between	
591	coastal and offshore changes in ocean chemistry. This study highlights the importance of	
592	considering other anthropogenic influences in the greater land-sea region that may contribute	
593	to coastal biogeochemical cycles (sensu Duarte et al. 2013) and alter projections of	
594	anthropogenic change in near-shore waters.	
595		
596	<b>Data availability</b> – Time-series data from Point B are available at Pangaea <sup>®</sup> (doi:	
597	10.1594/PANGAEA.727120)	
598		
599	Author contribution – JPG initiated the study, LM supervised data collection, SA	
600	performed SeaFET deployments and calibration, JPG and LK designed and JPG conducted	
601	statistical analyses, and LK prepared the manuscript with contributions from all authors.	
602		
603	<b>Competing interests</b> - The authors declare that they have no conflict of interest.	

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606	Acknowledgements – Thanks are due to the Service d'Observation Rade de Villefranche	
607	(SO-Rade) of the Observatoire Océanologique and the Service d'Observation en Milieu	
608	Littoral (SOMLIT/CNRS-INSU) for their kind permission to use the Point B data. Discrete	
609	samples were analyzed for $C_{\rm T}$ and $A_{\rm T}$ by the Service National d'Analyse des Paramètres	
610	Océaniques du CO2. The authors thank Jean-Yves Carval, Anne-Marie Corre, Maïa	Deleted: Thanks are also due to
611	Durozier, Ornella Passafiume and Frank Petit for sampling assistance, to Steeve Comeau and	
612	Alice Webb for help with data analysis, and to Bernard Gentili for producing Fig. 1.	
613	Atmospheric CO2 data from Plateau Rosa was collected by Ricerca sul Sistema Energetico	
614	(RSE S.p.A.); we are grateful for their contribution. We acknowledge L. Coppola for	
615	providing DYFAMED data (Coppola et al., 2016) and Météo-France for supplying the	
616	meteorological data and the HyMeX database teams (ESPRI/IPSL and SEDOO/Observatoire	
617	Midi-Pyrenees) for their help in accessing them. The Agence de l'Eau Rhône-Méditerranée-	
618	Corse kindly provided data on the chemistry of local rivers. Alexandre Dano, Gilles Dandec	
619	and Dominique Chassagne provided the high-resolution bathymetric data for the volume	
620	estimate of the Bay. We are grateful for helpful comments from Nicolas Metzl on the	
621	manuscript and those from two anonymous reviewers. This work is a contribution to the	
622	European Project on Ocean Acidification (EPOCA; contract # 211384) and the MedSeA	
623	project (contract # 265103), which received funding from the European Community's	
624	Seventh Framework Programme, and to the United States National Science Foundation	
625	Ocean Sciences Postdoctoral Research Fellowship (OCE-1521597) awarded to LK.	
626		

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

929 <u>'Total' indicates estimates made for the whole Mediterranean Sea.</u> TrOCA is the 'Tracer

Comment [LK23]: #10

930 combining Oxygen, inorganic Carbon, and total Alkalinity' method, NR means 'not

931 reported', and PI is 'pre-industrial era'. \*indicates studies where the reported pH change was

#### 932 assumed to be at *in situ* temperatures.

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

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#### 936 **Table 2.** Time-series anomaly regression analyses on seawater carbonate chemistry at Point

B for salinity (S), temperature (T), dissolved inorganic carbon ( $C_{\rm T}$ ), total alkalinity ( $A_{\rm T}$ ), pH<sub>T</sub>,

p38  $pH_T$  normalized to 25 °C (pH<sub>T25</sub>), pCO<sub>2a</sub> calcite ( $\Omega_c$ ) and aragonite ( $\Omega_a$ ) saturation state, and

salinity-normalized  $A_T$  (n $A_T$ ) and  $C_T$  (n $C_T$ ), at 1 and 50 m. Slopes represent the change in the

940 variable unit per year.  $P \leq 0.001$  indicates *p*-values far smaller than 0.001.

Depth (m)	Variable	$Slope \pm SE$	Intercept $\pm SE$	<u>N</u>	F	df	Slope P	$R^2$
	S	$-0.0017 \pm 0.0044$	$3.38 \pm 8.82$	417	0.147	1,415	0.702	0
	T <u>(°C)</u>	$0.072 \pm 0.022$	$-145 \pm 44$	413	10.999	1,411	0.001	0.026
	C <sub>т</sub> (µmol kg <sup>-1</sup> )	$2.97 \pm 0.20$	$-5965 \pm 400$	416	221.87	1,414	<< 0.001	0.349
	A <sub>T_</sub> (μmol kg <sup>-1</sup> )	$2.08 \pm 0.19$	$-4189 \pm 379$	417	122.429	1,415	<< 0.001	0.228
	pH <sub>T</sub>	$-0.0028 \pm 0.0003$	$5.72 \pm 0.66$	412	74.205	1,410	<< 0.001	0.153
1	pH <sub>T25</sub>	$-0.0017 \pm 0.0002$	$3.46 \pm 0.43$	412	64.204	1,410	<< 0.001	0.135
	pCO <sub>2</sub> (µatm)	$3.53 \pm 0.39$	$-7105 \pm 776$	412	83.927	1,410	<< 0.001	0.17
	$\Omega_{\rm c}$	$-0.0109 \pm 0.0022$	$22.0 \pm 4.5$	412	24.08	1,410	<< 0.001	0.055
	$\Omega_{\rm a}$	$-0.0064 \pm 0.0015$	$12.9 \pm 3.1$	412	17.33	1,410	<< 0.001	0.04
	nA <sub>T</sub> (μmol kg <sup>-1</sup> )	$2.20 \pm 0.28$	$-4425 \pm 560$	412	62.34	1,410	<< 0.001	0.13
	nC <sub>T</sub> (μmol kg <sup>-1</sup> )	$3.12 \pm 0.29$	$-6275 \pm 579$	412	117.486	1,410	<< 0.001	0.22
	S	$0.0063 \pm 0.0020$	$-12.8 \pm 4.1$	412	9.858	1,410	0.002	0.023
	T <u>(°C)</u>	$0.088 \pm 0.019$	$-177 \pm 38$	<u>408</u>	21.927	1,406	<< 0.001	0.05
	C <sub>T</sub> <u>(µmol kg<sup>-1</sup>)</u>	$2.16 \pm 0.21$	$-4344 \pm 418$	<u>411</u>	108.105	1,409	<< 0.001	0.209
	A <sub>T</sub> (μmol kg <sup>-1</sup> )	$1.59 \pm 0.15$	$-3192 \pm 309$	412	106.947	1,410	<< 0.001	0.206
	pH <sub>T</sub>	$-0.0026 \pm 0.0002$	$5.28\pm0.50$	407	112.111	1,405	<< 0.001	0.216
50	pH <sub>T25</sub>	$-0.0013 \pm 0.0003$	$2.55 \pm 0.54$	407	21.863	1,405	<< 0.001	0.051
	pCO <sub>2</sub> (µatm)	$2.79 \pm 0.25$	$-5603 \pm 501$	407	125.1	1,405	<< 0.001	0.23
	$\Omega_{\rm c}$	$-0.0070 \pm 0.0027$	$14.0 \pm 5.4$	407	6.648	1,405	0.01	0.016
	$\Omega_{\mathrm{a}}$	$-0.0038 \pm 0.0019$	$7.6 \pm 3.7$	407	4.155	1,405	0.042	0.010
	nA <sub>T</sub> (μmol kg <sup>-1</sup> )	$1.15 \pm 0.13$	$-2309 \pm 254$	407	82.309	1,405	<< 0.001	0.168
	$nC_{\rm T}$ (µmol kg <sup>-1</sup> )	$1.82 \pm 0.19$	$-3661 \pm 376$	407	94.98	1,405	<< 0.001	0.19

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## **Comment [LK24]: #9 Deleted:** , °C

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- P48 **Table 3.** Deconvolution of  $pH_T$  anomalies  $(\frac{dpH_T}{dt}, units pH_T yr^{-1})$  at 1 and 50 m.
- 949 <u>Sensitivity of pH<sub>T</sub> with respect to variables  $\left(\frac{\partial pH_T}{\partial var}\right)$ , where the variable var is either</u>
- p50 temperature (T), salinity (S), total alkalinity ( $A_T$ ), <u>or</u> dissolved inorganic carbon ( $C_T$ ), <u>was</u>
- 951 <u>multiplied by the anomaly of var ( $\frac{dT}{dt}$ , Table 2). SE is standard error and RMSE is root-mean-</u>
- 952 squared error. Rounding was performed at the end of the calculations, prior to estimating
- 953 percent contributions.

Depth (m)	var	$\frac{\partial pH_T}{\partial var} \pm SE$	$\frac{\partial pH_T}{\partial var}\frac{dvar}{dt} \pm RMSE$	Contribution (%)	$\frac{dpH_T}{dt} \pm RMSE$
	T (°C)	$-0.0153 \pm < 0.0001$	$-0.0011 \pm 0.0003$	41	
1	S	$-0.0117 \pm < 0.0001$	$<\!0.0001 \pm 0.0001$	0	$-0.0027 \pm 0.0005$
1	$A_{\rm T}$ (µmol kg <sup>-1</sup> )	$0.0015 \pm < 0.0001$	$0.0031 \pm 0.0003$	-115	-0.0027 ± 0.0003
	$C_{\rm T}$ (µmol kg <sup>-1</sup> )	$-0.0016 \pm < 0.0001$	$-0.0047 \pm 0.0003$	174	
	T (°C)	$-0.0154 \pm < 0.0001$	$-0.0014 \pm 0.0003$	54	
50	S	$-0.0116 \pm < 0.0001$	$-0.0001 \pm < 0.0001$	4	0.0026 ± 0.0005
50	$A_{\rm T}$ (µmol kg <sup>-1</sup> )	$0.0015 \pm < 0.0001$	$0.0024 \pm 0.0002$	-92	$-0.0020 \pm 0.0003$
	$C_{\rm T}$ (µmol kg <sup>-1</sup> )	$-0.0016 \pm < 0.0001$	$-0.0035 \pm 0.0003$	135	

## **Table 4.** Deconvolution of pCO<sub>2</sub> anomalies $\left(\frac{dpCO_2}{dt}, \mu atm yr^{-1}\right)$ at 1 and 50 m. Details are the

### 956 <u>same as in Table 3.</u>

Depth (m)	var	$\frac{\partial pH_T}{\partial var} \pm SE$	$\frac{\partial pH_T}{\partial var}\frac{dvar}{dt} \pm RMSE$	Contribution (%)	$\frac{dpH_T}{dt} \pm RMSE$
	T (°C)	$16.49\pm0.05$	$1.19 \pm 0.36$	37	
1	S	$10.14 \pm < 0.01$	$-0.02 \pm 0.05$	-1	$2.22 \pm 0.57$
1	$A_{\rm T}$ (µmol kg <sup>-1</sup> )	$-1.478 \pm 0.005$	$-3.08 \pm 0.28$	-95	5.25 ± 0.57
	$C_{\rm T}$ (µmol kg <sup>-1</sup> )	$1.735 \pm 0.006$	$5.14 \pm 0.35$	159	
	T (°C)	$15.55 \pm 0.03$	$1.37 \pm 0.29$	48	
50	S	$9.355 \pm < 0.001$	$0.06\pm0.02$	2	$2.84 \pm 0.40$
50	$A_{\rm T}$ (µmol kg <sup>-1</sup> )	$-1.327 \pm 0.002$	$-2.11 \pm 0.20$	-74	2.04 ± 0.49
	$C_{\rm T}$ (µmol kg <sup>-1</sup> )	$1.629 \pm 0.005$	$3.52 \pm 0.34$	124	

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



962 Figure 2. Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity,

963 and seawater carbonate chemistry at Point B, 1 m. Regression slopes are drawn  $\pm$  SE (in

964 grey) and noted with a star for significance at  $\alpha = 0.05$ .



965

966 Figure 3. Time-series observations (a-g) and anomaly trends (h-n) for temperature, salinity,

967 and seawater carbonate chemistry at Point B, 50 m. Regression slopes are drawn  $\pm$  SE (in

968 grey) and noted with a star for significance at  $\alpha = 0.05$ .



969

- 970 **Figure 4.** Monthly distribution of seawater
- 971 carbonate chemistry at Point B, 1 m, using a
- 972 combination of a violin plot showing the relative
- 973 frequency of the observations (shaded blue area)
- 974 and a boxplot showing the median, first and third
- 975 quartiles, as well as outliers (blue).
- 976





- 977 **Figure 5.** Monthly trends of total alkalinity ( $A_T$ , blue) and dissolved inorganic carbon ( $C_T$ ,
- 978 green) for the period 2007-2015. Errors bars are  $\pm$  SE of the slope estimate and significance
- 979 is noted (\*) at  $\alpha$ =0.05.





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