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# A Time-Series View of Changing Surface Ocean Chemistry Due to Ocean Uptake of Anthropogenic CO<sub>2</sub> and Ocean Acidification

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**ABSTRACT.** Sustained observations provide critically needed data and understanding not only about ocean warming and water cycle reorganization (e.g., salinity changes), ocean eutrophication, and ocean deoxygenation, but also about changes in ocean chemistry. As an example of changes in the global ocean carbon cycle, consistent changes in surface seawater CO<sub>2</sub>-carbonate chemistry are documented by seven independent CO<sub>2</sub> time series that provide sustained ocean observations collected for periods from 15 to 30 years: (1) Iceland Sea, (2) Irminger Sea, (3) Bermuda Atlantic Time-series Study (BATS), (4) European Station for Time series in the Ocean at the Canary Islands (ESTOC), (5) Carbon Retention In A Colored Ocean sites in the North Atlantic (CARIACO), (6) Hawaii Ocean Time-series (HOT), and (7) Munida in the Pacific Ocean. These ocean time-series sites exhibit very consistent changes in surface ocean chemistry that reflect the impact of uptake of anthropogenic CO<sub>2</sub> and ocean acidification. The article discusses the long-term changes in dissolved inorganic carbon (DIC), salinity-normalized DIC, and surface seawater pCO<sub>2</sub> (partial pressure of CO<sub>2</sub>) due to the uptake of anthropogenic CO<sub>2</sub> and its impact on the ocean's buffering capacity. In addition, we evaluate changes in seawater chemistry that are due to ocean acidification and its impact on pH and saturation states for biogenic calcium carbonate minerals.

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Igor Shkvorets,  
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## INTRODUCTION

Perturbation of the global carbon cycle through the production and release of anthropogenic carbon dioxide ( $\text{CO}_2$ ) to the atmosphere has important implications for Earth's climate (Solomon et al., 2007) and for ocean chemistry. In the atmosphere-terrestrial biosphere-ocean system, the marine carbon cycle is the largest active carbon reservoir on time scales relevant to human societies. Interacting physical and biogeochemical processes that are spatially and temporally variable influence the uptake of anthropogenic  $\text{CO}_2$  from the atmosphere by the global ocean (e.g., Sabine and Tanhua, 2010; Tanhua et al., 2013) and exhibit feedbacks that can significantly impact Earth's climate system in the future. The scale of sequestration of anthropogenic  $\text{CO}_2$  by the ocean and terrestrial biosphere over the next few centuries is slowly being understood through the systematic collection of time-series observations that quantify the uncertainties in physico-biogeochemical feedbacks in the atmosphere-terrestrial biosphere-ocean system. These measurements are required to help predict scenarios about future  $\text{CO}_2$  emissions, socio-economic drivers of  $\text{CO}_2$  release, and evolving mitigation/adaptation strategies.

The uptake of anthropogenic  $\text{CO}_2$  from the atmosphere by the global ocean also has significant implications for surface ocean chemistry, individual marine organisms, and ocean ecosystems. The ocean's pH is controlled by the acid-base buffering capacity of seawater that in turn is primarily controlled by equilibrium reactions of  $\text{CO}_2$  with seawater. These reactions give rise to a chemical system that involves carbonic acid [ $\text{H}_2\text{CO}_3$ ], carbonate ion [ $\text{CO}_3^{2-}$ ], and bicarbonate ion [ $\text{HCO}_3^-$ ] (Box 1; Zeebe and Wolf-Gladrow, 2001). At present, the global

ocean remains generally mildly alkaline, with a pH of surface waters typically in the range of 8.1 to 8.2. However, the uptake of anthropogenic  $\text{CO}_2$  by seawater alters the natural chemical equilibrium of the present-day seawater  $\text{CO}_2$ -carbonate system, resulting in gradual acidification of seawater in a process termed "ocean acidification" (OA; e.g., Caldeira and Wickett, 2003; Doney et al., 2009). Ocean acidification can be viewed as a decrease of the chemical bases in seawater that results in increasing protons ( $\text{H}^+$ ) and reduction of pH. It also decreases the  $\text{CO}_3^{2-}$  concentration and saturation state ( $\Omega$ ) of calcium carbonate ( $\text{CaCO}_3$ ) minerals such as calcite ( $\Omega_{\text{calcite}}$ ) and aragonite ( $\Omega_{\text{aragonite}}$ ). Such changes in seawater chemistry have complex direct and indirect impacts on marine organisms and ecosystems (e.g., Gattuso and Hansson, 2011).

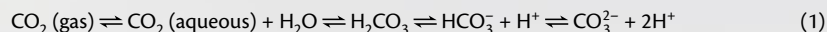
Sustained time-series observations provide a wealth of data about ocean physics and biogeochemistry that can be used to examine, test, and refine many paradigms and hypotheses about the functioning of the ocean. Such time series generate information not only about ocean warming and water cycle reorganization (e.g., salinity changes), ocean eutrophication, and ocean deoxygenation but also about changes in surface ocean chemistry. In this article, we examine recent changes in surface seawater  $\text{CO}_2$ -carbonate chemistry at the locations of seven ocean  $\text{CO}_2$  time series that have been gathering sustained observations from 15 to 30 years (Figure 1). This cohort of ocean time-series sites exhibits consistent changes in surface ocean chemistry that reflect the impact of uptake of anthropogenic  $\text{CO}_2$  and ocean acidification.

The ocean  $\text{CO}_2$  time series considered here are based on shipboard observations

and include two sites in the subpolar North Atlantic Ocean (Figure 1; Iceland Sea and Irminger Sea; Olafsson et al., 2009, 2010) and five sites in tropical/subtropical/temperate waters of the North Atlantic and Pacific Oceans (Figure 1; (1) Bermuda Atlantic Time-series Study [BATS], Bates et al., 2012; (2) European Station for Time Series in the Ocean near the Canary Islands [ESTOC], González-Dávila et al., 2010; (3) Hawaii Ocean Time-series [HOT], Dore et al., 2009; (4) Carbon Retention In A Colored Ocean [CARIACO], Cariaco Basin, Astor et al., 2005, 2013; Muller-Karger et al., 2010; Taylor et al., 2012; and (5) Munida, R/V *Munida* time series, Currie et al., 2011). While we focus here on surface observations, the entire water column from surface to near the seafloor is typically sampled with a frequency that ranges from approximately four to 16 repeat occupations of each site per year (Table 1). Thus, individual time series are integrated studies with a broad suite of sustained water-column observations, including hydrography, biogeochemistry (e.g., dissolved oxygen, inorganic nutrients, chlorophyll, and dissolved and particulate organic carbon and nitrogen), and rate measurements (including  $^{14}\text{C}$  primary production, bacterial production, and organic matter export flux), and various taxonomic and molecular observations. Therefore, our cohort of ocean  $\text{CO}_2$  time-series programs benefits from synergies and connectivity with broad understanding gained about ocean physics, biology, and chemistry at each site. As aptly noted by many earlier writers, "the sum is greater than the individual parts" when ocean time-series nodes are considered as a whole or as a nexus of scientific endeavor where substantial observations support concomitant process studies.

## BOX 1. SEAWATER CO<sub>2</sub>-CARBONATE CHEMISTRY

The chemical basis of the seawater CO<sub>2</sub>-carbonate system is the reaction of CO<sub>2</sub> with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and other carbonate species (Zeebe and Wolf-Gladrow, 2001). The chemical equilibria are defined as



Dissolved inorganic carbon (DIC) is the sum of bicarbonate ([HCO<sub>3</sub><sup>-</sup>]), carbonate ([CO<sub>3</sub><sup>2-</sup>]), and CO<sub>2</sub> in natural waters (Dickson et al., 2007) and thus defined as

$$\text{DIC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2^*] \quad (2)$$

where [CO<sub>2</sub><sup>\*</sup>] is equivalent to [CO<sub>2</sub>]<sub>aq</sub> + [H<sub>2</sub>CO<sub>3</sub>]. Total alkalinity (TA) can be defined in its simplest terms as

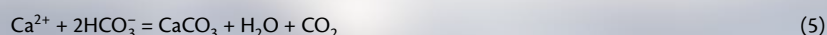
$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})^-] + [\text{OH}^-] - [\text{H}^+] + \dots \quad (3)$$

where [B(OH)<sup>-</sup>] is total borate concentration in seawater and “...” reflects a suite of minor constituents that influence alkalinity (see Dickson et al., 2007, for a full definition of alkalinity).

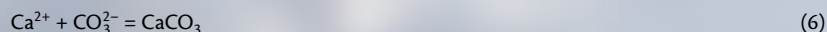
DIC, TA, pH, and pCO<sub>2</sub> (partial pressure of CO<sub>2</sub>) are the common measurable parameters, and all components of the seawater CO<sub>2</sub>-carbonate system, including [HCO<sub>3</sub><sup>-</sup>], [CO<sub>3</sub><sup>2-</sup>], and saturation states for calcium carbonate (CaCO<sub>3</sub>) minerals such as calcite (Ω<sub>calcite</sub>) and aragonite (Ω<sub>aragonite</sub>), can be computed from any two of these measured parameters. Here, Ω is defined as

$$[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{sp}} \quad (4)$$

where K<sub>sp</sub> is the solubility product of calcite and aragonite, respectively. Physico-biochemical processes such as ocean release of CO<sub>2</sub> by air-sea gas exchange or fixation of CO<sub>2</sub> via photosynthesis (i.e., primary production) act to decrease DIC and pCO<sub>2</sub> and increase pH, Ω<sub>aragonite</sub>, and Ω<sub>calcite</sub> (e.g., Zeebe and Wolf-Gladrow, 2001). In contrast, ocean uptake of CO<sub>2</sub> and respiration act oppositely (increasing DIC and pCO<sub>2</sub> and decreasing pH, Ω<sub>aragonite</sub>, and Ω<sub>calcite</sub>), while TA remains unchanged (except for minor changes associated with nitrate uptake or release). Precipitation or calcification (i.e., the formation of CaCO<sub>3</sub> in shells, tests, or skeletons of organisms) and dissolution of CaCO<sub>3</sub> are defined by



and



with calcification/CaCO<sub>3</sub> precipitation reducing TA, and dissolution increasing TA.

Seawater CO<sub>2</sub>-carbonate system parameters, including pCO<sub>2</sub> (μatm), Ω<sub>aragonite</sub> and Ω<sub>calcite</sub>, and pH (total scale) were computed from salinity (S), temperature (T), TA, and DIC data using CO2calc software (Robbins et al., 2010). The carbonic acid dissociation constants pK<sub>1</sub> and pK<sub>2</sub> (Mehrbach et al., 1973, as refit by Dickson and Millero, 1987) were used for these computations. The DIC-TA pair was typically used to calculate pCO<sub>2</sub>, pH, Ω<sub>aragonite</sub>, and Ω<sub>calcite</sub>, but other observed pairs were also used for the computation (See Table 1). We estimated the calculation error range for pCO<sub>2</sub>, pH, and Ω<sub>aragonite</sub> and Ω<sub>calcite</sub> to be ±5 μatm ± 0.001, and ± 0.02 (assuming a DIC and TA analytical error of ±2 μmol kg<sup>-1</sup>), respectively. pH is determined on the seawater scale but has no units. The Revelle factor (β) is a measure of the ocean's capacity to absorb CO<sub>2</sub> from the atmosphere or the buffer capacity of the ocean (Revelle and Suess, 1957). It is defined as the fractional change in [CO<sub>2</sub>] relative to fractional change in DIC.

$$\beta = \partial \ln [p\text{CO}_2] / \partial \ln \text{DIC} \quad (7)$$

with higher Revelle factors indicating lower capacity of the ocean to absorb CO<sub>2</sub> (see Egleston et al., 2010, for further discussion on ocean CO<sub>2</sub> buffer capacity).

Ocean Data View 4 (ODV, <http://odv.awi.de>) software was used to visualize the data.

## A BRIEF HISTORY OF SUSTAINED OCEAN CARBON CYCLE OBSERVATIONS

Sustained ocean time series began with repeated observations of select areas of the ocean and establishment of ocean weather station ship observations in the early half of the twentieth century. One of the first efforts was continuous plankton recorder (CPR) observation of ocean phytoplankton communities initiated by Sir Alistair Hardy in 1931—and continuing today (<http://www.safhos.co.uk>). The California Cooperative Oceanic Fisheries Investigations (CalCOFI; <http://www.calcofi.org>) organization was formed in 1949, and its hydrographic and biogeochemical sampling of the California coast commenced in earnest in the early 1960s; it also continues to present, as do other coastal programs, such as the Helgoland Roads time series in the North Sea (Wiltshire et al., 2010). In the open ocean, Henry Stommel of the Woods Hole Oceanographic Institution (WHOI) initiated water column sampling of hydrography (e.g., salinity, temperature) at Hydrostation S (known as the *Panulirus* site in its early days) off Bermuda in 1954 (e.g., Menzel and Ryther, 1964).

The first comprehensive survey and collection of seawater CO<sub>2</sub>-carbonate chemistry in the open ocean occurred as part of the Geochemical Ocean Sections Study (GEOSECS; Takahashi et al., 1982), and it was followed soon thereafter by annual reoccupation of ocean sections such as Line P, initiated in 1973 in the North Pacific Ocean (Wong et al., 2010). The GEOSECS program provided the foundation for subsequent scientific expeditions such as the Transient Tracers in the Ocean (TTO) expedition of the North and tropical Atlantic Oceans in the early



1980s (Brewer et al., 1985), and the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) in the late 1980s and 1990s. The initiation of time series such as BATS and HOT in the late 1980s and subsequent expansion of sustained observations around the globe owe much to these earlier efforts and to the growing recognition that understanding of the time-varying components of the ocean carbon cycle and related inorganic nutrient dynamics (e.g., nitrogen, phosphorus, and silica) required identification of the relevant physical, chemical, and ecosystem processes responsible for observed variability.

Several other factors promoted the expansion of ocean CO<sub>2</sub> time series (including repeating ocean sections) in both open-ocean and coastal environments in order to detect changes in the ocean carbon cycle due to both natural processes and anthropogenic perturbation. Improvements in chemical instrumentation (e.g., Johnson et al., 1987, 1993) allowed sample analyses to be conducted with sufficient sensitivity to detect gradual change. These developments were complemented by rigorous standard operating protocols for chemical analysis (Dickson et al., 2007) and refinement of chemical equilibria models of the seawater CO<sub>2</sub>-carbonate system (e.g., Zeebe and Wolf-Gladrow, 2001). In the early 1990s, Andrew Dickson of Scripps Institution of Oceanography (SIO) developed and distributed certified reference material (CRMs)—seawater with carefully measured and standardized DIC and TA concentrations that allowed assessments to be made of the long-term accuracy of other measurements. Incorporation of seawater CO<sub>2</sub>-carbonate chemistry data into global climatology products such as the

Global Ocean Data Project (GLODAP; Key et al., 2004; Sabine et al., 2005) and PACIFICA (PACIFIC ocean Interior Carbon; Suzuki et al., 2013) is credited as critically important for improvement of global models and for understanding

global ocean carbon cycle feedbacks and synergies necessary to detect changes in the ocean carbon cycle due to both natural processes and anthropogenic perturbation (e.g., Sabine and Tanhua, 2010; Tanhua et al., 2013).

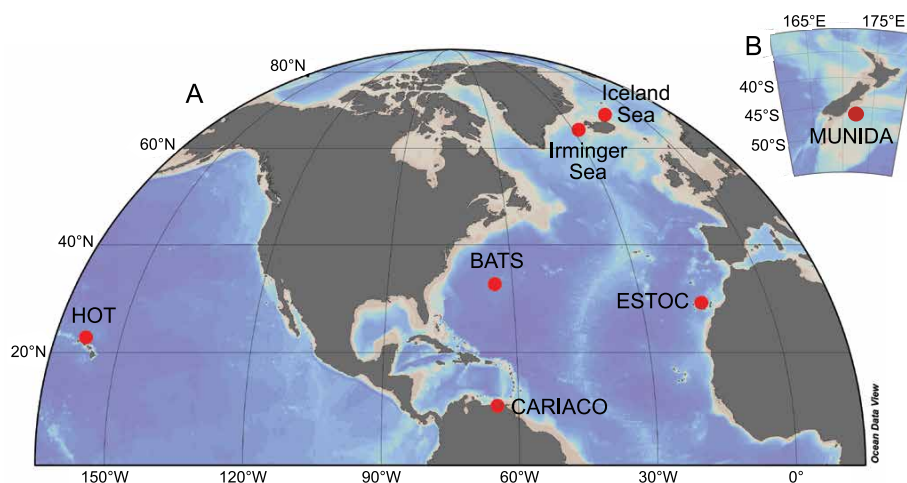


Figure 1. Location map of the seven ocean carbon time-series sites, including Iceland Sea, Irminger Sea, Bermuda Atlantic Time-series Study (BATS), European Station for Time series in the Ocean at the Canary Islands (ESTOC), Hawaii Ocean Time-series (HOT), CARbon Retention In A Colored Ocean (CARIACO), and Munida (see Table 1 for detailed information about locations and sampling frequency). Such sustained ocean carbon cycle time series complement collection of water-column hydrography and biogeochemistry (e.g., dissolved oxygen, inorganic nutrients, chlorophyll, and dissolved and particulate organic carbon and nitrogen) and rate measurements (including <sup>14</sup>C primary production, bacterial production, and export flux) at several of these sites.

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SEASONAL AND LONG-TERM CHANGES IN SURFACE SEAWATER CO<sub>2</sub>-CARBONATE CHEMISTRY

Types of Time-Series and Repeated Ocean Section CO<sub>2</sub> Observations Sustained, high-accuracy observations of seawater CO<sub>2</sub>-carbonate chemistry changes extend three decades into the past. Here, we focus on surface ocean CO<sub>2</sub> observations that have been carried out with relatively high frequency (monthly or seasonal sampling) in fixed ocean time series that include comprehensive ocean biogeochemistry and ecology data collection (Table 1; Iceland Sea, Irminger Sea, BATS, ESTOC, HOT, CARIACO, and Munida). Importantly, these ocean CO<sub>2</sub> time series contribute to understanding of the dynamics of the ocean carbon cycle and related nutrient cycles, and the continuing elucidation of the paradigms and model function of each ocean system. Several other relatively high-frequency ocean time-series sites not included in this review are DYFAMED (DYnamique des Flux Atmosphériques en MEDiterranée, Mediterranean Sea, Touratier and Goyet, 2009), KNOT (Kyodo North

Pacific Time-series, Wakita et al., 2005; Watanabe et al., 2011), and other Pacific Ocean sites (e.g., Ishii et al., 2011; Midorikawa et al., 2012). Other time-series data have also contributed to establishing long-term trends in seawater CO<sub>2</sub>-carbonate chemistry (see online Supplementary Table S1 for details), including: (1) annual reoccupations of a fixed location or ocean section (e.g., Line P, North Pacific Ocean, Wong et al., 2010; Ocean Weather Station Mike, Norwegian Sea, Skjelvan et al., 2008), (2) long-term opportunistic surface sampling efforts that are irregular in time and space but sufficient to establish long-term trends in ocean regions (e.g., surface pCO<sub>2</sub> trends; Takahashi et al., 2009; McKinley et al., 2011), and (3) lower-frequency sampling along an ocean section reoccupied through projects like WOCE and CLIVAR/CO<sub>2</sub> Repeat Hydrography (e.g., North Pacific Ocean: Byrne et al., 2010; Midorikawa et al., 2012; Rockall Trough: McGrath et al., 2012; Southern Ocean: van Heuven et al., 2011). Ocean climate stations such as HOT (Hawaii, Pacific Ocean, 2003–present), KEO (Kuroshio Extension Observatory, North Pacific Ocean,

2004–present), and Ocean Station Papa (50°N, 145°W, 2007–present) represent emerging moored surface seawater CO<sub>2</sub>-carbonate chemistry data collection systems that will provide multidecadal understanding in the future.

How to Establish Trends in Surface Seawater CO<sub>2</sub>-Carbonate Chemistry Using Irregularly Sampled Seasonal Data

The seven comprehensive surface ocean biogeochemistry and ecology time series highlighted in this paper have a frequency of occupation ranging from three or four times per year to as many as 16 times per year, often with irregularly spaced sampling times. The irregularity of sampling, non-uniform time intervals between cruises, and considerable seasonality (e.g., at BATS, Bates et al., 1996; at HOT, Dore et al., 2003; at Munida, Brix et al., 2013; Figure 2) exhibited at each time-series site complicates statistical trend analyses of seawater CO<sub>2</sub>-carbonate chemistry data. For example, at the BATS site, additional bloom cruises increase the sampling frequency to bimonthly during the January to April period, which

Table 1. Information about sustained ocean carbon cycle time series described in the text. DIC = dissolved inorganic carbon. TA = total alkalinity. pCO<sub>2</sub> = partial pressure of carbon dioxide.

Time-Series Site	Sampling Region	Location	Time Series Duration	Frequency (per year)	Principal Scientists	Ocean C Cycle Measurements
Iceland Sea	Iceland Sea	68°N, 12.66°W	1983–present	3–4	J. Olafsson	DIC/pCO <sub>2</sub>
Irminger Sea	Irminger Sea	64.3°N, 28°W	1983–present	3–4	J. Olafsson	DIC/pCO <sub>2</sub>
BATS	Sargasso Sea	32°N, 64°W	1983–present	14–16	N.R. Bates	DIC/TA
ESTOC	Canary Islands	29.04°N, 15.50°W	1995–present	4–6	M. González-Dávila, M. Santana-Casiano	DIC/TA
HOT	North Pacific	22°45'N, 158°W	1988–present	10	J. Dore, M. Church	TA/pH
CARIACO	Cariaco Basin	10°30'N, 64°40'W	1995–present	12	Y. Astor, L. Lorenzoni, F. Muller-Karger	TA/pH
Munida	South Pacific	45.7°S, 171.5°E	1998–present	~ 4–6	K. Currie, K. Hunter	pCO <sub>2</sub> /TA

Relevant Web addresses for data access:

Irminger Sea: [http://cdiac.ornl.gov/oceans/Moorings/Iceland\\_Sea.html](http://cdiac.ornl.gov/oceans/Moorings/Iceland_Sea.html)  
Iceland Sea: [http://cdiac.ornl.gov/oceans/Moorings/Irminger\\_Sea.html](http://cdiac.ornl.gov/oceans/Moorings/Irminger_Sea.html)  
BATS: <http://www.bios.edu/research/projects/bats>  
HOT: [http://hahana.soest.hawaii.edu/hot/hot\\_jgofs.html](http://hahana.soest.hawaii.edu/hot/hot_jgofs.html)

ESTOC: <http://www.eurosites.info/estoc.php>  
CARIACO: <http://www.imars.usf.edu/CAR/index.html>  
Munida: <http://cdiac.ornl.gov/oceans/Moorings/Munida.html>

can result in a statistical bias to winter observations (Bates et al., 2012). Several techniques can and should be used to seasonally detrend both hydrographic and seawater CO<sub>2</sub>-carbonate chemistry data, including harmonic detrending and comparison of differences between observations and mean climatological seasonal values at each time-series site. Here, we use the latter approach, and for better comparison have compiled mean seawater CO<sub>2</sub>-carbonate parameter values (i.e., DIC, TA, pCO<sub>2</sub>, pH, Revelle factor, and  $\Omega_{\text{aragonite}}$  values) into four seasons per year (i.e., January to March, April to June, July to September, October to December) at each individual

time-series site (Figure 2). The differences (i.e., anomalies) between observed concentrations and their climatological means are then plotted against time. This approach removes most of the seasonality observed at each time series and dampens potential seasonal bias of sampling (please note that Munida is in the Southern Hemisphere and has opposite seasonality to the Northern Hemisphere).

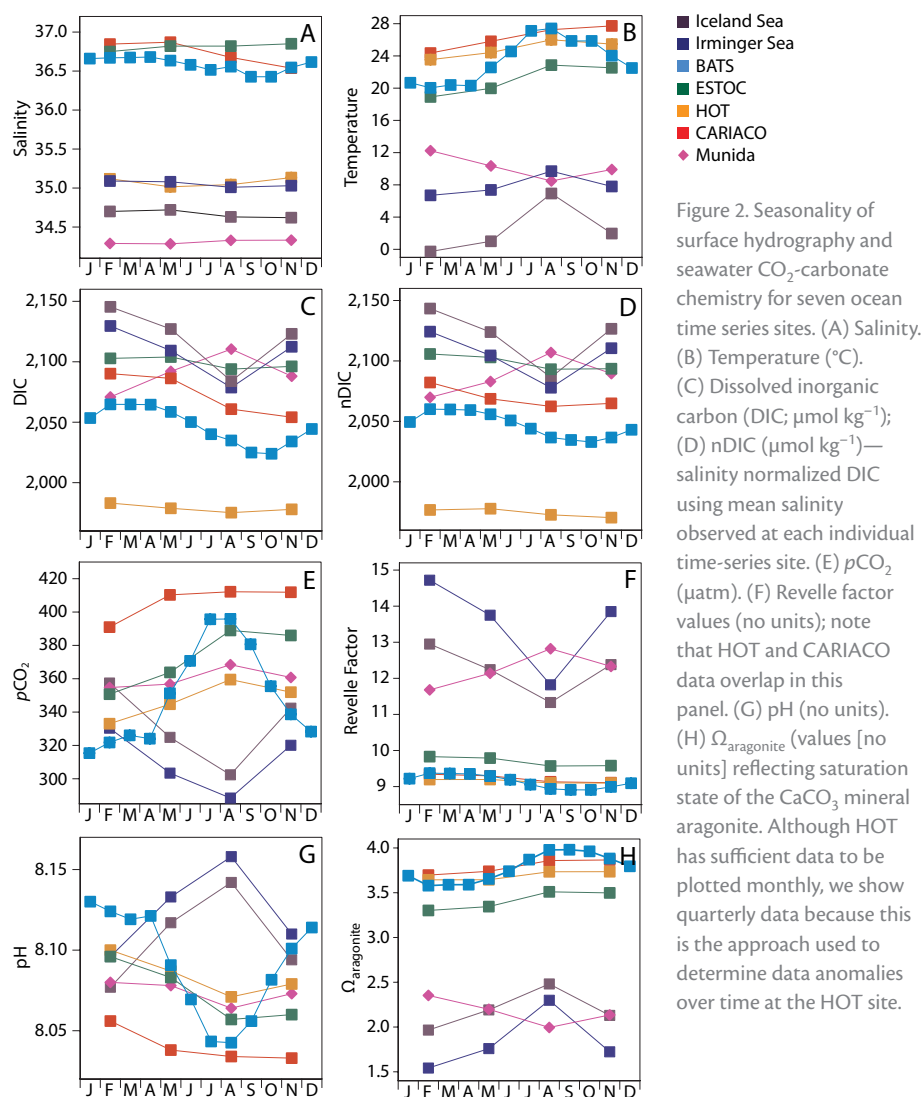
Figure 3 shows observed DIC data (shown as salinity normalized DIC, or nDIC; i.e.,  $\text{nDIC} = S_{\text{mean}}/S_{\text{observed}} \times \text{DIC}_{\text{observed}}$ ) along with nDIC anomalies against time at each time-series site (see also Figure 2 and Table 2). Normalization of DIC to the

mean observed salinity minimizes the influence of evaporation and precipitation (i.e., freshwater flux) on DIC at each time-series site. This normalization results in an increase of the  $r^2$  values of the trends and a reduction in the standard error (Table 2). The exception to this quarterly seasonal detrending in Figure 3 was for BATS data, where monthly mean climatological values were determined. For other time-series data collected at HOT and CARIACO, for example, the choice of seasonal detrending (whether quarterly or monthly) did not alter the trend analysis significantly. As Table 2 shows, the regression statistics for seasonally detrended data at several time-series sites were statistically significant.

The CO<sub>2</sub> time series are thus processed similarly here. However, it must be noted that in high-latitude waters where the seasonal CO<sub>2</sub>-chemistry changes are both large and not sinusoidal, other detrending methods may give somewhat different trend results.

### Seasonality of Hydrography and Seawater CO<sub>2</sub>-Carbonate Chemistry

The data from the ocean CO<sub>2</sub> time-series sites exhibit seawater CO<sub>2</sub>-carbonate chemistry that reflects different environments ranging from subpolar water (Iceland Sea, Irminger Sea), to sub-Antarctic surface water (Munida), to a subtropical gyre (BATS, ESTOC, HOT) and a semi-enclosed marginal tropical sea (CARIACO in the Caribbean Sea; Figure 1). Figure 2 shows mean climatological hydrographic properties (salinity and temperature), seawater CO<sub>2</sub>-carbonate chemistry parameters (DIC, nDIC, pCO<sub>2</sub>, pH, and  $\Omega_{\text{aragonite}}$ ), and the buffering capacity of the ocean (Revelle factor,  $\beta$ ) for the period of observation at each individual time-series site. The



seasonality of hydrography and the seawater CO<sub>2</sub>-carbonate system (as well as of inorganic nutrients, phytoplankton community structure, biomass, and rate of primary, new, and export production, for example) at each time-series site has been reported in many previous studies (e.g., Steinberg et al., 2001; Astor et al., 2005; Muller-Karger et al., 2010; Taylor et al., 2012; Church et al., 2013; Lorenzoni et al., 2013; see references within these papers). Here, we briefly compare the seasonality evident at the cohort of time-series sites as context for a later discussion of long-term trends in the ocean carbon cycle.

### Salinity and Temperature

Five of the time series had low salinity seasonality (< 0.1), while the BATS and CARIACO sites had considerable seasonal variability. This variability

was caused by winter mixing at BATS, upwelling at the CARIACO site, and fresher surface waters in summer/fall due to increased precipitation at both sites (Figure 2a). The latitudinal gradient between time series was pronounced for temperature, with all sites exhibiting seasonality (to ~ 8°C). The Iceland Sea (~ 6°C) and BATS (~ 8°C) had the highest seasonal temperature variability (Figure 2b).

### DIC and nDIC

The range of DIC and nDIC varied from ~ 1,980 to ~ 2,150 μmol kg<sup>-1</sup> for the seven time-series sites (Figure 2c,d). With the exception of HOT, all other time series showed considerable seasonal variability for DIC and nDIC (Figure 2c,d), ranging from < 10 to ~ 60 μmol kg<sup>-1</sup> (with the subpolar time-series sites exhibiting the largest

wintertime to summertime decrease). The seasonal changes of nDIC were notably attenuated when compared to DIC seasonality, reflecting the influence of salinity changes on DIC. The residual seasonal variability in nDIC is a composite of biological and physical processes such as net community production (NCP), air-sea CO<sub>2</sub> gas exchange, mixing, and advection that varies at each individual site (e.g., Takahashi et al., 1993, 2009; Bates, 2001, 2007; González-Dávila et al., 2007).

### pCO<sub>2</sub> and Revelle Factor

Surface pCO<sub>2</sub> ranged from ~ 280 μatm to 420 μatm (Figure 2e). The subpolar time-series sites exhibited a summertime drawdown of surface pCO<sub>2</sub> of ~ 60 μatm (due to net community production, which is similar to net primary production but typically determined geochemically over time through changes in DIC, dissolved oxygen, or inorganic nutrients; Figure 2e; Takahashi et al., 1993, 2009), while the Munida site showed a small summer decrease during the austral summer (Figure 2e; Currie et al., 2011). In contrast, the subtropical gyre sites showed summertime increases of ~ 30 μatm to 80 μatm (primarily due to the influence of seasonal warming, which was especially pronounced at the BATS site). At all of the time-series sites, except for CARIACO in the Caribbean Sea, surface seawater pCO<sub>2</sub> was lower when compared to the average range of atmospheric pCO<sub>2</sub> of ~ 375–385 μatm. All sites showed increasing surface pCO<sub>2</sub> with time due to uptake of anthropogenic CO<sub>2</sub> during the sampling period. As demonstrated in many previous studies, most of these ocean time-series sites were net annual ocean sinks for atmospheric CO<sub>2</sub>, especially during boreal summer in the subpolar gyre and boreal

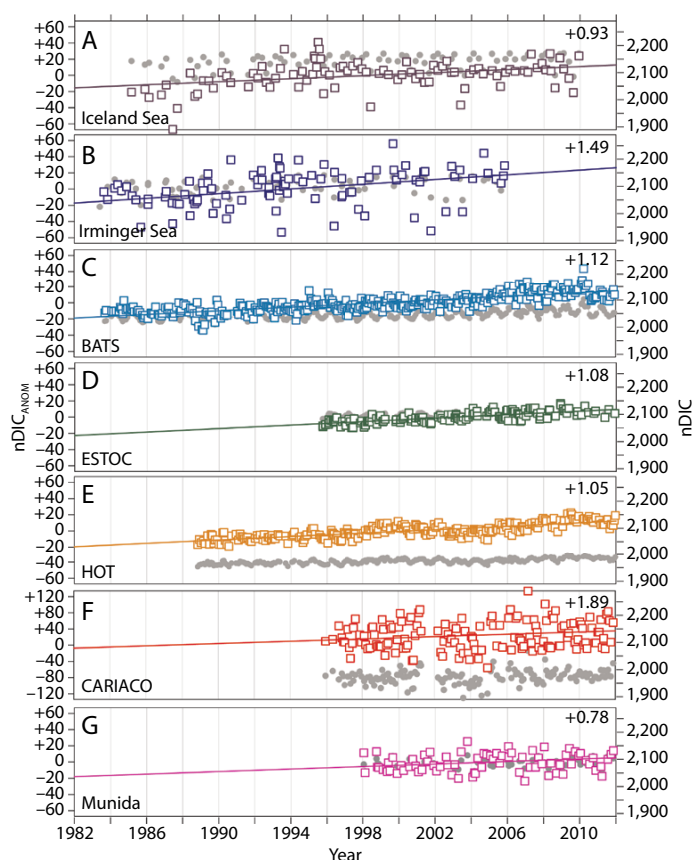


Figure 3. Time series of surface seawater anomalies of nDIC (colored symbols) and observed nDIC (gray symbols; μmol kg<sup>-1</sup>), with trends (μmol kg<sup>-1</sup> yr<sup>-1</sup>) reported in Table 2 shown in top right-hand corner of each panel. The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site. Note that the CARIACO data anomalies have a different scale than the other time series.



winter in the subtropical gyre (e.g., Winn et al., 1994; Bates, 2007; Santana-Casiano et al., 2007; Dore et al., 2009). At BATS and ESTOC, summertime warming increases surface  $p\text{CO}_2$ , so these waters seasonally transition to being net sources of  $\text{CO}_2$  to the atmosphere for a few months each year. This also occurs at the HOT site during the warmest months when the surface ocean briefly transitions to being a weak source of  $\text{CO}_2$  to the atmosphere. In contrast to the other sites, surface  $p\text{CO}_2$  at CARIACO in the Caribbean Sea was typically close to or exceeded atmospheric  $p\text{CO}_2$  values (Astor et al., 2013; this study), providing conditions favorable for release of  $\text{CO}_2$  to the atmosphere during much of the year except during times of high net community production (Astor et al., 2005; Muller-Karger et al., 2010).

The Revelle factor or buffering

capacity of surface waters was highly variable, ranging from  $\sim 9$ –10 in the subtropics to  $\sim 12$ –15 at the subpolar time-series sites where there was pronounced seasonality (Figure 2f). Similar latitudinal gradients have been shown previously (e.g., Sabine et al., 2004), with the higher Revelle factor values reflecting reduced capacity to absorb  $\text{CO}_2$  from the atmosphere. This seeming contradiction reflects the complexities of the  $\text{CO}_2$ -carbonate equilibria in seawater. At the subpolar sites, high Revelle factor values indicate relatively reduced efficiency of absorption of  $\text{CO}_2$  from the atmosphere, but the large air-sea  $\text{CO}_2$  gradients at the subpolar time series facilitate strong uptake of  $\text{CO}_2$  from the atmosphere (Olafsson et al., 2010). In contrast, subtropical waters, with lower Revelle factor values, have the highest capacity to absorb  $\text{CO}_2$  per unit volume of seawater.

### *pH and $\Omega_{\text{aragonite}}$*

Surface water pH was lowest at the CARIACO site ( $\sim 8.02$  to  $8.05$ ), while the highest seasonal values were observed at BATS and the two subpolar sites (up to  $8.16$ ; Figure 2g); pH seasonality was considerable at these latter sites. As expected from the equilibrium thermodynamics of the seawater  $\text{CO}_2$ -carbonate system, surface  $p\text{CO}_2$  and pH exhibit mirrored seasonal changes (Figure 2e,g). For  $\Omega_{\text{aragonite}}$ , large differences are evident between the subpolar sites ( $\sim 1.5$  to  $2.5$ ) and the subtropical sites ( $\sim 3.3$  to  $\sim 4.0$ ), with most sites exhibiting considerable seasonality as demonstrated for other parameters such as DIC, nDIC,  $p\text{CO}_2$ , and pH. Note that the long-term changes in pH and  $\Omega_{\text{aragonite}}$  due to ocean acidification, discussed later, have to be viewed in the context of large natural seasonal variability at most of the sites.

Table 2. (A) Seawater  $\text{CO}_2$ -carbonate seawater trends and standard error for the seven ocean time-series sites listed in Table 1. (B) Regression statistics  $r^2$  ( $r^2$  values of  $> 0.30$  are in bold type),  $n$  (number of samples), and  $p$ -value are given (\* =  $p$ -value  $< 0.01$ ; § =  $p$ -value  $> 0.01$ , not statistically significant). The seawater  $\text{CO}_2$ -carbonate seawater parameters were seasonally detrended to remove seasonality of the observations and calculated parameters. In the method, climatological mean values were determined for data collected at individual time-series sites during each of four seasons (January to March, April to June, July to September, October to December). The observed values were then compared to mean values to determine anomalies in the seawater  $\text{CO}_2$ -carbonate seawater parameters. Similar methods have been used previously to determine trends from seasonally impacted and irregularly sampled data in time (e.g., Bates et al., 2012). nDIC is salinity normalized DIC corrected to the mean salinity observed at each individual time-series site.

Time-Series Site	DIC ( $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$ )	nDIC ( $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$ )	$p\text{CO}_2$ ( $\mu\text{atm yr}^{-1}$ )	Revelle Factor	pH	$\Omega_{\text{aragonite}}$
A. Time-Series Ocean Carbon Cycle Trends						
Iceland Sea	$1.22 \pm 0.27$	$0.93 \pm 0.24$	$1.29 \pm 0.36$	$0.019 \pm 0.001$	$-0.0014 \pm 0.0005$	$-0.0018 \pm 0.0027$
Irminger Sea	$1.62 \pm 0.35$	$1.49 \pm 0.35$	$2.37 \pm 0.49$	$0.030 \pm 0.012$	$-0.0026 \pm 0.0006$	$-0.0080 \pm 0.0040$
BATS	$1.37 \pm 0.07$	$1.12 \pm 0.04$	$1.69 \pm 0.11$	$0.014 \pm 0.001$	$-0.0017 \pm 0.0001$	$-0.0095 \pm 0.0007$
ESTOC	$1.09 \pm 0.10$	$1.08 \pm 0.08$	$1.92 \pm 0.24$	$0.019 \pm 0.002$	$-0.0018 \pm 0.0002$	$-0.0115 \pm 0.0023$
HOT	$1.78 \pm 0.12$	$1.05 \pm 0.05$	$1.72 \pm 0.09$	$0.014 \pm 0.001$	$-0.0016 \pm 0.0001$	$-0.0084 \pm 0.0011$
CARIACO	$0.64 \pm 0.40$	$1.89 \pm 0.45$	$2.95 \pm 0.43$	$0.011 \pm 0.003$	$-0.0025 \pm 0.0004$	$-0.0066 \pm 0.0028$
Munida	$0.88 \pm 0.30$	$0.78 \pm 0.30$	$1.28 \pm 0.33$	$0.028 \pm 0.008$	$-0.0013 \pm 0.0003$	$-0.0085 \pm 0.0026$
B. Statistics for Above Trends ( $r^2$ , $n$ , and * = statistically significant $p$ -value $< 0.01$ level)						
Iceland Sea	0.18 (91)*	0.23 (91)*	0.14 (84)*	0.06 (83)§	0.09 (83)*	0.05 (83)§
Irminger Sea	0.18 (101)*	0.15 (101)*	0.21 (87)*	0.07 (83)*	0.18 (82)*	0.05 (83)*
BATS	<b>0.55</b> (373)*	<b>0.64</b> (373)*	<b>0.39</b> (378)*	<b>0.44</b> (378)*	<b>0.35</b> (378)*	<b>0.35</b> (378)*
ESTOC	<b>0.46</b> (152)*	<b>0.55</b> (152)*	<b>0.30</b> (152)*	<b>0.51</b> (152)*	<b>0.30</b> (152)*	<b>0.43</b> (152)*
HOT	<b>0.49</b> (232)*	<b>0.62</b> (232)*	<b>0.62</b> (232)*	<b>0.51</b> (232)*	<b>0.55</b> (232)*	<b>0.39</b> (232)*
CARIACO	$< 0.05$ (159)§	0.10 (153)*	0.24 (153)*	0.06 (153)*	0.20 (153)*	0.04 (153)*
Munida	0.10 (79)*	0.08 (79)*	0.17 (79)*	0.13 (79)*	0.16 (78)*	0.12 (79)*

## MULTIDECADAL CHANGES IN SURFACE SEAWATER CO<sub>2</sub>- CARBONATE CHEMISTRY

The longest of the ocean CO<sub>2</sub> time-series sites considered here extend back in time about 30 years. This time period is sufficient to establish seasonal and some interannual changes in seawater CO<sub>2</sub>-carbonate chemistry that reflect changes in the natural carbon cycle and anthropogenic perturbation. Over relatively short time scales (< 10 years or so), observed trends in seawater CO<sub>2</sub>-carbonate chemistry can be caused by natural variations of the carbon cycle imparted by climate modes of variability, and by variability of deep, intermediate, and mode water formation (e.g., Gruber et al., 2002; Bates et al., 2002; Bates, 2012). The impact of such phenomena on the ocean carbon cycle has been reported in many previous

studies and includes the influence of, for example, the El Niño-Southern Oscillation (ENSO; e.g., Feely et al. 1994), the North Atlantic Oscillation (NAO; e.g., Bates, 2001; Santana-Casiano et al., 2007; Levine et al., 2011), and the Pacific Decadal Oscillation (PDO; e.g., McKinley et al., 2006). Winn et al. (1994) first observed the variability of the ocean carbon cycle at HOT in response to subtropical gyre variability, and it can be seen in the quasi-decadal variation of surface DIC around the long-term trend (Dore et al., 2003, 2009).

Over multidecadal time scales, direct observations over the past 25 to 30 years indicate that surface seawater *p*CO<sub>2</sub> (and DIC) is increasing at a similar rate to the increase in atmospheric *p*CO<sub>2</sub> (Takahashi et al., 2009; McKinley et al., 2011; Bates et al., 2012). However, we are

mindful that it is difficult to assess any longer time scale impact on ocean carbon cycle variability by such phenomena as the Atlantic Multidecadal Variability (AMV; McKinley et al., 2004, 2011;) and the Atlantic Meridional Overturning Circulation. At some of the time-series sites, the statistical significance of trends is weak, but when considered with statistically significant trends evident at other time-series sites (Table 2), the cohort of time series discussed here show very similar trends. As Table 2B shows, while only BATS, ESTOC, and HOT had *r*<sup>2</sup> values > 0.30 for trends, nearly all long-term trends were statistically significant with *p*-values < 0.01. We also compare these trends to trends derived from data collected from annual and episodic reoccupation of ocean sites or sections (Supplementary Table S1). A further caveat is that trends estimated from two or more repeat occupations are likely to be subject to ocean variability and uncertainty imparted by seasonal and interannual variability, depending on the timing of sampling and the length of time between repeat occupation of ocean sections or specific ocean sites. Combined, the long-term changes in ocean CO<sub>2</sub> content (i.e., DIC, nDIC, *p*CO<sub>2</sub>, and pH, or buffer capacity indicators such as Revelle factor values) exhibit globally consistent and coherent changes in response to the uptake of anthropogenic CO<sub>2</sub> by the ocean.

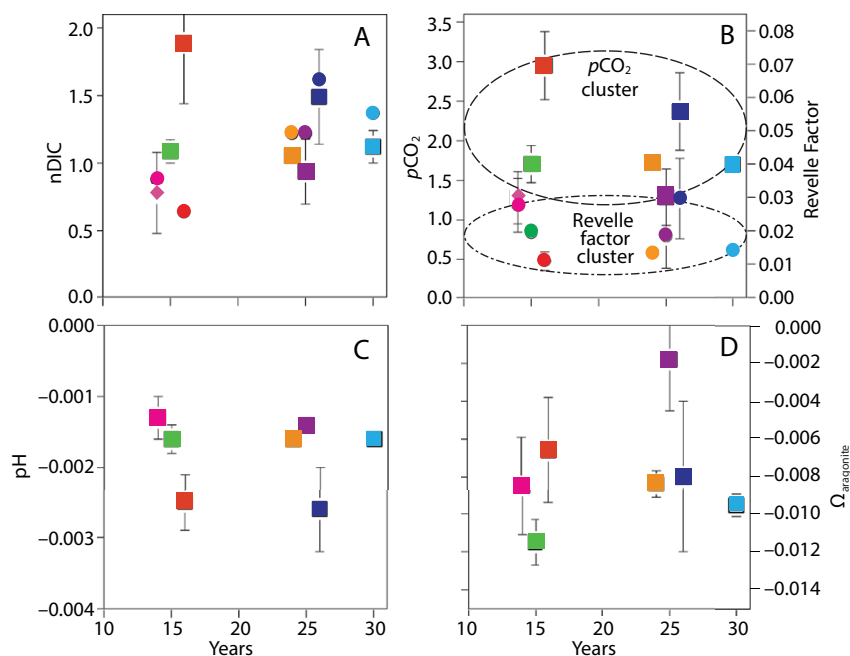


Figure 4. Trends of surface seawater CO<sub>2</sub>-carbonate chemistry for seven ocean time series plotted against length of time series (years), including: Iceland Sea (purple), Irminger Sea (blue), BATS (cyan), ESTOC (green), HOT (orange), CARIACO (red) and Munida (pink). The standard errors of the trends are also shown in the figure with the regression statistics given in Table 2. (A) nDIC (μmoles kg<sup>-1</sup> yr<sup>-1</sup>) trends indicated by square symbols. Seasonally detrended nDIC trends are also indicated for each time-series site with circle symbols. (B) *p*CO<sub>2</sub> (μatm yr<sup>-1</sup>) trends indicated by square symbols. Revelle factor (yr<sup>-1</sup>) trends are also shown for each time-series site with circle symbols. (C) pH (yr<sup>-1</sup>) trends indicated by square symbols. (D) Ω<sub>aragonite</sub> (yr<sup>-1</sup>) trends indicated by square symbols (i.e., saturation state of CaCO<sub>3</sub> mineral).

## Long-Term Trends in Surface DIC and nDIC at the Seven Time-Series Sites

At the Atlantic and Pacific Ocean time-series sites, surface/mixed-layer DIC has increased by +0.64 to +1.78 μmol kg<sup>-1</sup> yr<sup>-1</sup> (Table 2; Figures 3 and 4a), with some of this variability in trends reflecting salinity changes at

several of the sites. The nDIC trends had a slightly higher range at  $+0.78$  to  $+1.89 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (Table 2; Figures 3 and 4a). The largest increase in nDIC was observed at CARIACO, reflecting changes in the ventilation of Subtropical Underwater in the region (Astor et al., 2013). The second largest increase in nDIC was observed in the Irminger Sea and has been attributed to strengthening of winter mixing (Olafsson et al., 2010). The other time-series sites clustered at an increase of  $+0.78$  to  $+1.12 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (HOT salinity increased by  $0.005 \text{yr}^{-1}$ ;  $r^2 = 0.18$ ; all other salinity trend  $r^2$  values  $< 0.10$ ). In summary, all seven time series exhibited positive trends in nDIC that were similar to trends expected due to ocean uptake of anthropogenic  $\text{CO}_2$  (e.g., Bates et al., 2012). The increase in DIC of  $\sim 0.78$  to  $1.89 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  observed at the time-series sites represents a 1.5% to 2.5% increase over the last three decades, with larger impacts for surface  $p\text{CO}_2$  and pH as discussed later.

Long-term trends for DIC observed at sites of annual reoccupation (e.g., Line P) or episodic reoccupation sites yielded similar results to those observed at the ocean  $\text{CO}_2$  time-series sites. The range of DIC increase reported for 10 sites in the North Atlantic and Pacific Oceans was  $\sim +0.86$  to  $+2.3 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (see Supplementary Table S1) over a variety of time scales of observation ( $\sim 6$  to  $\sim 20$  years). As discussed by Tanhua et al. (2013), the shorter duration time-series data tend to chart highly variable trends, reflecting the difficulties of assessing long-term trends in regions where there is considerable short-term spatio-temporal variability and insufficient reoccupation of sites to evaluate change over time. Furthermore, the underlying interannual variability associated with climatic variations such as the NAO,

ENSO, and PDO requires that observations be made over a sufficient duration to account for their influences.

Assessment of trends from annual reoccupation of ocean sites can also be complicated if the time of sampling is not the same each year, especially in ocean regions where there is large seasonal variability (refer to earlier section on How to Establish Trends in Seawater  $\text{CO}_2$ -Carbonate Chemistry Using Irregularly Sampled Seasonal Data). Sampling along sections such as Line P are not uniform in time each year (see Supplementary Table S1), and thus long-term trends are highly influenced by larger seasonal variability (for DIC and other seawater  $\text{CO}_2$ -carbonate parameters) than the secular changes due to uptake of anthropogenic  $\text{CO}_2$  or natural ocean basin variability over time scales of a few decades. The trends in DIC increase (as well as other seawater  $\text{CO}_2$ -carbonate chemistry parameters) tend to increase along Line

P as well as in the records of other annual or episodic reoccupations that have low statistical significance. Nonetheless, they have important and meaningful value when viewed in the context of similar changes observed in the cohort of ocean  $\text{CO}_2$  time series. As discussed earlier regarding seasonality at individual time-series sites, collection of seasonal data provides a critically needed context for assessing robust trends over relatively short time scales of one to three decades.

### Long-Term Trends in Surface $p\text{CO}_2$ and Revelle Factor at the Seven Time-Series Sites: Have the Rates of Ocean Uptake of $\text{CO}_2$ and the Buffering Capacity of the Ocean Changed?

The rate of change of seawater  $p\text{CO}_2$  was  $+1.29$  to  $2.95 \mu\text{atm yr}^{-1}$  at the seven ocean  $\text{CO}_2$  time-series sites (Table 2; Figures 4b and 5) or about  $+12.9$  to  $+29.5 \mu\text{atm decade}^{-1}$ . Over the last

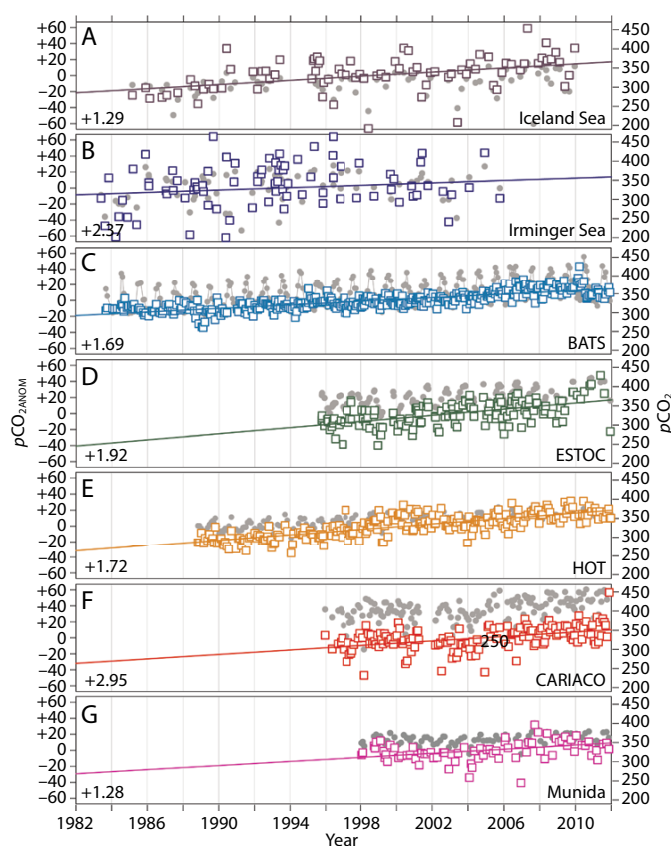


Figure 5. Time series of surface seawater anomalies of  $p\text{CO}_2$  (colored symbols) and observed  $p\text{CO}_2$  (gray symbols;  $\mu\text{atm}$ ), with trends ( $\mu\text{atm yr}^{-1}$ ) reported in Table 2 shown in bottom left-hand corner of each panel. Seawater  $\text{CO}_2$ -carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site. Note that the scale of the CARIACO data anomalies is different from that of the other time series.

30 years, surface seawater  $p\text{CO}_2$  has increased by  $\sim 15\text{--}20\%$ . At the ESTOC, HOT, and BATS sites, the increase in surface  $p\text{CO}_2$  was similar to the increase observed in atmospheric  $p\text{CO}_2$  (e.g., Dore et al., 2009; González-Dávila et al., 2010; Bates et al., 2012). These rates are also similar to those determined from the past three decades of seawater  $p\text{CO}_2$  collected from shipboard underway seawater systems (e.g., Takahashi et al., 2009; McKinley et al., 2011). At some time-series sites, surface seawater  $p\text{CO}_2$  (and DIC) has kept pace with the contemporaneous increase in atmospheric  $p\text{CO}_2$  during the last two to three decades. The implication of this finding is that one of the two primary driving forces for air-sea  $\text{CO}_2$  gas exchange ( $\Delta p\text{CO}_2$ ; the difference in  $p\text{CO}_2$  between ocean and atmosphere) has remained fairly constant across the subtropical gyres.

In the Iceland Sea, surface seawater

$p\text{CO}_2$  has not kept pace with atmospheric  $p\text{CO}_2$  over time, favoring increased uptake of  $\text{CO}_2$  from the atmosphere. Similarly, at the Munida site in the sub-Antarctic surface waters of the South Pacific Ocean off New Zealand, surface  $p\text{CO}_2$  has increased at a rate lower than that of the atmosphere (partly due to a cooling trend of  $\sim 0.3^\circ\text{C}$  per decade). In contrast, surface seawater  $p\text{CO}_2$  has increased at rates greater than the atmosphere in the Irminger Sea and in the Cariaco Basin. At the CARIACO site, earlier estimates of the trend in  $p\text{CO}_2$  have lower values ( $+1.77 \pm 0.43$ ; 1996–2008; Astor et al., 2013) than those estimated for the period 1996–2012 (Table 2). As Figure 2 shows, these trends suggest that the potential for ocean uptake of  $\text{CO}_2$  has decreased in the Irminger Sea over time, while the potential for efflux of  $\text{CO}_2$  to the atmosphere in the Caribbean Sea at CARIACO may have increased slightly in

the last few years.

The global complexity and heterogeneity of changes in surface  $p\text{CO}_2$  and sinks and sources of atmospheric/anthropogenic  $\text{CO}_2$  is further evidenced by the variability exhibited at annual reoccupation or episodic reoccupation sites (Supplementary Table S1). The rates of change vary from  $\sim 0.5$  to  $2.6 \mu\text{atm yr}^{-1}$ . The  $\Delta p\text{CO}_2$  gradients across the global ocean are highly variable over the short term, and the sink for  $\text{CO}_2$  over the last couple of decades has been decelerating or accelerating for select periods (Olsen et al., 2003; Schuster and Watson, 2007; Watson et al., 2009; Schuster et al., 2013). In the Pacific Ocean, short-term variability in  $\Delta p\text{CO}_2$  gradients and sinks and sources of  $\text{CO}_2$  appear strongly influenced by physical changes in the ocean basin (salinity changes associated with changes in evaporation versus precipitation at HOT; Dore et al., 2003; Midorikawa et al., 2005, 2012; Currie et al., 2011) and associated with ENSO and PDO changes (Feely et al., 1999, 2006; McKinley et al., 2006; Takahashi et al., 2009).

The seven ocean  $\text{CO}_2$  time series analyzed here show different trends in surface  $p\text{CO}_2$ , but, universally, they also show positive increases in the Revelle factor (Figures 4b and 6), ranging from  $+0.011 \text{ yr}^{-1}$  to  $+0.019 \text{ yr}^{-1}$ . The exception is the Irminger Sea, which exhibits greater increases in the Revelle factor of  $0.030 \text{ yr}^{-1}$ , reflecting the highest rate of surface  $p\text{CO}_2$  increases (Figure 4b). The increase in Revelle factor indicates that the buffering capacity of subtropical to subpolar surface waters to absorb  $\text{CO}_2$  has gradually reduced over time. This confirms theoretical considerations of the global ocean response to continued uptake of anthropogenic  $\text{CO}_2$  from the atmosphere. It also confirms previous

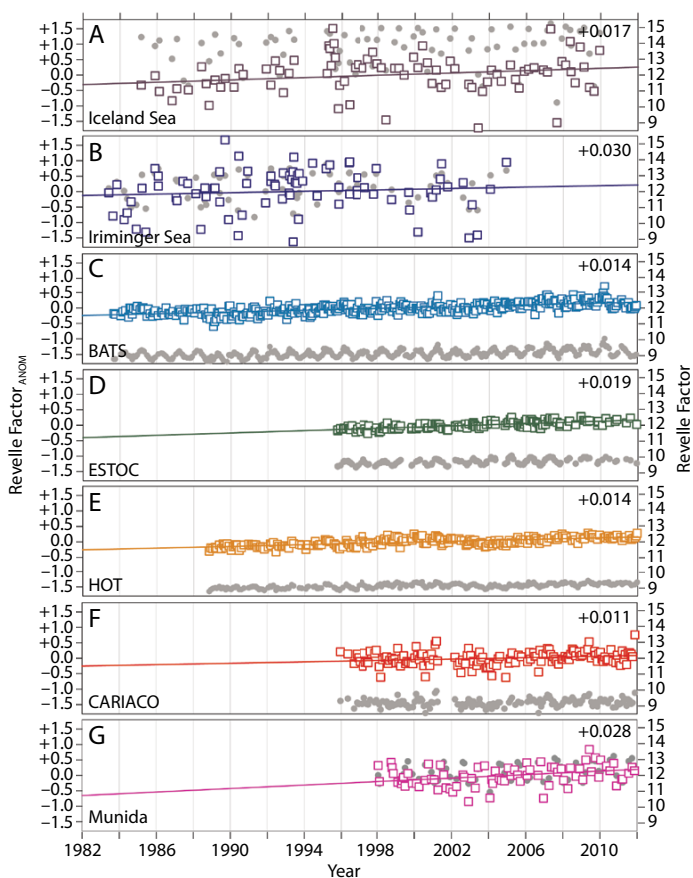


Figure 6. Time series of surface seawater anomalies of Revelle factor (buffer capacity of surface water; colored symbols) and observed Revelle factor (gray symbols; no units), with trends ( $\text{yr}^{-1}$ ) reported in Table 2 shown in top right-hand corner of each panel. Seawater  $\text{CO}_2$ -carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel, illustrating the most northerly ocean time-series site.



model studies that predict an increasing trend in Revelle factor and reduction of the ocean's capacity to absorb  $\text{CO}_2$  at the BATS site and for the North Atlantic Ocean over time (Thomas et al., 2007).

### Long-Term Trends in Surface pH and $\Omega_{\text{aragonite}}$ (A Response to Gradual Ocean Acidification)

The slow acidification of the surface ocean is evident at the seven ocean  $\text{CO}_2$  time-series sites (Figures 4c and 7; Table 2). As anticipated from model predictions on changing seawater pH due to uptake of anthropogenic  $\text{CO}_2$  (Caldeira and Wickett, 2003), surface seawater pH has declined at rates of  $-0.0013 \text{ yr}^{-1}$  to  $-0.0025 \text{ yr}^{-1}$ . Over the last three decades, such pH changes in the surface ocean indicate that the hydrogen ion concentration of the ocean has increased by  $\sim 20\%$  to  $35\%$ , depending on the ocean region. As shown for surface  $p\text{CO}_2$  time series with the highest rates of increase in  $p\text{CO}_2$  (Irminger Sea, CARIACO) have the highest rate of pH decrease (up to  $-0.0025 \text{ yr}^{-1}$  or about  $-0.025 \text{ pH decade}^{-1}$ ).

At CARIACO, lower pH is expected because of the upwelling of Subtropical Underwater, which is rich in DIC, and yet pH has continued to decrease in this region despite reduced upwelling and primary productivity decrease over the last decade (Taylor et al., 2012). The Iceland Sea, BATS, HOT, ESTOC, and Munida sites have a rather narrow range of pH decline, with rates of  $-0.0013$  to  $-0.0018 \text{ yr}^{-1}$ . Contemporaneous with such changes in ocean pH are similar declines in carbonate ion concentration ( $[\text{CO}_3^{2-}]$ , not shown here) and saturation state for calcium carbonate ( $\text{CaCO}_3$ ) minerals such as aragonite ( $\Omega_{\text{aragonite}}$ ; Figures 4d and 8).  $\Omega_{\text{aragonite}}$  values have declined at all time-series sites within

a range of  $-0.0066$  to  $-0.0115 \text{ yr}^{-1}$ . The changes in pH and  $\Omega_{\text{aragonite}}$  have long-term and gradual direct (and indirect) impacts on marine organisms and ecosystems, especially calcifiers and environments dominated by calcification or dissolution of  $\text{CaCO}_3$  (e.g., Andersson et al., 2008; Gattuso and Hansson, 2011). The long-term changes in pH and  $\Omega_{\text{aragonite}}$  superimpose their impacts (either mitigating or enhancing pH and  $\Omega_{\text{aragonite}}$  decreases) on seasonal changes observed in the open ocean (e.g., Feely et al., 1988), upwelling systems (e.g., Feely et al., 2008), or coastal environments strongly impacted by high rates of primary production and export of organic carbon (e.g., Bates et al., 2009, 2013).

## CONCLUSIONS AND OUTLOOK

Ocean  $\text{CO}_2$  time-series data are important for understanding the rate of uptake of  $\text{CO}_2$  and for ground truthing indirect

assessments of the rate of the ocean's uptake and inventories of anthropogenic  $\text{CO}_2$  (Tanhua et al., 2013). On societally relevant time scales (i.e., decades to centuries), physical, chemical, and biological processes sequester large quantities of atmospheric  $\text{CO}_2$  (including anthropogenic  $\text{CO}_2$ ) into the ocean. Several indirect methods exist to determine the rates of uptake and cumulative inventories of anthropogenic  $\text{CO}_2$  in the global ocean, including back calculation (e.g.,  $\Delta C^*$ , MIX, TrOCA) and tracer-based (e.g., transit-time distributions [TTDs] estimates; Sabine and Tanhua, 2010). Estimates of the uptake of anthropogenic  $\text{CO}_2$  vary from  $0.1$  to  $2.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$  (Tanhua et al., 2013; references therein), reflecting not only the spatio-temporal variability of sinks and sources in the global ocean (e.g., Takahashi et al., 2009) but also significant uncertainties and caveats in rate and inventory estimates

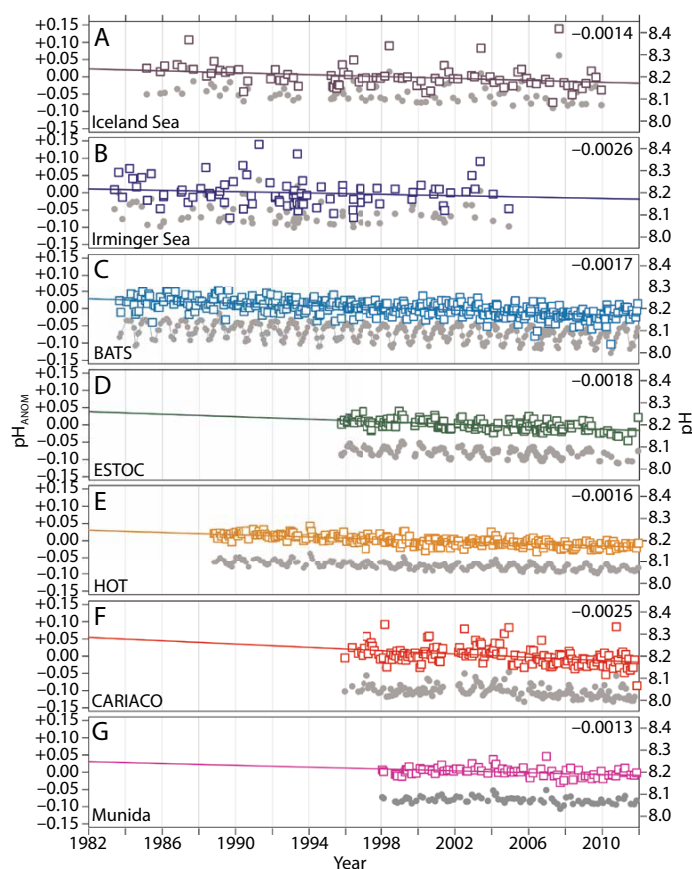


Figure 7. Time series of surface seawater anomalies of pH (colored symbols) and observed pH (gray symbols; no units), with trends ( $\text{yr}^{-1}$ ) reported in Table 2 shown in top right-hand corner of each panel. Seawater  $\text{CO}_2$ -carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site.

determined by back calculation and TTD methods. Observationally based, direct assessments of DIC or  $p\text{CO}_2$  changes over time from a variety of sustained time series are thus important to validate these indirect approaches.

The cohort of seven comprehensive ocean biogeochemistry- and ecology-based  $\text{CO}_2$  time-series sites considered here have exhibited similar changes in surface seawater chemistry over the last three decades. Although based in different geographical locations and oceanic biomes, these time series provide some of the best information we have about temporal variability of ocean  $\text{CO}_2$ , and thus provide unprecedented understanding of the response of the ocean carbon cycle to natural variability and anthropogenic perturbation. The DIC and  $p\text{CO}_2$  content of surface waters has increased in most sites at a similar rate in response

to changes in atmospheric  $p\text{CO}_2$  induced by the release of anthropogenic  $\text{CO}_2$ . The exceptions are the Irminger Sea and the CARIACO sites, where DIC and  $p\text{CO}_2$  have increased at a rate higher than expected from equilibration with increasing atmospheric  $p\text{CO}_2$  contents. This is due to the compounding effects of changes in the biological and physical factors at play at these locations (Astor et al., 2013). At the same time, the ocean's capacity to absorb  $\text{CO}_2$  from the atmosphere has declined, as evidenced by the ubiquitous increases in Revelle factor values. These observations confirm model predictions for changing surface ocean chemistry and the declining future ability of the global ocean to absorb the anthropogenic  $\text{CO}_2$  transient in the atmosphere. The cohort of seven ocean  $\text{CO}_2$  time series also exhibit significant long-term decreases in pH and

saturation states for  $\text{CaCO}_3$  minerals in response to ocean acidification and uptake of anthropogenic  $\text{CO}_2$ .

Looking into the future, climate variability and accompanying changes in ocean chemistry define a requirement for sustained, seasonally robust, long-term observations to determine rates of uptake of anthropogenic  $\text{CO}_2$ , ocean storage of anthropogenic  $\text{CO}_2$ , and the chemical context for the complex impacts on and responses of marine organisms and ecosystems to ocean acidification. Emerging technologies and autonomous sensors will complement shipboard sampling of the seawater  $\text{CO}_2$ -carbonate system in the next decade or two, providing seasonal and greater spatial context for understanding changes in the ocean carbon cycle. In time, these evolving technologies will likely provide sensors that can observe pH and  $p\text{CO}_2$  with sufficient sensitivity and accuracy to contribute to the assessment of long-term global ocean changes in seawater chemistry. New satellite-based sensors are urgently needed to accomplish repeated, frequent, long-term observations over synoptic scales. Ocean climate stations such as those at the Papa and KEO sites in the North Pacific Ocean, and data assimilation studies of existing and future surface  $p\text{CO}_2$  data such as those entrained into the Surface Ocean Carbon Atlas (SOCAT; e.g., Bakker et al., 2013), will improve understanding of the spatio-temporal variability of  $p\text{CO}_2$  (i.e., Rödenbeck et al., 2013) and of interannual changes. These data products combined with ocean time series and autonomous sensor data will provide a powerful cohort of observations that will allow detailed assessments of changing surface ocean chemistry to be made in the open ocean and coastal seas in the future.

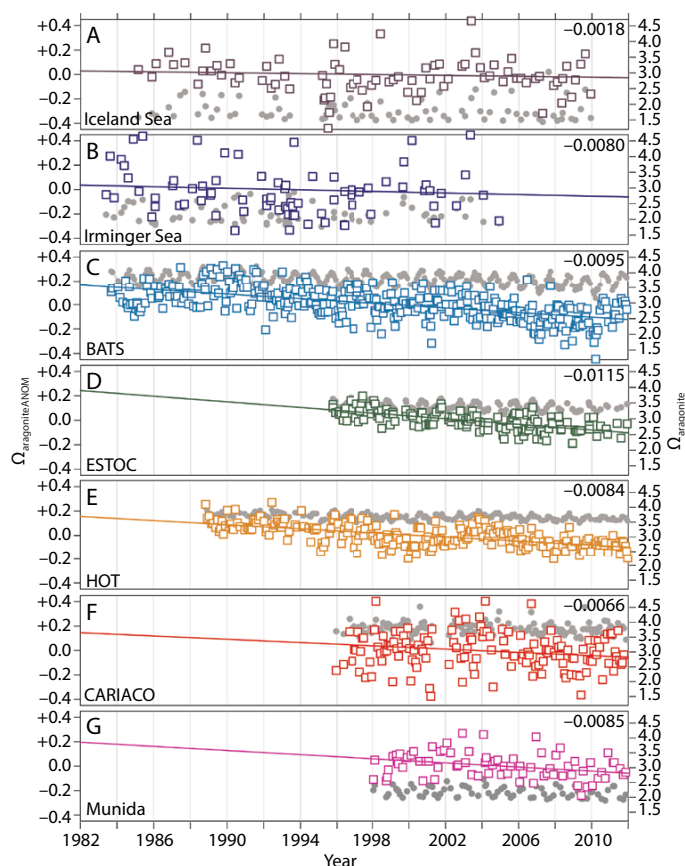



Figure 8. Time series of surface seawater anomalies of  $\Omega_{\text{aragonite}}$  (saturation state of  $\text{CaCO}_3$  mineral; colored symbols) and observed  $\Omega_{\text{aragonite}}$  (gray symbols; no units), with trends ( $\text{yr}^{-1}$ ) reported in Table 2 shown in top right-hand corner of each panel. Seawater  $\text{CO}_2$ -carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site.

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