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Spring 2024

Investigating Ocean Carbonate System Changes Across Latitudes in the North Atlantic Basin with a Time-series Mooring System

Anna Trujillo SIT Study Abroad

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Investigating Ocean Carbonate System Changes Across Latitudes in the North Atlantic Basin with a Time-series Mooring System

Anna Trujillo SIT Iceland: Climate Change and the Arctic Spring 2024

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Abstract

The world ocean, specifically the Arctic, serves as one of the greatest mitigators for anthropogenic carbon dioxide release, making the study of high latitude ocean carbonate chemistry an increasingly important topic. While much work has been done concerning the science of acidification and future model projections, analyzing data to detect decadal anthropogenic trends and effects is also highly important. Aiming to add to this data pool, this study investigated the ocean carbonate system at three North Atlantic mooring locations at polar, subtropical, and tropical latitudes from 2013 - 2021. Time series datasets of the pH and $pCO₂$ of surface water along with boundary layer air $pCO₂$ from each mooring location were analyzed, and a partial pressure ratio (pCO_2sw/pCO_2air) was calculated to investigate saturation and flux more effectively. Important findings included decreasing pH, increasing seawater $pCO₂$ and increasing air $pCO₂$ at all three moorings, along with significant correlation between seawater pCO₂ and air-sea CO₂ flux direction across all latitudes. Comparison with past research indicated clearer trends likely occur with larger data availability and strong implications for future Arctic ocean carbon uptake.

Introduction

The world ocean possesses complex and intricate systems which help balance chemical processes and fluxes. One of these is known as the ocean carbonate system, responsible for the regulation of carbon in seawater. In the face of anthropogenic activities and rising greenhouse gas levels, ocean uptake and sequestration of carbon is becoming increasingly important. Effects of carbon dioxide rise are prevalent in the carbonate system and will continue to grow as anthropogenic warming continues.

The Seawater Carbonate System

In seawater, there is a natural equilibrium between different forms of inorganic carbon known as the carbonate system (McGovern et al 2023). The four forms consist of carbonic acid (H $_2$ CO₃), bicarbonate (HCO $_3$ ⁻), carbonate (CO $_3$ ²⁻), and carbon dioxide (CO₂) (McGovern et al, 2023). The system

can be quantified by measuring at least two of four measurable variables: total alkalinity (TA), dissolved inorganic carbon (DIC), pH, and the partial pressure of $CO₂$ (pCO₂) (McGovern et al, 2023). The carbonate system creates a natural buffer capacity wherein equilibrium reactions prevent large changes in ocean acidity ("Fact," 2012; McGovern et al, 2023). This buffer capacity is the most important factor regulating the pH of the world ocean ("Fact," 2012; McGovern et al, 2023; Middleburg, Soetart, & Hagens, 2020; "Surface," 2019).

$$
CO2(g) + H2O (l) \approx H2CO3 (aq) \approx H+ (aq) + HCO3- (aq)
$$

\n
$$
CO2(g) + H2O (l) + CO32- (aq) \approx 2HCO3- (aq)
$$

\n
$$
CO32- (aq) + H+ (aq) \approx HCO3- (aq)
$$
 (McGovern et al, 2023)

As forms of inorganic carbon rise and fall, the above reactions shift to maintain equilibrium, a phenomenon which follows Le Chatelier's Principle ("Fact," 2012). In the context of anthropogenic activities, an increase in $CO₂$ causes the equilibrium to move right, resulting in an increase in hydrogen and bicarbonate ions ("Fact," 2012; McGovern et al, 2023). In general, these multiple co-occurring equilibria result in approximately 19 out of 20 of the molecules of $CO₂$ entering the ocean being converted into bicarbonate and carbonate ions (Middleburg et al, 2020). Buffer capacity is not constant throughout the world ocean; carbonate concentrations, sea surface temperature, salinity, and more can affect how well equilibrium reactions redistribute $CO₂$ and regulate ocean acidity (McGovern et al, 2023).

Ocean Acidification

pH is one of the measurable variables of the carbonate system and numerically expresses how acidic or basic a solution is. Mathematically, pH is defined as follows ("Fact," 2012; McGovern et al, 2023):

 $pH = -\log[H^*]$ (McGovern et al, 2023)

Due to the nature of the logarithmic function, small changes in pH represent large changes in hydrogen ion concentration (McGovern et al, 2023). A greater hydrogen ion concentration results in a lower pH, or a more acidic solution, and vice versa ("Fact," 2012; McGovern et al, 2023). Excluding anthropogenic forcings, larger changes in hydrogen ion concentration are generally mitigated by the ocean's buffer capacity; a large portion of H⁺ produced by dissolving carbonic acid are neutralized by carbonate ions (McGovern et al, 2023). However, carbonate ions in seawater originate from long term processes, such as weathering of carbonate minerals on land and dissolution of sediments. In extreme cases, these processes can't keep up with consumption of carbonate due to $CO₂$ uptake (McGovern et al, 2023). In such cases, hydrogen ion concentration can rise enough to produce decreases in pH, making the ocean more acidic. If sustained for long enough, the result is ocean acidification, a reduction in the pH of the ocean over an extended period of time caused primarily by the uptake of $CO₂$ from the atmosphere ("What," 2024). Areas with a lower buffer capacity are more susceptible to ocean acidification as they are less capable of

redistributing $CO₂$ and neutralizing hydrogen ions (McGovern et al, 2023). Ocean acidification has high implications for marine organisms, as many corals, pteropods, molluscs, bivalves, and fish utilize aragonite and calcite, two mineral forms of calcium carbonate, to create their shells and skeletons ("BIOACID," n.d.; McGovern et al, 2023). In an acidic solution, calcium carbonate dissolves, and therefore declining ocean pH threatens calcite and aragonite structures (McGovern et al, 2023). One way to quantify this relationship is the carbonate saturation state Ω , defined as the level of calcium carbonate saturation in seawater. ("BIOACID," n.d.). If Ω < 1, conditions are corrosive and calcium carbonate will dissolve ("BIOACID," n.d.; McGovern et al, 2023). Corals and other marine organisms benefit from a saturation state as high as 3, making declining pH a strong threat to these organisms and their ecosystem. ("BIOACID," n.d.).

The Arctic CO₂ **Sink**

The Arctic is of special importance in the context of ocean acidification, as it is a crucial carbon sink but possesses a low buffer capacity (Fransner et al, 2022; McGovern et al, 2023). Generally, CO2 is undersaturated in Arctic surface waters, creating an air-sea $CO₂$ disequilibrium which turns the flux of $CO₂$ to the ocean and positions the Arctic as a carbon sink (Jiang et al, 2019). At these high Arctic latitudes, surface waters possess a larger uptake potential due to greater CO₂ solubility in cold water (McGovern et al, 2023). Uptake potential is further increased by freshwater input from rivers, glacial runoff, and sea-ice melt (McGovern et al, 2023). Seasonally, phytoplankton blooms in the spring and strong cooling in the winter additionally increases the Arctic's potential to hold $CO₂$ (McGovern et al, 2023). Furthermore, the Arctic possesses a naturally low carbonate saturation state Ω , and freshwater melt additionally lowers saturation levels through dilution (McGovern et al, 2023). Resulting low levels of carbonate means little neutralization of hydrogen ions in equilibrium reactions (McGovern et al, 2023). These characteristics combine to pose the Arctic ocean as an area with a strong incoming $CO₂$ flux, but lacking the chemical tools to regulate large increases via equilibrium reactions.

Background

Since the industrial revolution, the effects of climate change have been observed and recorded in the ocean (Fransner et al, 2022; Wang et al, 2015; McGovern et al, 2023; Sutton et al, 2019; Yamamoto et al, 2012). Looking into the future, consequences of rising temperatures and $CO₂$ levels will dominate the natural world over the next century (Fransner et al, 2022; Jiang et al, 2019; "Surface," 2019). As the Arctic is an integral region for $CO₂$ uptake, examining how polar water responses to anthropogenic activities differ from lower latitude locations is highly important.

Declining pH and Rising pCO²

Global mean surface ocean pH has decreased by 0.1 since the industrial era $(\sim 8.2 \text{ to } 8.1)$, translating to around 30% more hydrogen ions in seawater (McGovern et al, 2023). The decrease in pH has been primarily caused by the increase in dissolved inorganic carbon due to uptake of anthropogenically released atmospheric CO₂ ("Fact," 2012; McGovern et al, 2023; "Surface," 2019).

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Figure 1: Trends in surface (< 50m) ocean carbonate chemistry. Both figures are calculated from observations obtained at the Hawaii Ocean Time-series (HOT) program in the North Pacific during 1988-2015. The upper figure shows $CO₂$ increases in the atmosphere (red) and in the surface ocean (blue) in equivalent air concentration (ppm). The bottom figure displays seawater pH (blue, primary y-axis) and carbonate ion concentration (green, secondary y-axis). (Figure from McGovern et al, 2023. Originally created by Dwight Gledhill, NOAA. Permission under CC-BY 4.0. Accessed at https://oan.

Both air $pCO₂$ and seawater $pCO₂$ display significant increases since 1980, consistent with declining pH and carbonate saturation levels (**Figure 1).** Ocean acidification from this sustained CO₂ uptake and pH drop has been occurring across the world oceans, such that decreasing pH and saturation state Ω can be identified over decadal time periods (**Figure 1,** McGovern et al, 2023). The speed with which the ocean is acidifying is "unprecedented in at least the last 66 million years," and therefore may not allow species the time to adapt to changing conditions (McGovern et al, 2023). In the Arctic region, ocean acidification is occurring faster than at global levels, with a stronger pH and Ω decline compared to lower latitudes (Fransner et al, 2022; McGovern et al, 2023; Yamamoto et al, 2012).

Future Projections

Future projections for pH, Ω , and CO₂ concentrations depend on emission scenario. For the esmRCP4.5 scenario, which roughly corresponds to the $CO₂$ reduction plan under the Paris Agreement, surface pH is simulated to drop by ~ 0.15 , reaching an average value of 7.93 ± 0.01 by 2100 (**Figure 2,** McGovern et al, 2023**)**. Under the higher esmRCP8.5 scenario, surface pH drops about 0.4-0.5 between present day and the future, with the largest decreases in polar waters (**Figure 2**).

Figure 2: pH evolution from 1850 to 2100 under different representative concentration pathways (RCPs). The Figure is separated into (a) past (1850-1980), (b) present (1981-2019), and (c) future (2020-2100). Black dots with error bars show observed annual mean pH with standard deviations, and the solid black line shows the trend from those observations. The gray, red, yellow, and blue lines show NorESM model outputs for emission driven simulations (esmRCP8.5, esmRCP4.5, and esmRCP2.6). Shading depicts the spatial variation. The vertical red bars represent pH range in CMIP5 model ensembles for historical and RCP8.5 simulations. Dashed lines display the evolution of global surface ocean pH from the same simulations. The numbers in black and blue are the calculated and significant linear trend with standard errors for 1981-2019. (Figure from Fransner et al, 2022. Permission under CC-BY 4.0. Accessed at [bg.copernicus.org/articles/19/979/2022/#abstrac](http://bg.copernicus.org/articles/19/979/2022/#abstract)t).

Spatial variability in future pH and corresponding ocean acidification is high due to the complexity of factors affecting pH, Ω , and CO₂ (Fransner et al, 2022; McGovern et al, 2023). Generally, higher emission scenarios result in a greater pH decline, greater Ω decrease, and higher CO₂ concentrations in surface waters, seen in **Figure 2 (**McGovern et al, 2023). In all scenarios, regardless of emissions, ocean acidification is projected to continue over the next century (Fransner et al, 2022; Jiang et al, 2019; McGovern et al, 2023; Pörtner et al, 2019; "Surface," 2019). Polar waters are expected to experience greater effects due to natural susceptibility to ocean acidification (Fransner et al, 2022; McGovern et al, 2023; Pörtner et al, 2019). The change in the carbonate system associated with projected pH decline would lead, in extreme cases, to corrosive waters $(Q < 1)$ for calcium carbonate structures and decreased availability of carbonate ions for marine organisms and equilibrium reactions ("BIOACID," n.d.; McGovern et al, 2023).

Reliance on ocean uptake

Rising atmospheric concentrations of $CO₂$ are tempered by oceanic uptake, and the future emission scenarios discussed above rely on the ocean to mitigate atmospheric carbon dioxide levels (McGovern et al, 2023; "Surface," 2019; Yamamoto et al, 2012). Without oceanic sequestration of CO₂, global temperatures and atmospheric greenhouse levels would be much more extreme (Pörtner et al, 2019). As discussed above, a large portion of $CO₂$ uptake occurs in polar waters where conditions are favorable. However, the capacity of ocean waters to take up anthropogenic $CO₂$ may be decreasing rapidly; the ocean's buffer capacity could decrease up to 34% by 2100 under higher emissions scenarios ("Surface," 2019). Additionally, a weakening of $pCO₂$ undersaturation of Arctic waters has been observed, meaning that surface ocean pCO_2 has risen faster than atmospheric pCO_2 in the past few decades (Fransner, 2022; McGovern et al, 2023; "Surface," 2019). A decreasing buffer capacity paired with declining $pCO₂$ undersaturation in essential polar waters suggests that while the ocean will continue to uptake $CO₂$ in the future, the proportion or rate of $CO₂$ entering the ocean will decrease ("Surface," 2019).

Past Research

In the context of increasingly pronounced acidification, projections of pH decline and $pCO₂$ rise, and possible decline of polar carbon uptake capacity, it is integral to study how the carbonate system is changing differently in Arctic waters. Past studies have been done with mooring time-series datasets to investigate how pH and pCO_2 are changing across latitudes over time (Sutton et al, 2019; Sutton et al, 2017; Sutton et al, 2014). However, at the time research was conducted, limited datasets were long enough or precise enough to estimate long-term anthropogenic trends (Sutton et al, 2019). These studies emphasize the importance of analyzing time-series data to detect significant anthropogenic impacts when datasets possess longer and more accurate measurement periods (Sutton et al, 2019). In accordance with this goal, this study attempts to expand on the importance of Arctic waters and possible trends in uptake capacity by examining carbonate systems with available time-series datasets. By analyzing pCO₂ and pH time series data from Arctic waters and lower latitude locations, this study aims to (1) determine if Arctic sensitivity to ocean acidification is apparent in data on less than decadal time periods, (2) assess changes in the saturation levels of $CO₂$ in surface waters at high and low latitudes inter annually, and (3) examine differences in carbonate system trends between the Arctic and lower latitudes on less than decadal time scales.

Data and Methods

The NOAA CO2 mooring system

In the later 2000s, the National Oceanographic and Atmospheric Administration (NOAA) began to improve their network of MAPCO₂ (Moored Autonomous Partial Pressure of $CO₂$) buoys with

additional sensors to track ocean acidification. Their mission was to evaluate the variability in air-sea CO₂ fluxes by conducting high resolution time-series measurements of atmospheric boundary layer and surface ocean CO_2 partial pressure (pCO₂) ("Buoys," n.d.). Currently, there are over 50 of these mooring locations in open-ocean, coastal, and coral reef environments collectively known as the NOAA global moored CO₂ network ("OCADS-CO2," 2022). The MAPCO₂ system includes four separate watertight cases that house the electronics, battery, transmitter, and a reference gas cylinder (**Figure 3**). An LI-820 $CO₂$ gas analyzer is used to determine $CO₂$ gas concentration through measuring the absorption of IR energy as gas flows through an optical path, shown in **Figure 3** (Sutton et al, 2014). The CO₂ concentration is determined with the difference ratio in the IR absorption between a reference and sample optical path (Sutton et al, 2014). $pCO₂$ air measurements are determined at a height of 0.5-1 m above surface water. To make seawater $CO₂$ measurements (< 0.5 m depth), the system equilibrates a closed loop of air with surface seawater in the h-shaped equilibrator (**Figure 3;** Sutton et al, 2014). While the air bubbles through the column of water, it comes to an equilibrium with the dissolved gasses in the surface seawater and can then be measured with the LI-820 detector (Sutton et al, 2014).

Figure 3: Schematic representation of main components and sampling paths and floating air-water equilibrator assembly in MAPCO₂ **System.** The left figure displays the overall system, while the right shows the floating air-water equilibrator in more detail. (Figure from Sutton et al, 2014. Permission under CC-BY 3.0. Accessed at <https://essd.copernicus.org/articles/6/353/2014/essd-6-353-2014.pdf>)

A typical MAPCO₂ measurement cycle takes approximately 20 minutes, and the system generates a zero standard at the beginning of each cycle for optimal measured values (Sutton et al, 2014). A GPS is used

for accurate position and time, and measurements are taken every 3 hours (Sutton et al, 2014). Overall uncertainty of the MAPCO₂ using in situ calibrations and standard operating procedures is $\leq 2\mu$ atm for seawater $pCO₂$ and $\leq 1 \mu$ atm for air $pCO₂$ (Sutton et al, 2014). pH is measured at 0.5 m depth with an uncertainty < 0.02 (Sutton et al, 2014). Data are quality controlled and flagged according to the SOCAT guidelines (Sutton et al, 2014). For this study, measurements of the partial pressure of $CO₂$ in the surface water, partial pressure of $CO₂$ in the boundary level air, and pH were utilized from the NOAA moored CO₂ network at specific mooring locations.

Iceland, The Gulf of Maine and La Parguera

For this study, three mooring locations were chosen from the NOAA moored CO₂ network; the Iceland mooring located at 68.0°N, 12.6°W, the Gulf of Maine (GOM) mooring located at 43.92°N, 70.54°W, and the La Parguera mooring at 17.95°N, 67.05°W. Coordinate locations are displayed in **Figure 4.**

Figure 4: North Atlantic Selected Ocean Moorings from the Global NOAA Moored CO₂ **Network.** Red location icons indicate the three moorings, each labeled with their location name. Latitude and longitude lines are in white to display a more exact location of the moorings. Yellow lines indicate degrees of importance and help position the three moorings within the climatic zones. Figure was created with Google Earth with location coordinates provided by NOAA's Moored CO₂ Network.

Iceland

The Iceland mooring is located to the northeast of the island, and was first deployed in 2013 ("Iceland," n.d.). Due to its distance from the coast of Iceland, this location falls under NOAAs open ocean mooring category ("Iceland," n.d.). The surface ocean to the northeast is dominated by the colder East Icelandic Current and the warmer North Icelandic-Irminger Current, which stems from the Gulf Stream. (Pardoe, 2009). Sea surface temperatures (SST's) in this region are currently around 0 to 4.0 ℃, sea surface salinity (SSS) ranges from 34.0 to 35.0 PSU, and pH ranges from 7.9 - 8.2. ("BGC-Argo," 2024).

The Gulf of Maine

The Gulf of Maine mooring is located about 10 km from the shore of Maine, making it a coastal mooring location ("GOM," n.d.). Data collection was initiated in 2006, with a surface seawater pH sensor added on September 9, 2010 ("GOM," n.d.). The two major surface currents in the region consist of the Labrador current, which brings cold, polar waters from the Arctic, and the Gulf Stream, which brings warm, tropical waters from the equator ("Gulf," 2023). SST's in this region are currently around 6 - 12 ℃, SSS's span from 32.0 to 34.0, and pH ranges from 7.8 to 8.2 ("BGC-Argo," 2024). **La Parguera**

The La Parguera Mooring is off the southwestern coast of Puerto Rico within the La Parguera Natural Reserve ("La," n.d.). The MAPCO₂ was deployed in this location on January 16, 2009, with a surface seawater pH sensor added in December 2011 ("La," n.d.). Due to its proximity to the coastal reef system, this mooring falls under the coral reef environment category ("La," n.d.). This region is dominated by the North Atlantic Equatorial Current which branches off into the Caribbean current, the Antilles current, and others (Oey, Ezer, & Lee, 2005). These branches flow around the Caribbean islands, into the Gulf of Mexico, and eventually rejoin to form the Gulf Stream (Oey et al, 2005). SST's in this area are around 26 - 29 °C, SSS's generally fall between 35.0 and 36.5, and pH is around 7.9 - 8.0 ("BCG-Argo," 2024)

Mooring Selection

Out of the moorings available through NOAA's moored $CO₂$ network, these three locations were optimal for this study's goal of examining how CO₂ concentrations and pH varied with latitude. Moorings were selected from the same ocean basin to minimize large scale differences in surface water qualities. The Atlantic basin was recognized as a more optimal region, as El Niño Southern Oscillation (ENSO) would likely have significant effects on decadal time series data in the Pacific (Sutton et al, 2017). The Atlantic southern hemisphere was negated so seasonality effects would be consistent. Time series activity periods were analyzed to identify mooring locations with similar measurement time scales that were recent and long enough for this study. Latitudinally, a mooring was selected from each climate zone based off of atmospheric cell placement; the Iceland moor at 68.0°N in the polar zone, the GOM moor at 43.02°N in the subtropics, and La Parguera at 17.95°N in the tropics. This allows for generalized comparison across zones, as well as organized information on climatic and oceanic conditions in each zone. These three moorings were furthermore selected due to their location relevant to the western and

warm current of the North Atlantic Subtropical Gyre, more commonly known as the Gulf Stream. Large scale base differences in SST, SSS, pH, and CO₂ content across the three mooring sites can be more easily recognized and quantified due to knowledge on how these qualities change throughout the Gulf Stream current, and therefore climatic zone separation is more easily recognized. Effects on pH and $pCO₂$ due to environmental mooring type (coastal, reef, or open ocean) should not be large enough to greatly impact wide scale changes due to anthropogenic global warming and therefore were not heavily considered when selecting mooring location (McGovern et al, 2023; Sutton et al, 2019; Sutton et al, 2014) However, it will be important to keep these differences in mind when analyzing results. The selected study time period from all three mooring locations is August 2013 - August 2021, with some gaps spanning from 2 days to 10 months. These gaps exist due to bad quality measurements, inactivity periods, or broken instruments and are left as no value entries in each data set so as not to affect results with filling techniques.

Data Analysis

Data preprocessing involved formatting no value entries, calculating the partial pressure ratio $(pCO₂ sw/pCO₂ air)$ at each location, and converting date formats to numeric representations for time series analysis. Summary statistics and boxplots were utilized to examine the spread of each dataset and to determine base states of pH, air $pCO₂$, and seawater $pCO₂$ in each location. Seasonality was examined by separating data from specific months at each mooring location; seasons were chosen from The Convention for the Protection of the Marine Environment of the North-East Atlantic ocean acidification assessment, where winter is defined as December-February, spring is defined as March-May, summer is June-August, and autumn is September-November (McGovern et al, 2023). Middle months (January, April, July, October) were chosen for optimal seasonality results. Smoothed time-series plots of seawater pCO₂ and partial pressure ratio at all moorings were created to display baseline carbonate system values at each location.

Both linear and polynomial regression models were fitted to the datasets to examine data trends, and both models produced significant results ($p < 0.05$). For overall analysis, the linear models were chosen due to a higher proportion of variability across the data being explained (higher \mathbb{R}^2). The models were used to establish trendlines for air $pCO₂$, seawater $pCO₂$, pH, and the partial pressure ratio over time for each mooring location. The significance of the trendlines was evaluated using linear regression analysis, with p-values indicating the significance of the slope and intercept, and low residuals, high \mathbb{R}^2 , and F-statistic indicating good fit. Trendlines were compared using slope and intercept values. Pearson's product-moment correlation tests were conducted to assess the relationships between $pCO₂$ in seawater and air, seawater pCO_2 and partial pressure ratio, as well as air pCO_2 and partial pressure ratio. Significant correlations were identified with p-value ($p < 0.05$) and strong correlations were ones with a correlation

coefficient greater than 0.95. Graphical analysis was further used to demonstrate correlation between seawater $pCO₂$ and partial pressure ratio.

Ethics

This study involved the analysis of publicly available data obtained from the National Oceanic and Atmospheric Administration Center for Environmental Information GlobaL CO₂ Time-Series and Moorings Project, and no interaction with human subjects was conducted. The data were freely accessible online and did not require permission for use in the context of this study. Ethical considerations related to informed consent, confidentiality, and potential harm to participants did not apply. No formal ethics review or approval was needed for this research. An IRB form was filed to ensure no ethical consideration was needed. The MAPCO₂ system should have little environmental impact if connected to the seafloor correctly, and therefore did not pose an ethical dilemma when utilizing data.

Results

Spreads, Baselines and Seasonality

The data displayed differences in the base levels of the carbonate system at each mooring location except for air pCO₂, which remained consistent regardless of latitudinal location and had little variability **(Figure 5).** Mean air pCO_2 difference between the datasets was only 14.1 *u*atm on an 8 year time scale. Seawater CO₂ partial pressure had much higher variability, with mean pCO₂ difference being 85.4 μ atm on the same timescale. As can be seen in **Figure 5,** the Maine mooring location had the largest spread of pCO₂ seawater values (\sim 300 μ atm), while Iceland and La Parguera had a similar range of \sim 150 μ atm.

Figure 5: Boxplots of CO, partial pressure time-series data at Iceland, the Gulf of Maine, and La Parguera. Air carbon dioxide partial pressure is displayed as the right box, and seawater partial pressure on the left. All y-axis possess scales of 250-550 *u*atm for easy comparison. Boxes display the interquartile range, with black lines representing the median. Maximum and minimum values are shown via T-whiskers. Outliers are excluded from the figure.

Figures 5 and 6 display that the surface water in Iceland overall had lower CO₂ partial pressure measurements than Maine and La Parguera respectively. La Parguera held much higher pCO₂ surface water measurements, while the Maine mooring fluctuated between the two (**Figure 6).** Comparing seawater partial pressure to air partial pressure revealed that the surface waters at each location differ in $CO₂$ saturation level. Iceland surface waters were dominated by a partial pressure ratio ≤ 1 , indicating undersaturation and CO₂ flux from air to sea (**Figure 6).** Contrastingly, La Parguera's partial pressure ratio was largely greater than 1 over the time series, suggesting $CO₂$ oversaturation and flux from sea to air (**Figure 6)**. The partial pressure ratio in the Gulf of Maine fluctuated around 1, indicating a more dynamic exchange of CO₂ between the air-sea interface **(Figure 6)**.

Figure 6: Seawater pCO, and Partial Pressure Ratio (pCO, sw/pCO, air) time-series data at all mooring **locations 2013-2021.** Seawater pCO_2 is depicted on the left, with partial pressure ratio on the right. pCO_2 is displayed in μ atm and the partial pressure ratio is unitless. Iceland is shown in green, Maine in blue and La Parguera in red in both figures. Data is smoothed to allow for easier comparison. Shading around lines represents the confidence interval.

Seasonality has an influence on the variability of pCO₂ values and differs between mooring locations. **Figure 7** displays the seasonal cycles of seawater carbon dioxide partial pressure over an annual term at each mooring location. The Gulf of Maine had a maximum seawater $pCO₂$ in either the Summer or Autumn, and a minimum in the Spring (**Figure 7)**. La Parguera maximum pCO₂ values occur in Summer as well, with minimum values measured in the Winter (**Figure 7)**. Contrastingly, Iceland minimum surface water pCO₂ occurred in the Summer, with maximum levels measured in the Winter (**Figure 7).**

Figure 7: Specific Month Seawater Partial Pressure Data at Iceland, the Gulf of Maine, and La Parguera 2013-2021. Iceland is shown in green, Maine in red, and La Parguera in blue. pCO_2 is displayed in μ atm for January (top left), April (top right), July (bottom left), and October (bottom right) to represent winter, spring, summer, and autumn respectively. Each dot represents a data point.

Consistently, the Gulf of Maine had the largest seasonal variation, shifting at most \sim 350 μ atm in an annual cycle (**Figure 7)**. La Parguera and Iceland displayed smaller maximum annual ranges of ~150 atm on the same timescale (**Figure 7)**. The three locations were most similar in partial pressure values in the Winter, while all other seasons displayed much larger variety by location (**Figure 7)**.

Declining pH and Rising pCO2

The data displayed significant decreasing trends in pH at all three mooring locations ($p < 0.05$, **Figure 8**). The Iceland mooring had the largest decrease (\sim 0.15) over the 8 year time period with a significant slope of -6.432e-05 (p < 0.05, **Figure 8)**. 91.98% of the variance in the Icelandic surface water pH was explained by the regression model, indicating a strong negative linear relationship between pH and time ($\mathbb{R}^2 = 0.9198$). It is important to note that the Iceland mooring location had limited pH data (2015 - 2019 = no entries), and therefore this trend may not be indicative of the 8 year period. The Gulf of Maine and La Parguera moorings displayed lower decreases in pH (\sim 0.02 - 0.05), with smaller significant slopes of -1.770e-05 and -8.162e-06 respectively (p < 0.05, **Figure 8**). While weaker than displayed by the Iceland mooring dataset, a significant negative linear relationship between pH and time was indicated at the Gulf of Maine and La Parguera.

Figure 8: pH time-series data from Iceland, the Gulf of Maine, and La Parguera 2013-2021. Raw data is displayed as black lines with gaps left unconnected and unfilled. Red lines represent trendlines calculated from the linear regression model. Y-axis is 7.9-8.4 on a total pH scale.

Initial pH levels differed based on latitudinal location; Iceland surface water pH had initial levels of \sim 8.2, Gulf of Maine initially measured at \sim 8.09 and La Parguera waters were at \sim 8.03 (**Figure 8**). At the end of the 8 year study period, all three locations were much closer, with Iceland at \sim 8.06, the Gulf of Maine at ~ 8.04, and La Parguera at ~8.02 (**Figure 8)**. This smaller spread in 2021 compared to 2013 may be indicative of changing base levels and a lessening of latitudinal impact on ocean acidity.

There were significant increasing trends in boundary layer air $pCO₂$ at all three mooring locations $(p < 0.05$, **Figure 9**). At the Iceland location, air $pCO₂$ was projected to increase by approximately 0.0075 μ atm per day over the study time period (p < 0.05). The Gulf of Maine and La Parguera had slightly smaller significant trends, with air $pCO₂$ projected to increase by approximately 0.0046 μ atm and 0.0055 *u*atm per day respectively ($p < 0.05$).

Figure 9: Air pCO₂ time-series data from Iceland, the Gulf of Maine, and La Parguera 2013-2021. Raw data is displayed as black lines with large gaps left unconnected and unfilled. Red lines represent trend lines calculated from the linear regression model. Y-axis scales are $370 - 480 \mu$ atm.

All three mooring locations shared similar initial and final air $pCO₂$ values, with an overall trend range of \sim 380 - 420 μ atm over the 8 year time period (**Figure** 9). This similarity, regardless of latitude, is consistent with the more even distribution of gaseous particles in the atmosphere and rise expected with climate change.

Similarly, there were significant increasing trends in surface water $pCO₂$ at all three mooring locations (p < 0.05, **Figure 10)**. At the Icelandic mooring and the Gulf of Maine mooring, seawater pCO₂ was projected to increase by $\sim 0.0055 \mu$ atm per day over the 8 year time period (p < 0.05). La Parguera had a larger increasing trend of $\sim 0.0098 \mu$ atm daily over the same time period (p < 0.05).

Figure 10: Seawater pCO2 time-series data from Iceland, the Gulf of Maine, and La Parguera 2013-2021. Raw data is displayed as black lines with large gaps left unconnected and unfilled. Red lines represent trend lines calculated from the linear regression model. Y-axis scales are $200-600 \mu$ atm.

Unlike air partial pressure, seawater $pCO₂$ initial and final values differed based on latitudinal location. The Iceland mooring displayed overall lowest $pCO₂$ concentrations, almost always staying below 400 μ atm over the 8 year period (**Figure 10**). Contrastingly, La Parguera pCO₂ values were largely over 400 μ atm over the study period, and the Gulf of Maine mooring pCO₂ values fluctuate above and below 400 atm (**Figure 10)**. Difference in intercept between the Gulf of Maine and Iceland was 18.564, indicating a baseline difference in CO₂ saturation level between the two locations, with the Gulf of Maine having a \sim 18.564 *u*atm greater pCO₂ level. Similarly, the difference between La Parguera and Iceland intercept is 33.226, indicating a baseline difference with La Parguera having a \sim 33.226 μ atm greater pCO₂ level. The differences in the seawater $pCO₂$ between the three moorings indicate that latitudinal position has an impact on CO₂ concentration in surface waters.

A significant increasing trend in the partial pressure ratio (pCO_2 sw/ pCO_2 air) was observed at all three mooring locations (p < 0.05, **Figure 11)**. Iceland was found to have a significant ratio increase of 9.109e-06 per day over the study period, and the Gulf of Maine and La Parguera had increases of 2.48e-06 and 9.52e-06 respectively ($p < 0.05$).

Figure 11: Partial Pressure Ratio Time-series Data from Iceland, the Gulf of Maine, and La Parguera 2013-2021. Raw data is displayed as black lines with large gaps left unconnected and unfilled. Red lines represent trend lines calculated from the linear regression model. Y-axis scales are not uniform for each graph. Data is displayed as unitless as it is a ratio.

As displayed in **Figure 6,** Iceland's partial pressure ratio is generally less than 1, indicating a state of CO₂ undersaturation in Iceland surface waters, and therefore an air-sea disequilibrium that suggests flux from air to sea. Contrastingly, La Parguera's ratio is generally over 1, suggesting a state of $CO₂$ oversaturation and flux from sea to air. The partial pressure ratio in the Gulf of Maine fluctuated around 1 over the time period, indicating a more complex saturation state based on this variable. These ratios indicate that saturation levels are dependent on latitudes, and implicate the Iceland waters as an area of $CO₂$ uptake.

Correlations

A weak significant positive correlation was found between air $pCO₂$ and seawater $pCO₂$ at the Iceland and Gulf of Maine moorings ($p < 0.05$, $0 < r < 0.4$), but statistical evidence was not strong enough to determine a significant relationship at La Parguera ($p > 0.05$). This suggests that the 8 year time period was not long enough to display the longer term variation of seawater $pCO₂$ caused by air $pCO₂$. A significant weak negative correlation was found between air $pCO₂$ and the partial pressure ratio (pCO_2 sw/pCO₂ air) at La Parguera and Maine ($p < 0.05$, $-0.4 < r < 0$), and a significant weak positive correlation was found between the same variables at the Iceland mooring ($p < 0.05$, $0 < r < 0.4$). While these correlations are significant, they likely had minimal impact on the partial pressure ratio datasets due to their weak nature, indicating that air $pCO₂$ does not display a large effect in the variability of the ratio and that air $pCO₂$ does not greatly affect the variability of seawater $pCO₂$ on this timescale.

A very strong significant positive correlation was found between seawater $pCO₂$ and the partial pressure ratio at the Iceland mooring ($p < 0.05$, $r = 0.956$), the Gulf of Maine mooring ($p < 0.05$, $r =$ 0.975), and the La Parguera mooring ($p < 0.05$, $r = 0.954$). This suggests that changes in the partial pressure ratio are closely associated with changes in the partial pressure level of $CO₂$ in the surface waters. In **Figure 13,** this correlation can be seen graphically.

Figure 13: Seawater pCO2 time-series data and Partial Pressure Ratio Time-series Data from Iceland, the Gulf of Maine, and La Parguera 2013-2021. Partial pressure ratio is displayed on the left with seawater pCO₂ on the right. Raw data is displayed as black lines with large gaps left unconnected and unfilled. Red lines represent trend lines calculated from the linear regression model. Y-axis scales are not uniform between graphs or variables.

Through side-by-side comparison, it can be seen that variations in the partial pressure ratio closely follows variations in seawater pCO₂ at all three mooring locations (**Figure 13)**. This relationship displayed through similar graphical behavior is apparent regardless of the latitudinal location, and high correlation values (> 0.95) at all three moorings imply that seawater $pCO₂$ strongly affects $CO₂$ saturation level, and therefore air-sea CO₂ flux.

Discussion

The time series data from Iceland, La Parguera, and the Gulf of Maine displayed significant trends in pH, surface water $pCO₂$ and boundary layer air $pCO₂$. These trends were often consistent with expected oceanic behavior due to anthropogenic climate change. The results of this study have important implications for future ocean carbon uptake, acidification impacts, and differences in response across latitudes.

Arctic Sensitivity, CO2 Saturation and Ocean Acidification

Surface seawater and air $pCO₂$ were found to increase significantly over the time period at all three mooring locations, consistent with rising atmospheric CO₂ levels and estimated ocean carbon uptake (Fransner et al, 2022; McGovern et al, 2023; "Surface," 2019; Sutton et al, 2019). Past studies done with the NOAA CO₂ mooring network have found that time-series data was not long enough to estimate long-term anthropogenic trends, but all three mooring locations displayed significant changes in $pCO₂$ (Sutton et al, 2019; Sutton et al, 2014). This may be due to the longer time period of measurements now available with the addition of recent years. Baseline $CO₂$ saturation level (pCO₂) in surface seawater was found to be lowest at the Icelandic mooring and highest at La Parguera, in accordance with lower DIC content found in Arctic waters as compared to lower latitudes (Fransner et al, 2022; García-Ibáñez et al, 2016; McGovern et al, 2023). Furthermore, the partial pressure ratio ($pCO_2\text{s}w/pCO_2\text{air}$) at the Iceland mooring location was generally less than 1, indicating $CO₂$ surface water undersaturation. Past research has found that Arctic surface water CO₂ content is generally lower than that of the atmosphere (partial pressure ratio < 1), making high latitude areas an important sink for atmospheric $CO₂$ (Fransner et al, 2022; García-Ibáñez et al, 2016; McGovern et al, 2023; Yamamoto et al, 2012). Compared to La Parguera (partial pressure ratio > 1) and the Gulf of Maine (partial pressure ratio ~ 1), the Iceland mooring data is consistent with past findings, indicating CO₂ flux from atmosphere to ocean and carbon storage at high latitudes.

All three partial pressure ratios were found to be increasing over the time period, indicating a trend towards surface water saturation. This trend is especially important in regard to Arctic waters, as undersaturation is necessary for ocean carbon uptake. Diminishing $pCO₂$ undersaturation has been observed in earlier research on the North Atlantic and could be a result of changes in several mechanisms, including cooling of northward flowing atlantic waters, primary production, and deep water formation (Fransner et al, 2022; McGovern et al, 2023; "Surface," 2019). It is important to note that the Iceland mooring *pCO*² air trend (+0.0075 μ atm/day) was greater than the *pCO*² sw (+0.0055 μ atm/day) even though the partial pressure ratio was found to be increasing. This disparity may be due to several factors affecting partial pressure values, such as temperature, biological productivity, and physical oceanographic processes (Fransner et al, 2022). Additionally, previous research has indicated that while the Arctic Ocean will continue to take up more $CO₂$, a decrease in buffer capacity will cause the proportion of anthropogenic carbon dioxide entering the ocean to decrease ("Fact," 2012; Jiang et al, 2019; Middleburg et al, 2020; "Surface," 2019). In other words, as the Arctic carbon sink becomes closer to CO₂ saturation, the rate at which the ocean can sequester $CO₂$ will slow. This may have caused different rates of increase that factor into why the ratio displayed an increasing trend even as $pCO₂$ *air* increased at a quicker rate than $pCO₂$ *sw*.

pH was identified to decrease at all three mooring locations over the study period, consistent with previous findings that ocean acidification is presently observable over around decadal time periods across the world oceans (Fransner et al, 2022; Garcia Ibanez et al, 2016; Jiang et al, 2019; McGovern et al, 2023). pH decline at the Iceland mooring location was greater than at the two lower latitude moorings, a pattern found in ocean acidification data with latitudinal variations, mainly due to low buffer capacity and high potential for CO₂ uptake at Arctic latitudes (Fransner et al, 2022; Garcia Ibanez et al, 2016; Jiang et al, 2019; McGovern et al, 2023). Additionally, negative mooring pH trends decreased with latitude from polar waters to subtropical waters to tropical $(-6.432e-05 < -1.770e-05 < -8.162e-06)$, a surface water pattern identified in past acidification research (Fransner et al, 2022; Garcia Ibanez et al, 2016; McGovern et al, 2023). However, pH decline identified at the Iceland moor $({\sim}$ -0.0235 yr⁻¹) was much higher than other average Arctic pH trends identified in previous research $(\sim$ -0.0021 to -0.0033 yr⁻¹) (Fransner et al, 2022; McGovern et al, 2023). This deviation may be a result of high spatial variability in Arctic waters; factors such as sea ice, currents, and temperature in specific areas have been found to cause strong ocean acidification trends such as -0.021 yr⁻¹, and therefore a specific mooring location may experience larger trends compared to the Arctic average (McGovern et al, 2023). Lack of data from 2015 - 2019 may have also contributed to the strong negative trend found at the Iceland mooring.

Variability of Seawater pCO²

Surface seawater pCO_2 had much more variation than air pCO_2 at all three mooring locations, consistent with previous research that has found $pCO₂$ of surface waters to vary up to 60% above and below atmospheric levels (Fay et al, 2021; Sutton et al, 2017; Takahashi et al, 2002). Long term variation in seawater $pCO₂$ has been found to be ultimately driven by increases in atmospheric $pCO₂$ levels. However, weak or no correlation was found between seawater $pCO₂$ and air $pCO₂$ at the three mooring locations (Fay et al, 2021; Takahashi et al, 2002). This may be due to shorter term variability of seawater $pCO₂$ having higher correlation with biological activity and seasonality fluctuations (Sutton et al, 2017; Orr J., Kwiatkowski L. & Portner H, 2022). Past research has found $pCO₂$ in surface ocean water to vary geographically and seasonally between 150-550 μ atm, consistent with seasonality spreads of \sim 100 - 400 atm between location and season identified in **Figure 7** (Takahashi et al, 2002; Wang et al, 2015)**.** Maximum $CO₂$ partial pressure was found in the winter for the Iceland mooring with minimum values in the summer, consistent with previous work observing a typical winter high and summer low in Arctic waters (Orr et al, 2022). La Parguera demonstrated the opposite trend, with maximum $pCO₂$ in the summer and minimum in the winter, again consistent with observations indicating consistently higher pCO₂ in the summer and lower in the winter at lower latitudes (Orr et al, 2022). The Gulf of Maine had less defined seasonality, with maximums occurring in both the summer and autumn, and minimums largely in the spring (**Figure 7).**

Past research has concluded that $pCO₂$ seasonality differences across latitude are likely due to the domination of different variables; in the tropics, temperature driven variations control seasonality through the CO₂ dissolution potential, whereas in polar regions seasonality is dependent on non-thermal effects such as biological activity (Orr et al, 2022; Sutton, 2017; Takahashi et al, 2002). Seasonality trends identified are consistent with these processes, as temperature spikes and biological productivity in Northern hemisphere summer would result in $pCO₂$ maximums at the equator and minimums in the poles (Orr et al, 2022; Sutton, 2017; Takahashi et al, 2002). The Gulf of Maine, being positioned in the subtropics, likely has $pCO₂$ fluctuations from both temperature and biological factors, explaining the higher variability in seasonality trends (Orr et al, 2022). Future projections indicate that Arctic seasonality may shift in coming years due to warming surface waters and sea ice coverage, with possible $pCO₂$ summer highs and winter lows at polar latitudes by 2100 (Orr et al, 2022). These shifts due to anthropogenic warming may create uniform cycles across the Atlantic Basin, such that Iceland and La Parguera would experience similar, thermally dominated pCO₂ fluctuations, and show yet another reason why Arctic regions are more sensitive to climate change driven consequences (Orr et al, 2022).

Partial Pressure Ratio Dependence

Notably high significant correlations were found between seawater $pCO₂$ and the partial pressure ratio (*pCO*₂*sw*/*pCO*₂*air*) at each mooring location, indicating that ratio value is greatly dependent on seawater CO₂ saturation level. Further enforced by the similar graphical behavior in **Figure 13,** this correlation is consistent with past research that finds the direction and magnitude of the sea-air CO₂ transfer flux at the ocean surface are mainly regulated by ocean pCO₂ (Fay et al, 2021; Orr et al, 2022; Sutton et al, 2017; Takahashi et al, 2002). The seasonal and geographical variability of surface water pCO₂ compared to atmospheric pCO₂ is identified as the main reason for this correlation (Orr et al, 2022; Takahashi et al, 2002). It is important to note that ratio dependence was present regardless of latitudinal location or mooring environment (coastal, reef, open ocean), indicating that surface ocean pCO_2 is the driving force governing $CO₂$ flux across the world oceans regardless of other surface water factors such as temperature, salinity, etc. This relationship is a considerable factor when examining future ocean trends, especially for the Arctic region where surface waters are mainly undersaturated. Seawater $pCO₂$ is influenced by a myriad of factors, including upwelling, sea-ice coverage, photosynthetic activity, surface currents, deep water formation and more, all of which are complex and difficult to conceptualize in model predictions (McGovern et al, 2023; Sutton et al, 2017; Takahashi et al, 2002; Wang et al, 2015). The correlation found between seawater $pCO₂$ and the partial pressure ratio implicates these processes as dominant influencers in air-sea $CO₂$ flux, and are therefore necessary variables to understand for future carbon uptake, ocean acidification, and CO2 saturation projections. In polar waters, where undersaturation is key for ocean uptake and atmospheric $CO₂$ mitigation, understanding these factors is even more

important as $pCO₂$ increases. Additionally, future projections of lowering buffer capacity, seasonality shifts, and decreased uptake capacity have high implications for the air-sea interface due to this correlation, and in some emission scenarios may result in a loss of the Arctic as a carbon sink (McGovern et al, 2023).

Marine Ecosystem Implications

All discussed findings and implications have high consequences for marine ecosystems. While some species may benefit from lower pH and higher $pCO₂$, most are likely to be negatively impacted as conditions shift (McGovern et al, 2023). For photosynthesizing organisms, higher $pCO₂$ and population decline of competitors may have a positive effect (McGovern et al, 2023). In general however, many marine organisms invest high amounts of energy in acid-base regulation to maintain pH homeostasis in cells and fluids; quickly changing conditions disrupt this regulation, require higher amounts of energy and put strain on marine organisms (McGovern et al, 2023). Species at high risk are marine calcifiers such as corals, mollusks, crustaceans, echinoderms, and some fish who use calcium carbonate to build their shells or skeletons (McGovern et al, 2023). The changes in the seawater carbonate system associated with the findings of this study may lead in extreme cases to corrosive water conditions $(Q < 1)$, inhibiting calcifiers from constructing shells or skeletons (McGovern et al, 2023). Additionally, a lowering buffer capacity would cause decreased availability of carbonate ions for the calcification process, furthering calcifier vulnerability (McGovern et al, 2023). Habitats that are shaped by carbonate structures or experience advanced anthropogenic impacts are under particular threat. In polar waters, biological impact is expected to be particularly high due to amplified acidification and warming conditions as well as northward species shifts (McGovern et al).

Examining biological responses across latitudes and in context with other stressors is greatly important but reveals high complexity. Additional drivers can directly influence carbonate chemistry and therefore biological response, and intricate ecosystem interactions can amplify or minimize acidification impacts (McGovern et al, 2023). Species environment determines baseline levels and natural fluctuating conditions of pH and pCO₂, and therefore 'stress' is highly relative to location (McGovern et al, 2023). Responses across and between species can depend on life history stage, gender, parental influence, adaptation to local conditions, and more (McGovern et al, 2023). Additionally, biological response may evolve over generations as ocean acidification persists, although this capacity depends on adaptation potential (McGovern et al, 2023). For several species, ocean acidification is progressing too quickly for generational adaptation, as is shown through the trends found in this 8 year study period (McGovern et al, 2023). In this regard, the emission scenario and subsequent $pH/pCO₂$ effect is highly important for biological capacity to adapt. It is integral to understand how multiple stressors and complexities will

affect marine organisms, especially as stressors often have a cumulative negative effect (McGovern et al, 2023).

Limitations and Future Research

This study was limited in scope through the use of only three mooring locations. Had data from other locations been available under the correct conditions, multiple moorings in each latitudinal zone would have been included. Different mooring environments may have further limited the study, as particularly strong ocean acidification trends are often found in near-shore and coastal regions (McGovern et al, 2023). La Parguera and Maine may therefore have had exaggerated pCO₂/pH trends compared to open water environments in their latitudinal zones. However, the usage of separate mooring environments did allow for some larger conclusions in regard to results occurring in all three habitats. Regardless, moorings from each environment type would have been included for every zone if available. Additionally, this study only looked at surface water variables; while most important for the air-sea interface and flux, pH and $pCO₂$ variation throughout the water column are necessary quantities to understand the changing ocean carbonate system. Finally, lack of previous experience combined with a large quantity of data made for a more generalized analysis. Had more time been available, more in depth statistical examination would have been carried out.

As suggested by the above limitations, further studies are necessary to fully understand pH and pCO₂ changes across latitudes. Knowledge could be gained by conducting a similar analysis with several moorings in each climatic zone. This could be done with locations spanning across the latitudinal spread, such as aiming for a mooring every 10 degrees, or with locations in different environmental regions at each zone, such as an open ocean, reef, and coastal moor every 30 degrees. While surface water qualities were central for the design of this study, future studies could be conducted with several mooring locations that measure pH and pCO₂ along the water column to better understand overall carbonate system effects. In a location such as Iceland where North Atlantic Deep Water is formed via the Atlantic Meridional Overturning Circulation (AMOC), examining how these quantities change with depth would be extremely interesting.

It would be very compelling to conduct similar studies in separate regions of the world ocean to examine how generalized the findings of this study in the North Atlantic basin are. A parallel analysis could be conducted with moorings in the southern climatic zones of the Atlantic to study the effects of continentality, seasonality, subtropical gyre and surface current location, and more on pH and pCO2. It would be important to keep in mind that the Southern Ocean is vastly different from Arctic waters at similar latitudes, and therefore pH and pCO₂ differences may be large and difficult to quantify. A possibly more significant analysis would be examining mooring locations in the North Pacific basin and comparing them to Atlantic findings to inspect Arctic sensitivity, basin dependence, and ENSO effects.

Both of these would allow for a deeper understanding of regional and worldwide carbonate system changes.

In order to accomplish the further research described above, longer and more reliable time-series datasets must be created. The 8 year time period utilized in this study was the longest available period for comparison across latitude of $pCO₂$ and pH . Carbonate system changes due to anthropogenic warming have been occurring since the atmospheric temperature rise of the industrial revolution, and while this study found significant trends and correlations, 2013-2021 is not representative of ocean impacts (McGovern et al, 2023). Furthermore, to compare hemisphere and/or ocean basin, longer term data will be necessary. The Global NOAA Moored CO₂ Network will continue recording time-series measurements to characterize natural variability and temporal trends in the ocean carbon cycle, but that data must then be utilized in analysis such as this study to understand how $pCO₂$ and pH change.

Conclusion

This study used a time series analysis approach to examine how ocean carbonate chemistry has changed differently across latitude over a less than decadal time period due to anthropogenic global warming. From the equator to the Arctic ocean, the data showed significant decreases in surface ocean pH along with significant increases of $CO₂$ partial pressure of the surface water and air. A comparison of these results to earlier studies displays the importance of continuing to analyze time series data as longer measurement periods become available. The data further showed significant correlations between the partial pressure ratio (pCO_2 *sw/pCO*₂*air*) and seawater pCO₂ at all latitudes, indicating that seawater CO₂ content is the primary factor affecting air-sea flux in the world ocean. As seawater pCO₂ was found to have much higher variation than air $pCO₂$, this correlation indicates complex variability and behavior of the air-sea interface. Trend agreement with predicted ocean behavior due to acidification was present across the data, but due to the short time period, data gaps and ocean variability nothing can be concluded for certain.

Rising ocean CO₂ content and ocean acidification makes the study of the carbonate system an increasingly important topic. With Arctic carbon uptake dependence, possible lowering buffer capacity, increasingly lower pH and subsequent marine organism stress it is unclear what the world ocean will look like by the end of the 21st century, especially at high latitude locations. While the ultimate goal with studies such as this is to advance towards conservation and adaptation, it is important to consider the possibility of a forever changed marine environment. Studying the ocean carbonate system is not only an opportunity to combat anthropogenic change, but to examine how humans may have to interact differently with the future world ocean as it shifts over the coming decades.

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