

Impact of Anthropogenic CO₂ Emissions on Surface Seawater Carbon Chemistry in the Pacific Ocean Near Hawaii (1988-2016).

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I. Motivation

Carbon dioxide levels in the atmosphere have increased substantially—by more than 20%—in less than 44 years, primarily due to human activities such as fossil fuel combustion and deforestation (U.S. Global Change Research Program, 2022). Carbon dioxide is a major greenhouse gas that contributes to global warming and disrupts the natural carbon cycle. The “Annual Greenhouse Gas Index” suggests that about 78% of the trapped heat in the atmosphere was due to increase in CO₂ (US EPA, 2017).

The Scripps Institution of Oceanography highlights the importance of accurately measuring seawater carbon dioxide to understand how much anthropogenic CO₂ from the atmosphere has been absorbed by the oceans (Dickson, A. G., 2010). The Pacific Ocean near Hawaii, a major sink for atmospheric CO₂, provides an ideal location for studying long-term interactions between atmospheric CO₂ and ocean carbon chemistry.

This project focuses on analyzing how anthropogenic CO₂ emissions, as measured by data from the Mauna Loa Observatory in Hawaii, influence surface seawater carbon chemistry. Specifically, it examines variations in dissolved inorganic carbon in the Pacific Ocean, using data collected from the Hawaii Ocean Time-series Station (ALOHA). These datasets offer critical insights into the ocean-atmosphere carbon exchange in the Pacific region and contribute to understanding the long-term implications of rising atmospheric CO₂ levels on global carbon cycling.

II. Methods

a. Data Acquisition and Description

The datasets were obtained from “The Scripps CO₂ Program” at the Scripps Institution of Oceanography, which was initiated by Charles David Keeling in 1956.

The ocean time-series data from *Hawaii Ocean Time-series (HOT) Station ALOHA* (`HAWI.mat`) contains measurements for seawater temperature and inorganic carbon chemistry from discrete bottle samples from surface seawater. ALOHA, short for A Long-Term Oligotrophic Habitat Assessment, is a research site located in the North Pacific subtropical gyre, approximately 100 kilometers (60 miles) north of the Island of Oahu, Hawaii (22.45°N, 158°W). Carbon chemistry includes the total dissolved inorganic carbon in micro mol/kg (DIC) and the reduced isotope ratio per mil ($\delta^{13}\text{C}$ -DIC). Surface water is in direct contact with the atmosphere, making it crucial for understanding carbon exchange between the ocean and the atmosphere.

The atmospheric data from *Mauna Loa Observatory, Hawaii* (19.5°N, 155.6°W) contains three separate files for different measurements: monthly flask CO₂ concentrations per mole (`monthly_flask_co2.mat`), monthly flask 13C/12C concentrations per mil (`monthly_flask_c13.mat`), and monthly flask 18O/16O concentrations per mil (`monthly_flask_o18.mat`). 13C/12C and 18O/16O are the measurements for the relative abundances of isotopes—atoms of the same element but different neutrons. Isotopic data is often used to track the sources of CO₂ and identify human contribution to rising CO₂ levels.

Monthly frequency data was selected as it is more suitable for analyzing long-term trends compared to daily frequency data. Although in-situ data measures CO₂ directly on-site using sensors in real time with very high temporal resolution, it was not chosen for this analysis because it is

better suited for short-term studies. Instead, flask data, consisting of air samples collected in flasks, was selected for long-term trend analysis due to its high precision.

b. Techniques and Procedures

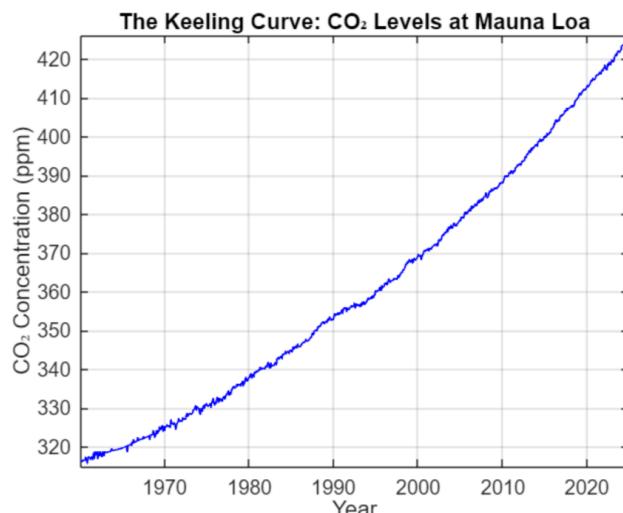
The analysis began by plotting time-series trends for atmospheric CO₂, δ13C-CO₂, and δ18O-CO₂ as well as seawater carbon chemistry variables, including DIC and δ13C-DIC from the Pacific Ocean. These plots were used to examine changes in concentration over the years. Subsequently, correlations between atmospheric CO₂ and seawater carbon chemistry were visualized to identify potential relationships. The correlation coefficient (R) was calculated and displayed as a slope to quantify the strength of these relationships. Additionally, seasonal variability and patterns in seawater DIC and temperature were also computed.

All datasets were initially downloaded as CSV files and converted into MAT files for MATLAB analysis. During the data processing phase, missing values were replaced with estimated values, and the quasi-regular seasonal cycle was removed to focus on long-term trends without distractions for the time-series and correlation analyses.

III. Results and Analysis

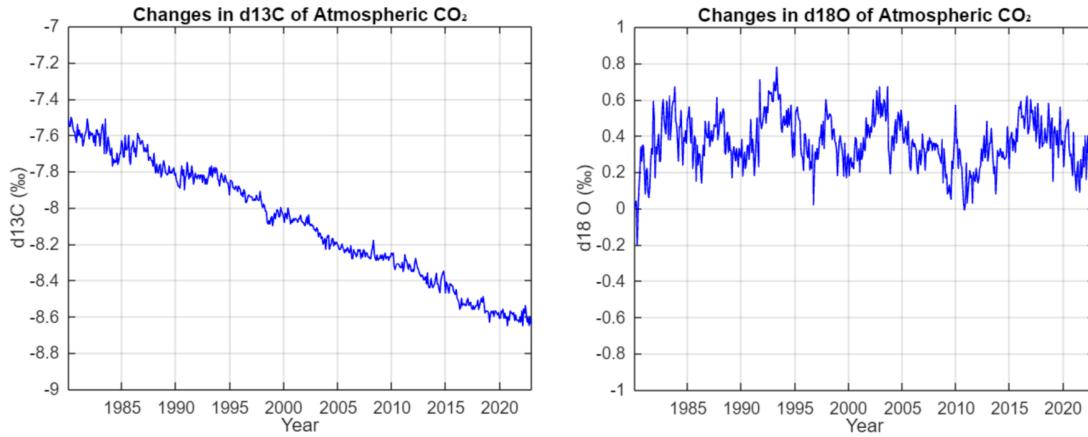
- a. Time-series analyses for atmospheric CO₂ concentration (1960-present) and isotopic ratio trends (1980-present) at Mauna Loa Observatory and seawater carbon chemistry at ALOHA over the years (1988-2016).

Fig. 1 The keeling curve (CO₂ concentrations over time)



The keeling curve was named after Charles David Keeling, it is a widely known iconic graph that depicts the long-term trend for atmospheric CO₂ concentrations at Mauna Loa, Hawaii. The curve shows an upward trend in CO₂ concentrations, starting from around 315 ppm to over 420 ppm from 1960 to the present. This reflects the increase of human activities, such as burning of fossil fuels, deforestation, and other industrial processes, which release large amounts of CO₂ into the atmosphere.

Fig. 2 (left) and **Fig. 3** (right) illustrate changes in atmospheric δ13C-CO₂ and δ18O-CO₂ concentrations from 1980 to the present.

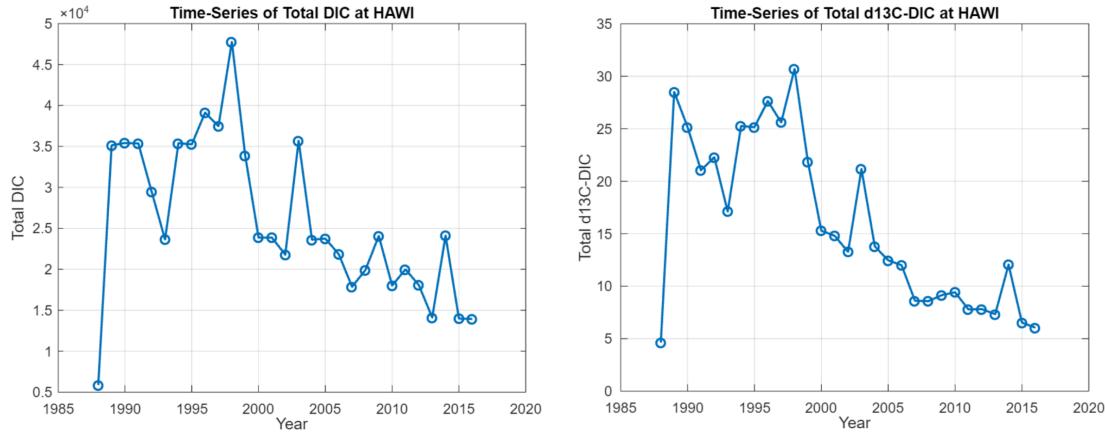


$\delta^{13}\text{C}$ (delta-13 C) refers to the ratio of two stable carbon isotopes: $^{13}\text{C}:^{12}\text{C}$.

$\delta^{18}\text{O}$ (delta-18 O) refers to the ratio of two stable oxygen isotopes: $^{18}\text{O}:^{16}\text{O}$.

In Figure 2, the data shows a clear downward trend in $d^{13}\text{C}-\text{CO}_2$ levels over the past 40 years. This decline reflects the addition of ^{12}C from fossil fuel combustion. Fossil fuels, derived from ancient organic matter, contain lower concentrations of ^{13}C compared to the atmosphere. When burned, they release carbon dioxide with a higher proportion of ^{12}C , reducing the overall atmospheric ^{13}C concentration. In contrast, the $d^{18}\text{O}-\text{CO}_2$ levels remain relatively stable over this period, showing minimal fluctuation in Figure 3.

Fig. 4 (left) and **Fig. 5** (right) depicts the time-series of total DIC and $d^{13}\text{C}-\text{DIC}$ at the station "HAWI" from 1988 to 2016.



In Figure 4, total DIC shows significant variability over the years, with an overall increase during the late 1980s and early 1990s, reaching a peak in 1998. After this peak, a gradual decline is observed, along with some fluctuations, until 2016. In Figure 5, the total $d^{13}\text{C}-\text{DIC}$ follows a similar pattern of variability but exhibits a sharper decline after its peak in 1998. When CO_2 from fossil fuels is absorbed by the ocean, it lowers the $d^{13}\text{C}-\text{DIC}$ concentration in seawater. The decreasing trend in $d^{13}\text{C}-\text{DIC}$ highlights the increasing contribution of isotopically lighter carbon, likely from fossil fuel-derived CO_2 , into the ocean.

b. **Fig. 6** (left) and **Fig. 7** (right) investigate correlations between atmospheric CO_2 & seawater carbon chemistry. The graphs plot data points by aligning CO_2 and DIC

measurements from the same year and month in the Hawaii region to ensure the accuracy of their relationship.

The correlation coefficient (R) was calculated and represented as a linear trendline to measure the strength of these relationships. $R>0.7$ indicates strong positive correlation; $0.7>R>0.3$ indicates moderate correlation, and $R<0.3$ indicates weak or no correlation.

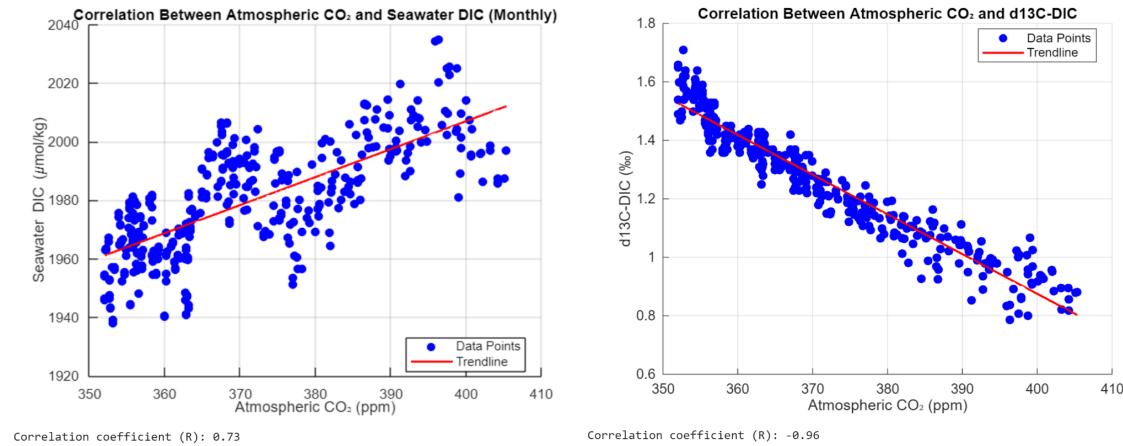
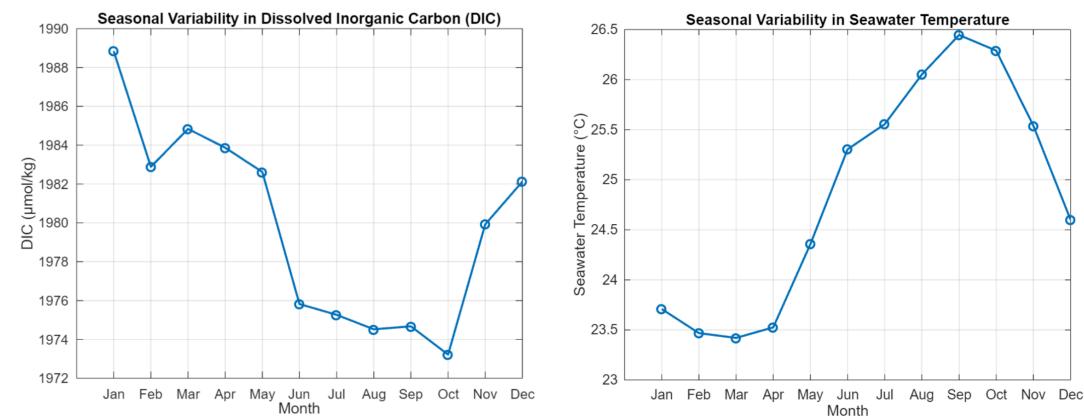


Figure 6 shows a correlation coefficient (R) of 0.73, indicating a strong positive correlation between atmospheric CO₂ and DIC in seawater. As atmospheric CO₂ concentrations increase, DIC levels in seawater also rise. This occurs because the ocean absorbs a significant portion of atmospheric CO₂, which then reacts with water to form carbonic acid. Carbonic acid dissociates into bicarbonate and carbonate ions, which are the primary components of DIC. Figure 7 shows a correlation coefficient (R) of -0.96, demonstrating a very strong negative correlation between atmospheric CO₂ and d13C-DIC in seawater. As atmospheric CO₂ concentrations increase, d13C-DIC values in seawater decrease. This occurs because a significant portion of the additional CO₂ in the atmosphere comes from the combustion of fossil fuels that contain lighter carbon isotope (d13C). When this fossil-fuel-derived CO₂ is absorbed by the ocean, it mixes with the existing dissolved inorganic carbon (DIC), diluting the d13C levels. This process leads to a reduction in the overall d13C-DIC values in surface seawater.

- c. **Fig. 8** (left) and **Fig. 9** (right) show the seasonal variability of DIC in seawater and ocean temperatures.



The plots depict an opposite relationship between DIC and seawater temperature, which implies that the concentration of DIC is the highest in winter (low seawater temperature) and lowest in summer/fall (highest seawater temperature.) This indicates that colder water can retain more dissolved CO₂, whereas rising temperatures reduce its solubility, resulting in lower DIC levels.

IV. Conclusion

Anthropogenic CO₂ emissions have increased over the last 40 years, and have impacted the surface seawater carbon chemistry in the Pacific Ocean near Hawaii. Rising atmospheric CO₂ levels, driven by fossil fuel combustion and other human activities, have increased DIC in seawater, as shown by a strong positive correlation ($R = 0.73$). Meanwhile, d13C-DIC has decreased due to the absorption of isotopically lighter carbon from fossil fuels, reflected in a strong negative correlation ($R = -0.96$).

Seasonal variations also reveal that colder seawater holds more dissolved CO₂, resulting in higher DIC during winter, while warmer temperatures in summer reduce CO₂ solubility, lowering DIC levels. These trends highlight the ocean's role as a major carbon sink, absorbing and altering atmospheric CO₂.

V. Limitation

1. The data is limited to the Pacific Ocean near Hawaii, which may not represent the global impact of CO₂ on seawater carbon chemistry.
2. The relationship between CO₂ and seawater carbon chemistry is complex and can be influenced by multiple other factors such as upwelling, ocean circulation, extreme weather and natural disaster.

References

Dickson, A. G. (2010). The carbon dioxide system in seawater: equilibrium chemistry and measurements. *Guide to best practices for ocean acidification research and data reporting*, 1, 17-40.

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