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Concomitant ocean acidification and increasing total alkalinity at a coastal site in the NW Mediterranean Sea (2007-2015)

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Abstract. Monitoring global ocean change is necessary in coastal zones due to their physical and biological complexity. Here, we document changes in coastal carbonate chemistry at the time-series station, Point B, in the NW Mediterranean Sea, from 2007 through 2015, at 1 and 50 m. The rate of surface ocean acidification (-0.0028 ± 0.0003 units pH_T yr^{-1}) was faster-than-expected based on atmospheric carbon dioxide forcing alone. Changes in carbonate chemistry were predominantly driven by an increase in total dissolved inorganic carbon (C_T, +2.97 ± 0.20 μmol kg^{-1} yr^{-1}), > 50 % of which was buffered by a synchronous increase in total alkalinity (A_T, +2.08 ± 0.19 μmol kg^{-1} yr^{-1}). The increase in A_T was unrelated to salinity and its cause remains to be identified. Interestingly, concurrent increases in A_T and C_T were most rapid from May to July. Changes at 50 m were slower compared to 1 m. It seems therefore likely that changes in coastal A_T cycling via a shallow coastal process gave rise to these observations. This study exemplifies the importance of understanding coastal ocean acidification through localized biogeochemical cycling that extends beyond simple air-sea gas exchange dynamics, in order to make relevant predictions about future coastal ocean change and ecosystem function.

Keywords – global ocean change, ocean acidification, time-series, pH, alkalinity, dissolved inorganic carbon, pCO_2, Mediterranean Sea, near-shore

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1. Introduction

Maintaining time-series of oceanographic data is essential for understanding anthropogenic change in the ocean (Tanhua et al., 2013). On land, fossil fuel burning, cement production and land use changes have contributed ~580 Gt carbon to the atmosphere during the period 1750-2013 (Le Quéré et al., 2015). An estimated 29 % of this anthropogenic carbon is absorbed by the ocean in the form of carbon dioxide (CO_2; Le Quéré et al., 2015), 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 region and range from -0.0013 units pH yr^{-1} (South Pacific) to -0.0026 units pH yr^{-1} (Irminger Sea, North Atlantic) and are reviewed in 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 ocean acidification time-series at weekly frequency for a coastal site in the Mediterranean Sea.

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

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anthropogenic CO_2 (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., 2011; Palmiéri et al., 2015; Schneider et al., 2010). In the Mediterranean Sea, the salinity-A_T relationship is driven by the addition of river discharge and Black Sea input, which are generally both 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 ΔpH_T 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 global ocean change with economic impacts (Lacoue-Labarthe et al., 2016), the Mediterranean Sea is a key location for time-series measurements.

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 (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

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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, 2011), especially 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). Variability 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). Introduction of nutrient-rich upwelled- or fresh-water masses influences biological processes and carbonate chemistry at higher frequencies. 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 pH variability in order to interpret the pH changes inferred from lower-frequency sampling, at time-series stations.

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,

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we documented pH variability 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).

2. Materials and methods

2.1. Site description

A carbonate chemistry time-series was initiated in 2007 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 riverine discharge, which for the Mediterranean Sea are generally high in A_T (Copin-Montégut, 1993; Schneider et al., 2007). For example, the Paillon River, 4 km west of Point B and whose plume on occasion reaches into the Bay (L. Mousseau, pers. obs.), was sampled on 18 Aug 2014 and had a A_T of 1585 ± 0.1 µmol kg^{-1} (N=2, J.-P. Gattuso, unpubl.). Due to low primary productivity, seasonal

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123 warming drives the main annual variability in carbonate chemistry at this location (De Carlo et
124 al., 2013).
125
126 **2.2. Point B data collection, processing, and analysis**
127 To document long-term changes in ocean carbonate chemistry at Point B, seawater was
128 sampled weekly starting in January 2007. Samples were collected at 1 and 50 m, using a 12-L
129 Niskin bottle at 9:00 local time. Seawater was transferred from the Niskin bottle to 500 mL
130 borosilicate glass bottles and fixed within an hour via addition of saturated mercuric chloride for
131 preservation of carbonate parameters, following recommendations by Dickson et al. (2007).
132 Duplicate samples were collected for each depth. For each sampling event, CTD casts were
133 performed either with a Seabird 25 or Seabird 25+ profiler whose sensors are calibrated at least
134 every two years. Accuracy of conductivity (SBE4 sensor) and temperature (SBE3 sensor)
135 measurements from CTD casts were 0.0003 S m^{-1} and 0.001°C, respectively.
136 Within 6 months of collection, bottle samples were analyzed for C_T and A_T via
137 potentiometric titration following methods described by Edmond (1970) and DOE (1994), by
138 *Service National d'Analyse des Paramètres Océaniques du* CO_2, at the Université Pierre et Marie
139 Curie in Paris, France. Precision of C_T and A_T was less than 3 µmol kg^{-1}, and the average
140 accuracy was 2.6 and 3 µmol kg^{-1}, as compared with seawater certified reference material
141 (CRM) provided by A. Dickson (Scripps Institution of Oceanography). Only obvious outliers
142 were omitted from the analyses: three C_T values at 1 m (> 2300 µmol kg^{-1}), one A_T value at 1 m
143 (> 2900 µmol kg^{-1}), one A_T value at 50 m (< 2500 µmol kg-1). The C_T and A_T measurements on
144 replicates bottle samples were averaged for analyses.

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145 Calculations of the carbonate system parameters were performed using the R package
146 seacarb version 3.1 with C_T, A_T, temperature and salinity as inputs (Gattuso et al., 2016). Total
147 concentrations of silicate ($SiOH_4$) and phosphate (PO_4^{3-}) were used when available from Point B
148 (L. Mousseau, unpubl.). Detection limits for nutrients were 0.05 µM for $SiOH_4$ and 0.003 to
149 0.006 µM for PO_4^{3-}; relative precision of these analyses is 5-10 % (Aminot and Kérouel, 2007).
150 Total boron concentration was calculated from salinity using the global ratio determined by Lee
151 et al. (2010). The following constants were used: K_1 and K_2 from Lueker et al. (2000), K_f from
152 Perez and Fraga (1987), and K_s from Dickson (1990). Reported measured parameters are
153 temperature, salinity, A_T, and C_T, and derived parameters are pH_T (total hydrogen ion scale), pH_T
154 normalized to 25 ºC (pH_{T25}), pCO_2, and aragonite (Ω_a) and calcite (Ω_c) saturation states. Salinity-
155 normalized changes in A_T (nA_T) and C_T (nC_T) were calculated by dividing by salinity and
156 multiplying by 38. Except for pH_{T25}, all parameters are reported at *in situ* temperatures.
157 The average uncertainties of the derived carbonate parameters were calculated according
158 to the Gaussian method (Dickson and Riley, 1978) implemented in the "errors" function of the R
159 package seacarb 3.1 (Gattuso et al., 2016). The uncertainties are ±2.7 x 10^{-10} mol H^+ (about
160 0.015 units pH_T), ±15 µatm pCO_2, and ±0.1 unit of the aragonite and calcite saturation states.
161 To quantify interannual changes in carbonate parameters, the data were detrended for
162 seasonality by subtracting monthly means from the time-series following methods in Bates et al.
163 (2014). The resulting anomalies were analyzed using a linear regression. All analyses were
164 performed in R (R Core Team, 2016).
165

166 **2.3. Deconvolution of pH_T and pCO_2**

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

172 $$\frac{dpH_T}{dt} = \frac{\partial pH_T}{\partial T}\frac{dT}{dt} + \frac{\partial pH_T}{\partial S}\frac{dS}{dt} + \frac{\partial pH_T}{\partial A_T}\frac{dA_T}{dt} + \frac{\partial pH_T}{\partial C_T}\frac{dC_T}{dt} \quad (1)$$

173 Here, $\frac{\partial pH_T}{\partial var}\frac{dvar}{dt}$ represents the slope contribution of changing *var* to the estimated change
174 in pH_T, where *var* is either T, S, A_T, or C_T. The rate of pH change due to *var* ($\frac{\partial pH_T}{\partial var}\frac{dvar}{dt}$) was
175 estimated by calculating pH_T using the true observations of *var* but monthly mean values of the
176 other three variables, and regressing it to time. The calculation was repeated for pCO_2 ($\frac{dpCO_2}{dt}$) in
177 order to compare the rate of increase with that of atmospheric CO_2.

178 As a sub-component of $\frac{\partial pCO_2}{\partial C_T}\frac{dC_T}{dt}$, the rate of anthropogenic CO_2 increase was estimated
179 from atmospheric CO_2 concentrations nearest to Point B (Plateau Rosa, Italy, courtesy of the
180 World Data Center for Greenhouse Gases, http://ds.data.jma.go.jp/gmd/wdcgg/). For these data,
181 missing daily values were linearly interpolated. A linear regression was performed where the
182 slope represents the rate of CO_2 increase in the atmosphere. Finally, to help identify different
183 processes that might have contributed to the observed trends, linear regressions were performed
184 on change in A_T and C_T by month and on the salinity-A_T relationship by year.
185

186 **2.4. SeaFET data collection, processing, and analysis**

187 To capture pH variability at higher-than-weekly sampling frequencies, a SeaFET™
188 Ocean pH sensor (Satlantic) was deployed on the EOL buoy (435 m from the Point B sampling

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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_T 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_T of the spectrophotometric measurement of Tris buffer from the CRM value).

3. Results

3.1. Time-series trends

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At Point B from January 2007 to December 2015, >400 samples were collected for carbonate chemistry at both 1 and 50 m. Anomaly trends detected at 1 m (Fig. 2, Table 2) were also significant at 50 m (Table S1, Fig. S1), with the exception that salinity increased at 50 m (0.0063 ± 0.0020 units yr^{-1}, P = 0.002). Changes in carbonate chemistry were faster at 1 m compared to 50 m, with the exception of salinity and temperature. The warming rate at 50 m was 22 % greater compared to 1 m, mostly due to increasing summer temperatures since 2007. Analyses for 50 m are available (Table S1, Fig. S1) but here, we focus on results from 1 m unless explicitly specified otherwise (Fig. 2, Table 2). For time-series anomalies at 1 m, carbonate chemistry anomalies were significant for pH_T (-0.0028 ± 0.0003 units yr^{-1}, N=412), A_T (+2.08 ± 0.19 µmol kg^{-1} yr^{-1}, N=417), C_T (+2.97 ± 0.20 µmol kg^{-1} yr^{-1}, N=416), pCO_2 (+3.53 ± 0.39 µatm yr^{-1}, N=412), and Ω_a (-0.0064 ± 0.0015 units yr^{-1}, N=412). At the same time, temperature anomaly increased (+0.072 ± 0.022 ºC yr^{-1}, *N=413*), but this significance was lost with the exclusion of the year 2015 (analysis not shown; changes in other carbonate chemistry parameters remained significant). No significant change in the salinity anomaly was detected (P=0.702, N=417).

Strong seasonal cycles in carbonate parameters were present at Point B at 1 m (Fig. 3). Calculated monthly means (2007-2015) are described briefly and listed in Table S2. 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. The opposing seasonal cycles of temperature and C_T, due to summer warming coinciding with the period of peak primary productivity (De Carlo et al. 2013), resulted in an annual pH_T range of 0.12 with peak pH in late winter (8.14 ± 0.01, February and March) and

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234 minimum pH in summer (8.02 ± 0.03, July and August). The corresponding pCO_2 range was
235 +128 µatm from February to August. The monthly means were subtracted from the time-series to
236 calculate anomalies.
237
238 **3.2. Deconvolution of pH_T and pCO_2**
239 Deconvolutions of pH and pCO_2 are presented in Table 3. For both $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$,
240 temperature and salinity had contributing (approx. 35% and 5% respectively) but non-significant
241 effects. The 2007-2015 observation period is likely not long enough to detect significance of the
242 relatively large temperature contribution to $\frac{dpH_T}{dt}$. The predominant driver of $\frac{dpH_T}{dt}$ and $\frac{dpCO_2}{dt}$ was
243 the increase in C_T (P <<0.001), 56 and 60 % of which was compensated for by a significant
244 increase in A_T (P = 0.002), respectively.
245 Atmospheric CO_2 at Plateau Rosa increased by 2.02 ± 0.03 ppm yr^{-1} ($F_{1,3285}$ = 5852.43, P
246 <<0.001, R^2 0.64), with an anomaly rate of 2.08 ± 0.01 ppm yr^{-1} ($F_{1,3285}$ = 46649.79, P <<0.001,
247 R^2 0.93) during the study period 2007-2015, and represents the anthropogenic CO_2 forcing of
248 ocean acidification. Considering the error associated with deconvolution of pCO_2 and assuming
249 air-sea CO_2 equilibrium, atmospheric CO_2 increase represents 31 to 44 % of the total C_T
250 contribution ($\frac{\partial pCO_2}{\partial C_T}\frac{dC_T}{dt}$) to $\frac{dpCO_2}{dt}$. This leaves 56 to 69 % of the total C_T contribution to pCO_2
251 unaccounted for. As A_T is not influenced by addition of anthropogenic CO_2 to seawater, the next
252 question was, thus, whether or not the changes in A_T and C_T were process-linked. Regressions of
253 annual monthly observations of A_T and C_T revealed similar seasonal cycles for both parameters
254 (Fig. 4). The fastest increases occurred simultaneously for both parameters, which peaked in
255 June. The smallest changes occurred in January. Significant increases in A_T occurred from May

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256 to July. Significant increases in C_T occurred from February-August and in November. Results of
257 regression analyses on monthly changes are listed in Table S3.
258
259 **3.3. Salinity and A_T relationships**
260 Given the coastal locale and the increase in A_T, it is interesting to look at the interannual
261 variability of the relationship between salinity and A_T (Fig. 5). With the exception of 2007,
262 salinity was a poor predictor of A_T. The R^2 value for each annual salinity-A_T linear regression
263 ranged from 0.00 (in 2013) to 0.87 (in 2007) with y-intercepts (A_{T0}, the freshwater end-member
264 alkalinity) ranging between -176 µmol kg^{-1} (in 2007) and 2586 µmol kg^{-1} (in 2013). The
265 interannual variability of the salinity-A_T relationship was driven by the variability in A_T observed
266 at salinity < 38.0 that was present from November through July.
267 The salinity cycle (monthly means) at Point B was small and ranged from 37.64 ± 0.26 to
268 38.21 ± 0.11 from May to September, following freshwater input in winter and spring and
269 evaporation throughout summer and fall (Fig. 3). Highest (> 38.0) and most stable salinity
270 observations were made in August through October, which coincided with the period of
271 maximum A_T (2562 and 2561 ± 9 µmol kg^{-1} in September and October, respectively). Minimum
272 A_T (2543 ± 14 µmol kg^{-1}) was observed in June. The reported salinity-A_T relationship is thus
273 generated from monthly means (R^2 = 0.74) where A_T units are µmol kg^{-1} and error terms are SE:

274 $$A_T = 1554.9(\pm 185.9) + 26.3(\pm 4.9) \times S \qquad (2)$$

275
276 **3.4. High-frequency pH data**
277 To verify the weekly sampling scheme at Point B, a total of 11 SeaFET deployments
278 were conducted from June 2014 to April 2016, averaging 58 ± 25 days and 5 ± 2 calibration

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279 samples per deployment (Fig. 6). Only 5 % of the data was removed during quality control, due
280 to biofouling in one deployment and a drained battery in another, yielding 610 days of good data.
281 The mean offset between calibration samples and the calibrated SeaFET pH time-series was ±
282 0.007 units pH_T, indicating a high-quality pH dataset (Fig. 6c). Sensor data corroborated the
283 seasonal pH and temperature cycle observed at Point B. Event-scale effects (e.g., pH_T change ≥
284 0.1 for days to weeks, *sensu* Kapsenberg and Hofmann 2016) were absent at this site suggesting
285 that weekly sampling was sufficient to describe seasonal and interannual changes in carbonate
286 chemistry at Point B. Magnitude of diel pH_T variability was small (the 2.5th to 97.5th percentiles
287 ranged between 0.01 and 0.05 units pH_T) and unrelated to seasonal warming or the concentration
288 of Chlorophyll-a (Fig. S2).
289
290 **4. Discussion**
291 **4.1. Observed changes in carbonate chemistry**
292 Anthropogenic forcing of CO_2 in seawater necessitates long-term monitoring, in order to
293 understand and study future ecological change in the coastal environment. In the coastal NW
294 Mediterranean Sea at EOL, near Point B, high-frequency pH data validated that weekly, morning
295 sampling at Point B was sufficient to capture water mass changes that were independent from
296 benthic, diel pH variability in seagrass beds inside the bay (Cox et al., 2016). Based on weekly
297 samples collected from 2007 through 2015, we detected anomaly changes in pH_T of -0.0028 ±
298 0.0003 units yr^{-1} and an increase in A_T of 2.08 ± 0.19 µmol kg^{-1} yr^{-1}. The corresponding pCO_2
299 increase of 3.53 ± 0.39 µatm yr^{-1} is 70 % greater than the atmospheric CO_2 anomaly of +2.08 ±
300 0.01 ppm yr^{-1} at Plateau Rosa, Italy. While Point B is a weak sink for CO_2 (De Carlo et al.,
301 2013), the increase in anthropogenic CO_2 in the atmosphere alone does not account for all of the

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observed changes in carbonate chemistry at this location. The increase in C_T was the dominant driver of pH_T change over the study period. An increase in A_T partially buffered this C_T increase such that the observed acidification rate is only slightly larger than those reported at other ocean time-series sites (-0.0026 to -0.0013 units yr^{-1}, Bates et al., 2014). Warming contributed to approximately 35 % of the pH decline, which agrees well with the 30 % approximation at DYFAMED, an open-sea site about 50 km offshore from Point B (Marcellin Yao et al., 2016). A longer time-series of temperature paired with pH observations will be necessary to definitively characterize this relationship. While anomalously warm summer temperatures in 2015 drove the warming trends in this study, this region has warmed steadily since 1980 (Parravicini et al., 2015) and this is observable at 50 m as well (Fig. S1). Finally, the co-evolution of A_T and C_T changes suggests that changes in C_T are also due to increasing A_T, which includes bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (Fig. 4). We assess the spatial extent of these trends and discuss potential drivers.

Fastest rate increases in A_T and C_T occurred from May through July; the period of seasonal transition (Fig. 3). At this time, various biophysical processes force the seasonality of the carbonate system. 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 (L. Mousseau, unpubl.). Mixing occurs down to more than 2000 m depth a few 10s of km from the study site and C_T is up to 100 µmol kg^{-1} higher in deep waters (Copin-

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325 Montégut and Bégovic, 2002). Following winter, C_T declines due to a combination of
326 phytoplankton bloom carbon uptake and freshwater dilution, until the onset of summer
327 stratification. Summer warming leads to pCO_2 off-gassing to the atmosphere (De Carlo et al.,
328 2013), thereby further decreasing C_T. The increases in A_T and C_T from 2007 through 2015 were
329 more pronounced at 1 m compared to 50 m, suggesting that the driving processes dominate at the
330 surface.

331 To estimate if the observed trends from Point B were also occurring offshore, we turn to
332 time-series station DYFAMED, approx. 50 km from Point B (Fig. 1). The acidification rate at
333 DYFAMED was estimated at -0.003 ± 0.001 units pH yr^{-1} from 1995 to 2011 (Marcellin Yao et
334 al., 2016), however, the uncertainty is large and makes the comparison with Point B unreliable.
335 A_T at the DYFAMED did not change significantly during the period 2007-2014 ($F_{1,51}$ 3.204, P =
336 0.0794, R^2 0.08, data from L. Coppola). This suggests that the processes driving changes in A_T
337 and C_T at Point B, in addition to being shallow, dissipate offshore.

338 Another coastal area of the Mediterranean Sea, in the North Adriatic Sea, exhibited
339 similar changes in carbonate chemistry as those observed at Point B. By comparing cruise data
340 between the winters of 1983 and 2008, Luchetta et al. (2010) determined an acidification rate of
341 pH_T -0.0025 units yr^{-1} and an increase in A_T of 2.98 µmol kg^{-1} yr^{-1} at depths < 75 m. As coastal
342 sites, Point B and the Gulf of Trieste in the N Adriatic Sea show a strong positive A_{T0} (i.e.,
343 freshwater end-member alkalinity) in surface waters (Cantoni et al., 2012; Ingrosso et al., 2016).
344 In contrast to Point B, the N Adriatic Sea exhibits a negative salinity-A_T relationship and faster
345 A_T increase (Luchetta et al., 2010), suggesting that rivers may play a stronger role in A_T trends
346 there compared to Point B. Rivers are significant sources of C_T to the Gulf of Trieste, making up
347 3-16 % of C_T in 2007 (Tamše et al., 2015). The authors note that 2007 was a year of record low

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river discharge. Notably, this is the only year at Point B for which A_{T0} was negative and salinity-A_T relationship was highly correlated, also indicating that 2007 was a year of low freshwater input.

The correlates between Point B and N Adriatic Sea suggest a common driver of changes in ocean carbonate chemistry at these two sites (possibly linked via shared watersheds of the Alps), and these independent studies may by symptomatic of changes occurring across wider coastal areas of the Mediterranean Sea. Monitoring efforts of carbonate chemistry in 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).

4.2. Potential drivers of changes in carbonate chemistry

Coastal ocean acidification rates vary greatly across different regions. In the NW Pacific coast, rapid acidification of surface waters (ΔpH_T -0.058 units yr^{-1}) at Tatoosh Island has been documented in the absence of concomitant 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 CO_2 (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 CO_2 rate by an order of magnitude while others exhibited an increase in pH (Provoost et al., 2010). These sites experience much greater sub-annual variability than Point B. As a coastal ocean acidification

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monitoring site, the relative simplicity of the Point B pH variability regime may therefore provide an opportunity to further investigate the underlying drivers of rapid coastal ocean acidification in the absence of additional noise from otherwise overshadowing processes.

While ocean acidification is often described in pH_T, at Point B, pH is largely a product of underlying changes in A_T and C_T. Sediment dissolution is unlikely to contribute to the observed increase in A_T as both aragonite and calcite were supersaturated throughout the study period; conditions that are not conducive to large rates of dissolution. An overall reduction in calcium carbonate ($CaCO_3$) precipitation rates is unlikely, as the dominant ecosystem in the Bay of Villefranche-sur-Mer is seagrass meadows, which harbor relatively few calcifying organisms and there has been no obvious changes in the abundance of calcifiers (J.-P. Gattuso, pers. obs.). All the same, the sheer volume of the Bay would likely dilute any signature of changes in calcification or dissolution of sediment or organisms. For the Mediterranean Sea, in general, the influence of biogenic $CaCO_3$ on A_T is small compared to the influence of river and Black Sea A_T (Copin-Montégut, 1993). Increased input from the eastern Mediterranean Sea waters could increase A_T, but this is questionable, because while eastern waters are higher in A_T, salinity and pH are also greater and C_T is a little lower, compared to the western waters (Álvarez et al., 2014; Touratier and Goyet, 2011).

For C_T, there are a few additional drivers to discuss. First, anthropogenic CO_2 partly accounted for the observed increase in C_T, independent of A_T. In summer, pCO_2 peaks and Point B becomes a weak source of CO_2 to the atmosphere (De Carlo et al., 2013). As atmospheric CO_2 is increasing it may contribute to summertime C_T retention, but this effect is likely too small for the observed increases in C_T. Second, increased remineralization rates could contribute to C_T, particularly in summer when the water is warmer, hence promoting respiration, and highly

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stratified and isolated from C_T-rich bottom waters. However, this would require either (1) a change in substrate (local or regional) for remineralization but no clear trend in particulate organic carbon was observable in the study period (L. Mousseau, unpubl.), or (2) a change in net community metabolism, but warming trends up through 2014 were not significant. Lastly, Chlorophyll-a biomass, a proxy of primary production, has decreased since 1995 and blooms have shifted towards earlier dates in the year, at Point B (Irisson et al., 2012). Both of these processes could influence the increasing rate of C_T in summer but would not account for the increase in A_T.

The lack of salinity change excludes additional processes as drivers of carbonate chemistry change at Point B. For example, increased summertime evaporation (concentration effect) and reduced riverine discharge (decreased dilution effect) would both be expected to cause an increase in salinity, which was not observed and so these are not suspected drivers. However, changes in the content of freshwater sources is conceivable.

The observed changes in A_T and C_T could be achieved via augmented limestone weathering increasing the A_T input from land to the sea via rivers and submarine groundwater springs. Increased A_T in freshwater was documented in North American rivers (Raymond and Cole, 2003; Stets et al., 2014) and groundwater (Macpherson et al., 2008). For the Mediterranean Sea, rivers are a significant source of both A_T and C_T (Copin-Montégut, 1993). Riverine contributions of A_T originate from erosion and are correlated with bedrock composition (e.g., McGrath et al., 2016). The annual variability in salinity-A_T relationships at Point B does suggest influence of river discharge, as has been observed elsewhere in the Mediterranean Sea (Cantoni et al., 2012; Turk et al., 2010). Signatures of limestone erosion can be observed in the A_T of local rivers near Point B (Var, Paillon, and Roya) and range between 1000 to 2000 µmol kg^{-1} (data

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417 from *Agence de l'Eau Rhône-Méditerranée-Corse*, http://sierm.eaurmc.fr). Even a rainwater
418 outfall at the entrance of Port de la Darse harbor, inside the Bay of Villefranche-sur-Mer, had an
419 A_T of 607 ± 5 µmol kg^{-1} (N=2) following a precipitation event. However, local precipitation was
420 not correlated with salinity or A_T, suggesting that rain runoff is not a driving factor of Point B
421 carbonate chemistry (Fig. S3). Lastly, submarine groundwater springs are a significant source of
422 nutrients, A_T, and C_T to the ocean (Cai et al., 2003; Slomp and Van Cappellen, 2004). Submarine
423 springs have been identified along the Point B coastline (Gilli, 1995), but their carbonate
424 chemistry contributions are currently unknown.

425 Rivers as a potential driver of A_T and C_T trends at Point B could be achieved if the A_T
426 content discharged by rivers was changing, as was proposed for the Adriatic Sea (Luchetta et al.,
427 2010). For example, terrestrial organic matter cycling influences riverine C_T (Vargas et al.,
428 2016), so changes in soil respiration could be expected to change A_T of rivers. Increasing river A_T
429 has been documented in North America and occurs via a number of processes including: (1) the
430 interplay of rainfall and land-use (Raymond and Cole, 2003), (2) anthropogenic limestone
431 addition (a.k.a., liming) used to enhance agriculture soil pH (Oh and Raymond, 2006; Stets et al.,
432 2014) and freshwater pH (Clair and Hindar, 2005), and (3) potentially indirect effects of
433 anthropogenic CO_2 on groundwater CO_2-acidification and weathering (Macpherson et al., 2008).
434 Such, and other, processes are hypothesized to have driven A_T changes in the Baltic Sea (Müller
435 et al., 2016). There, A_T increased at a rate of +3.4 µmol kg^{-1} yr^{-1} during the period 1995 to 2014
436 (mean salinity = 7). In contrast to Point B, where salinity is about 38, the increase in Baltic Sea
437 A_T was not noticeable at salinity > 30 (Müller et al., 2016). This contrast clouds the perspective
438 that changes in A_T of freshwater sources can influence A_T at Point B, and a more in depth study
439 will be necessary to address this.

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Given the discussion above, the simplest plausible mechanisms causing changes in carbonate chemistry at Point B would be through (1) increasing anthropogenic atmospheric CO_2, and (2) increasing A_T of freshwater sources (i.e., rivers, groundwater). Freshwater has a shallow and coastal influence and is also dominant in the N Adriatic Sea, which exhibits similar trends as those observed at Point B. If so, there is a lag effect, as freshwater influence peaks in May but A_T and C_T increased fastest from May through July. Consequently, this hypothesis needs further investigation. The influence of a coastal boundary processes influencing seawater A_T and C_T presents a potentially major difference between coastal and offshore ocean acidification rates. Until the source of A_T increase is properly identified, use of this observation (e.g., in modeling) should be implemented with great caution.

5. Conclusion

Predictions of coastal ocean acidification remain challenging due the complexity of biogeochemical processes occurring at the ocean-land boundary and the lack of long-term monitoring. At the Point B coastal monitoring station in the NW Mediterranean Sea, the ocean acidification trend is greater than expected from assuming atmospheric equilibrium. We postulate that the enhanced acidification trend could stem from changes in freshwater inputs from land which are also the source of interannual variability in A_T at this site. This study highlights the importance of considering other anthropogenic influences in the greater land-sea region that may (1) contribute to coastal biogeochemical cycles (*sensu* Duarte et al. 2013) and (2) inform projections of anthropogenic change in near-shore waters and experimental design in global ocean change biology.

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463 **Data availability –** Time-series data from Point B are available at Pangaea® (doi:
464 10.1594/PANGAEA.727120)
465
466 **Author contribution** – JPG initiated the study, LM supervised data collection, SA performed
467 SeaFET deployments and calibration, JPG and LK designed and JPG conducted statistical
468 analyses, and LK prepared the manuscript with contributions from all authors.
469
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758 **Table 1.** Ocean acidification studies estimating or documenting pH change in the Mediterranean
759 Sea. TrOCA is the 'Tracer combining Oxygen, inorganic Carbon, and total Alkalinity' method,
760 N.R. means 'not reported', and PI is 'pre-industrial era'. *indicates studies where the reported
761 pH change was assumed to be at *in situ* temperatures.

Region	*Site*	*Method*	*Study period*	*pH scale*	*°C*	*ΔpH yr^{-1} ± SE*	*Total ΔpH*	*Reference*
NW	Point B	time-series, anomaly	2007-2015	total	*in situ*	-0.0028 ± 0.0003	-0.0252	This study
NW	Point B	time-series, anomaly	2007-2015	total	25	-0.0017 ± 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	17.34	-0.003 ± 0.001	-0.051	Marcellin Yao et al. (2016)
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 ± 0.001	Palmiéri et al. (2015)
Gibraltar Strait	Espartel sill	pH, pCO2 sensors	2012-2015	total	25	-0.0044 ± 0.00006	-	Flecha et al. (2015)

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764 **Table 2.** Time-series (observed values and anomalies) regression analyses on seawater carbonate
765 chemistry, at Point B, 1 m, for salinity (S), temperature (T, ºC), dissolved inorganic carbon (C_T,
766 µmol kg^{-1}), total alkalinity (A_T, µmol kg^{-1}), pH_T, 25 ºC-normalized pH_T (pH_{T25}), calcite (Ω_c) and
767 aragonite (Ω_a) saturation state, and salinity-normalized A_T (nA_T) and C_T (nC_T). Slope is change
768 yr^{-1}. P <<0.001 indicate p-values far smaller than 0.001.

	Variable	*Slope ± SE*	*Intercept ± SE*	*F*	*df*	*Slope P*	R^2
	S	0.0031 ± 0.0054	31.7 ± 10.8	0.326	1,415	0.568	0.001
	T	0.12 ± 0.08	-226 ± 157	2.429	1,411	0.12	0.006
	C_T	2.71 ± 0.31	-3208 ± 626	75.671	1,414	<<0.001	0.155
	A_T	2.24 ± 0.21	-1945 ± 418	115.895	1,415	<<0.001	0.218
	pH_T	-0.0031 ± 0.0009	14.3 ± 1.8	11.674	1,410	0.001	0.028
Observed	pH_{T25}	-0.0012 ± 0.0004	10.5 ± 0.9	6.861	1,410	0.009	0.016
	pCO_2	3.78 ± 0.98	-7214 ± 1976	14.82	1,410	<<0.001	0.035
	Ω_c	-0.0043 ± 0.0052	13.9 ± 10.5	0.684	1,410	0.409	0.002
	Ω_a	-0.0017 ± 0.004	6.74 ± 7.98	0.177	1,410	0.674	0
	nA_T	2.01 ± 0.31	-1489 ± 632	41.067	1,410	<<0.001	0.091
	nC_T	2.57 ± 0.47	-2918 ± 944	29.927	1,410	<<0.001	0.068
	S	-0.0017 ± 0.0044	3.38 ± 8.82	0.147	1,415	0.702	0
	T	0.072 ± 0.022	-145 ± 44	10.999	1,411	0.001	0.026
	C_T	2.97 ± 0.20	-5965 ± 400	221.87	1,414	<<0.001	0.349
	A_T	2.08 ± 0.19	-4189 ± 379	122.429	1,415	<<0.001	0.228
	pH_T	-0.0028 ± 0.0003	5.72 ± 0.66	74.205	1,410	<<0.001	0.153
Anomaly	pH_{T25}	-0.0017 ± 0.0002	3.46 ± 0.43	64.204	1, 410	<<0.001	0.1354
	pCO_2	3.53 ± 0.39	-7105 ± 776	83.927	1,410	<<0.001	0.17
	Ω_c	-0.0109 ± 0.0022	22.0 ± 4.5	24.08	1,410	<<0.001	0.055
	Ω_a	-0.0064 ± 0.0015	12.9 ± 3.1	17.33	1,410	<<0.001	0.041
	nA_T	2.20 ± 0.28	-4425 ± 560	62.34	1,410	<<0.001	0.132
	nC_T	3.12 ± 0.29	-6275 ± 579	117.486	1,410	<<0.001	0.223

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771 **Table 3.** Contribution of temperature (*T*), salinity (*S*), total alkalinity (A_T), and dissolved
772 inorganic carbon (C_T) to observed changes in pH_T and pCO_2 (µatm) yr^{-1}. The sum of the slopes
773 ($\frac{dpH_T}{dt}$, $\frac{dpCO_2}{dt}$) is slightly inflated compared to the observed trends reported in Table 2 (-0.0037 vs. -
774 0.0031 yr^{-1} for pH_T, and 4.26 vs. 3.78 µatm yr^{-1} for pCO_2). These differences are negligible
775 relative to the error associated with the slope estimates. Incomplete sum of % contributions are
776 due to rounding. *P* of <<0.001 indicate p-values far smaller than 0.001.

	Variable	***Slope ± SE***	***% contribution***	***Slope P***
$\frac{\partial pH_T}{\partial var}\frac{dvar}{dt}$	*T*	-0.0013 ± 0.0009	35	0.15
	S	-0.0002 ± 0.0008	5	0.793
	A_T	0.0028 ± 0.0009	-76	0.002
	C_T	-0.0050 ± 0.0009	135	<<0.001
$\frac{dpH_T}{dt}$		-0.0037	99	
$\frac{\partial pCO_2}{\partial var}\frac{dvar}{dt}$	*T*	1.43 ± 0.97	34	0.143
	S	0.24 ± 0.89	6	0.792
	A_T	-2.94 ± 0.94	-69	0.002
	C_T	5.53 ± 0.96	130	<<0.001
$\frac{dpCO_2}{dt}$		4.26	101	

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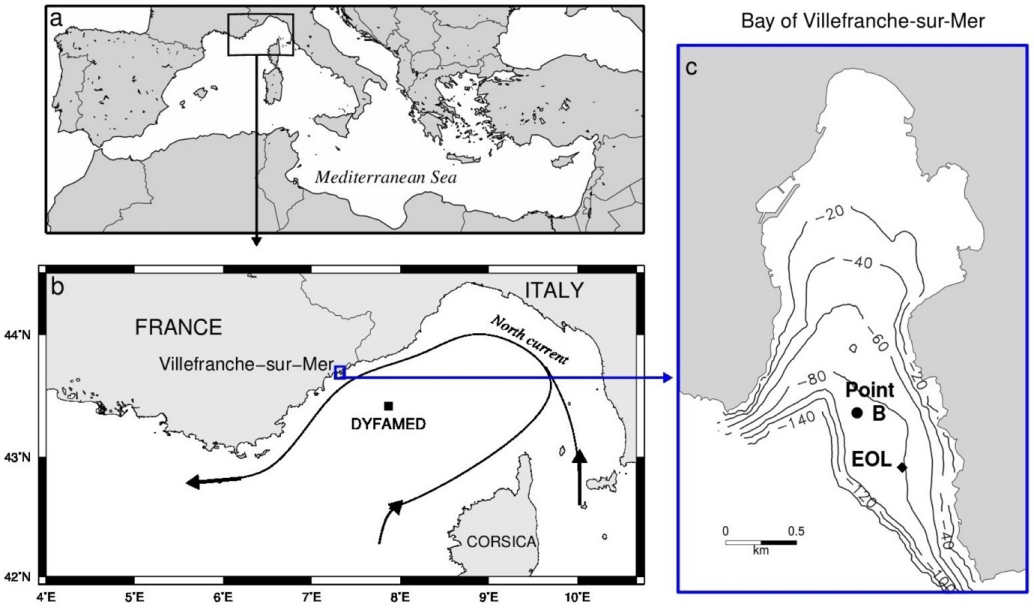
778 **Figure 1.** Map of study region in the NW Mediterranean Sea (a) along the North current (b) in
779 the Bay of Villefranche-sur-Mer, France (c). Point B station, EOL buoy, and offshore time-series
780 station DYFAMED are marked. Bathymetric line units are m (c).



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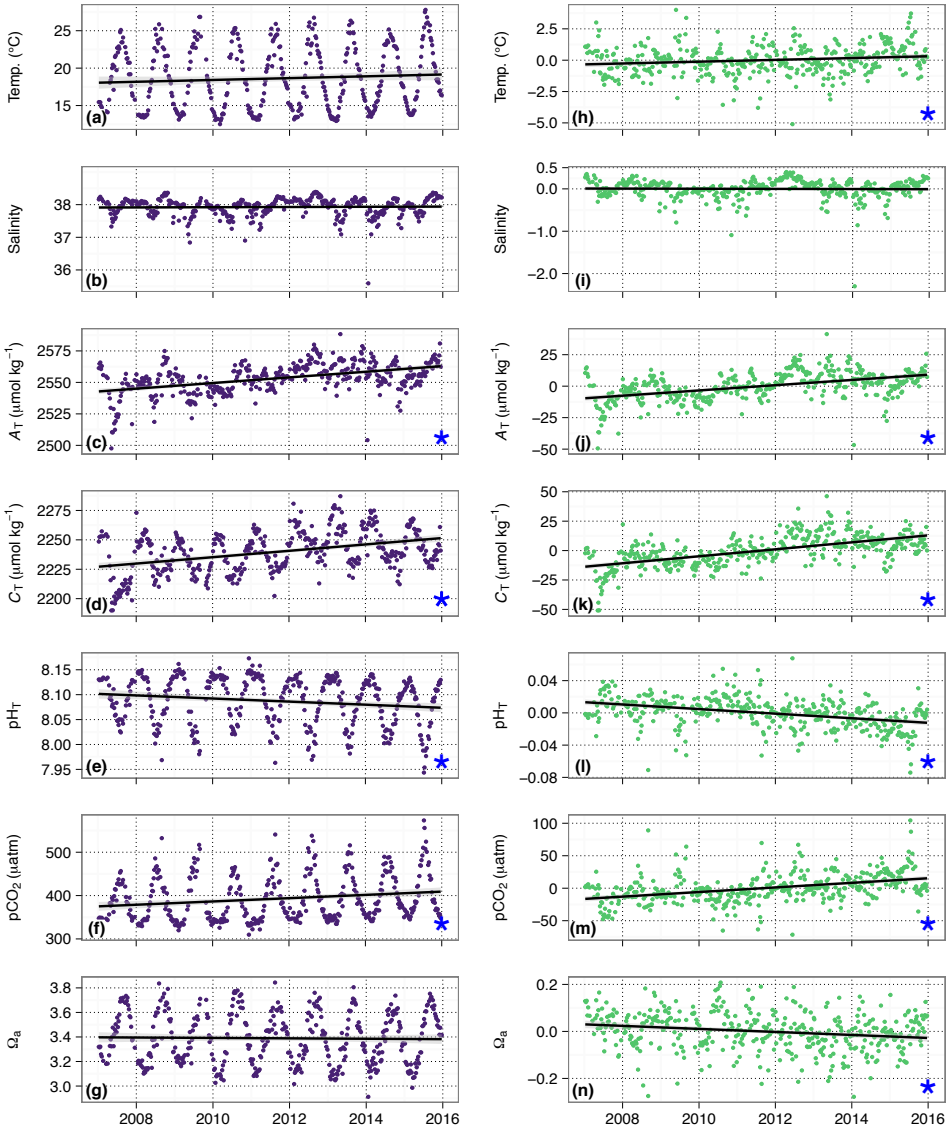
782 **Figure 2.** Time-series observations (a-g) and anomalies (h-n) of temperature, salinity, and
783 seawater carbonate chemistry at Point B, 1 m. Regression slopes are drawn ± SE (in grey) and
784 noted with a star for significance at α=0.05.



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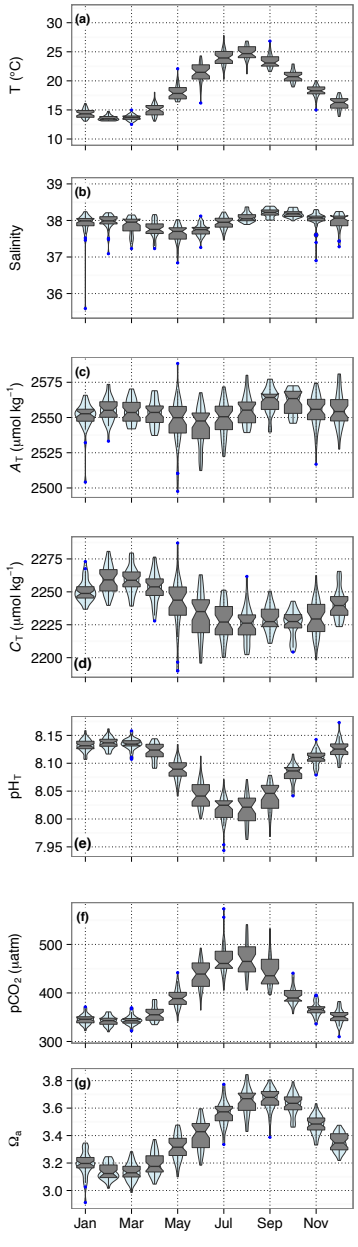
786 **Figure 3.** Monthly distribution of seawater carbonate chemistry at Point B, 1 m., using a
787 combination of a violin plot showing the relative frequency of the observations (shaded blue
788 area) and a boxplot showing the median, first and third quartiles, as well as outliers (blue).



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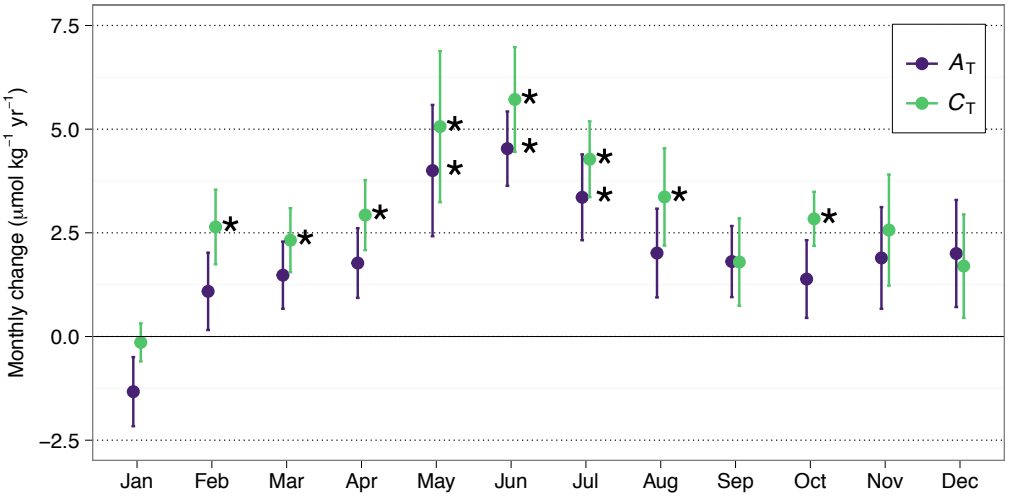
790 **Figure 4.** Increase in total alkalinity (A_T, purple) and dissolved inorganic carbon (C_T, green) by
791 month for the period 2007-2015. Errors bars are ± SE of the slope estimate and significance is
792 noted (*) at α=0.05.



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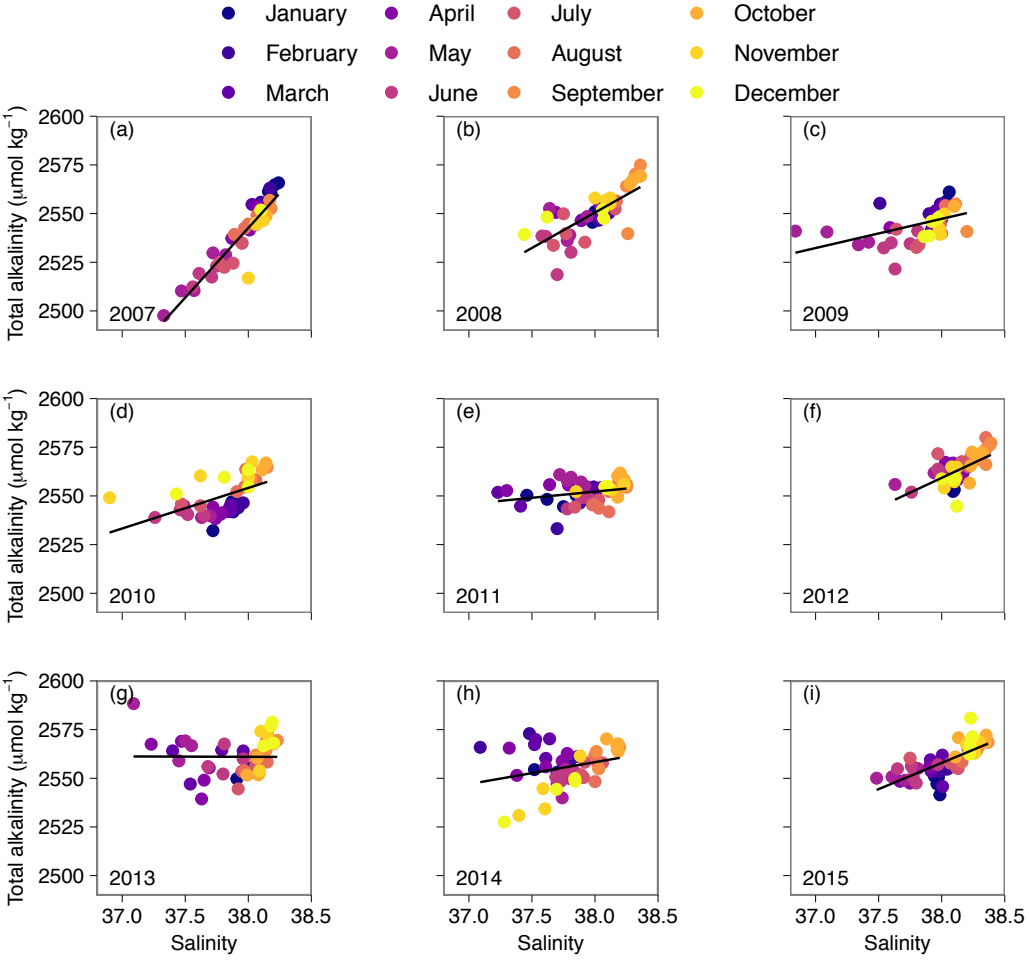
794 **Figure 5.** Salinity and total alkalinity relationships by year for the period 2007-2015, at Point B,

795 1 m. Data points are colored for month.



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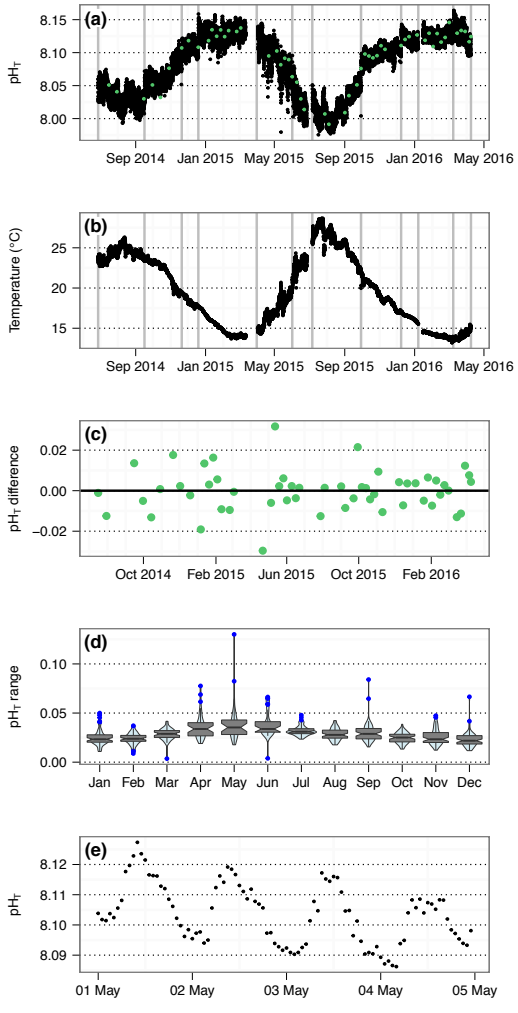
797 **Figure 6.** Time-series pH (a) and temperature (b) from autonomous SeaFET pH sensor at EOL
798 buoy, 2 m. Discrete calibration samples are noted in green, and grey vertical lines bracket
799 deployment periods (a). Mean offset of calibration samples from processed pH time-series was
800 pH_T ±0.007 (c). Diel pH range was small and peaked in April and May (d) and exhibits a clear,
801 small, diel cycle (e, representative example from May 2015).



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