

Impact of Anthropogenic CO₂ Emissions on Surface Seawater Carbon Chemistry in the Pacific Ocean Near Hawaii (1980-2023).

Jiayi Xue

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 research project investigates the long-term impacts of rising anthropogenic CO₂ emissions on surface seawater carbon chemistry, focusing on ocean-atmosphere carbon exchange in the Pacific and its implications for global carbon cycling. Using atmospheric data from the Mauna Loa Observatory and oceanic data from the Hawaii Ocean Time-series Station (ALOHA), the study analyzes variations in dissolved inorganic carbon (DIC) to assess how increasing CO₂ influences seawater chemistry.

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 two files with different measurements: monthly flask CO₂ concentrations per mole (`monthly_flask_co2.mat`) and monthly flask $^{13}\text{C}/^{12}\text{C}$ concentrations per mil (`monthly_flask_c13.mat`). The $^{13}\text{C}/^{12}\text{C}$ ratio is the raw measurement of heavy to light carbon isotopes in a sample. However, because this ratio is a very small number and the differences between samples are subtle, it is typically expressed as $\delta^{13}\text{C}$ -CO₂ — a standardized, relative measurement that compares a sample’s $^{13}\text{C}/^{12}\text{C}$ ratio to a known reference (usually VPDB) and reports the result in per mil (‰) units. Isotopic data such as $\delta^{13}\text{C}$ -CO₂ is often used to trace the sources of rising atmospheric CO₂, such as human contributions from fossil fuel combustion. Fossil fuels, derived from ancient plant material, are depleted in ^{13}C and therefore have a low $^{13}\text{C}/^{12}\text{C}$

ratio. As fossil fuel-derived CO₂ releases into the atmosphere, it lowers the δ¹³C-CO₂. Similarly, as it absorbs in the ocean, it lowers the δ¹³C of dissolved inorganic carbon (δ¹³C-DIC) in seawater.

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.

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.

b. Techniques and Procedures

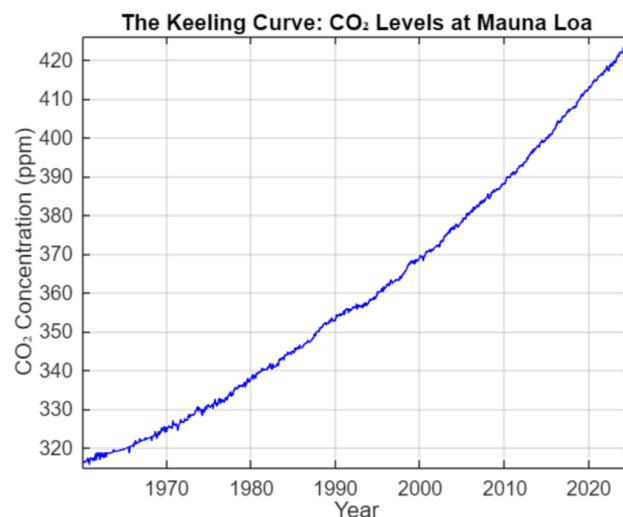
The analysis began by plotting time-series trends for atmospheric CO₂ and δ¹³C-CO₂, alongside seawater carbon chemistry metrics such as dissolved inorganic carbon (DIC) and δ¹³C-DIC from the Pacific Ocean. These plots provided a visual representation of long-term changes in concentration over the last 40 years.

To further investigate the influence of rising atmospheric CO₂ on seawater chemistry, correlation analyses were performed between atmospheric and oceanic variables. Specifically, three key relationships were examined: CO₂ vs DIC, δ¹³C-CO₂ vs δ¹³C-DIC, and CO₂ vs δ¹³C-CO₂. These plots were used to assess the strength and direction of associations between CO₂ concentration and its isotopic or dissolved counterparts in the ocean. Linear trendlines were fitted to each scatterplot, and correlation coefficients (R) were calculated to quantify the degree of linear association.

III. Results and Analysis

- Time-series analyses for atmospheric CO₂ concentration (1960-2023) and isotopic ratio trends (1980-2023) at Mauna Loa Observatory and seawater carbon chemistry at ALOHA over the years (1988-2016).

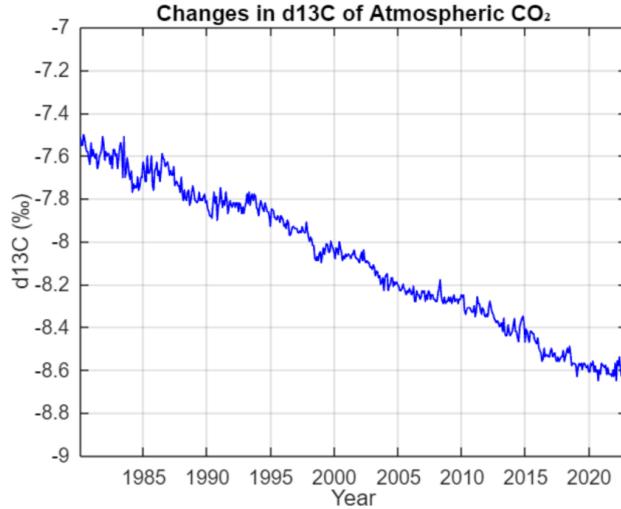
Fig. 1 The keeling curve (CO₂ concentrations over time)



The keeling curve was named after Charles David Keeling, it is a widely known iconic graph that represents the long-term trend for atmospheric CO₂ concentrations. The curve shows

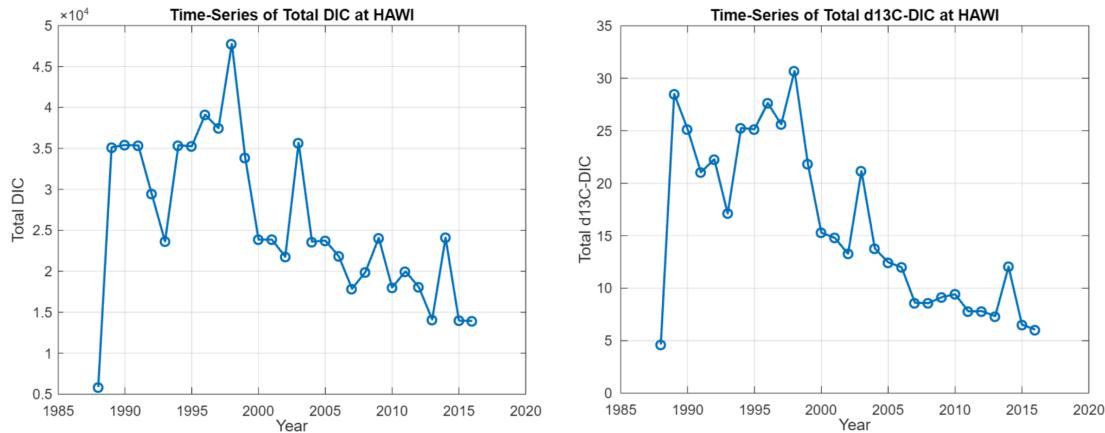
an upward trend in CO₂ concentrations, starting from around 315 ppm to over 420 ppm from 1960 to 2023. This reflects the increase of human activities, such as burning of fossil fuels, deforestation, and other industrial processes, which release large amounts of CO₂ into the atmosphere.

Fig. 2 Changes in atmospheric δ¹³C-CO₂ concentrations from 1980 to 2023



This time-series plot illustrates the long-term decline in δ¹³C-CO₂ over the past 40 years. As fossil fuel-derived CO₂ accumulates in the atmosphere, it lowers the overall δ¹³C-CO₂ values. This steady decline serves as a clear isotopic signature of rising anthropogenic CO₂ emissions.

Fig. 3 (left) and **Fig. 4 (right)** depicts the time-series of total DIC and d13C-DIC at the station "HAWI" from 1988 to 2016.



In Figure 3, 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 4, the total d13C-DIC follows a similar pattern of variability but exhibits a sharper decline after its peak in 1998. When CO₂ from fossil fuels is absorbed by the ocean, it lowers the d13C-DIC concentration in seawater. The decreasing trend in d13C-DIC highlights the increasing contribution of isotopically lighter carbon, likely from fossil fuel-derived CO₂, into the ocean.

- b. Correlation analyses between atmospheric and oceanic carbon chemistry metrics were examined: CO_2 vs DIC, $\delta^{13}\text{C}-\text{CO}_2$ vs $\delta^{13}\text{C}-\text{DIC}$, and CO_2 vs $\delta^{13}\text{C}-\text{CO}_2$. 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; $0.3 < R < 0.7$ indicates moderate correlation, and $R < 0.3$ indicates weak or no correlation.

Fig. 5 (left) CO_2 vs DIC . **Fig. 6** (right) $\delta^{13}\text{C}-\text{CO}_2$ vs $\delta^{13}\text{C}-\text{DIC}$.

The points in these scatterplots were generated by matching atmospheric and seawater measurements from the same year and month in the Hawaii region to ensure accurate temporal alignment.

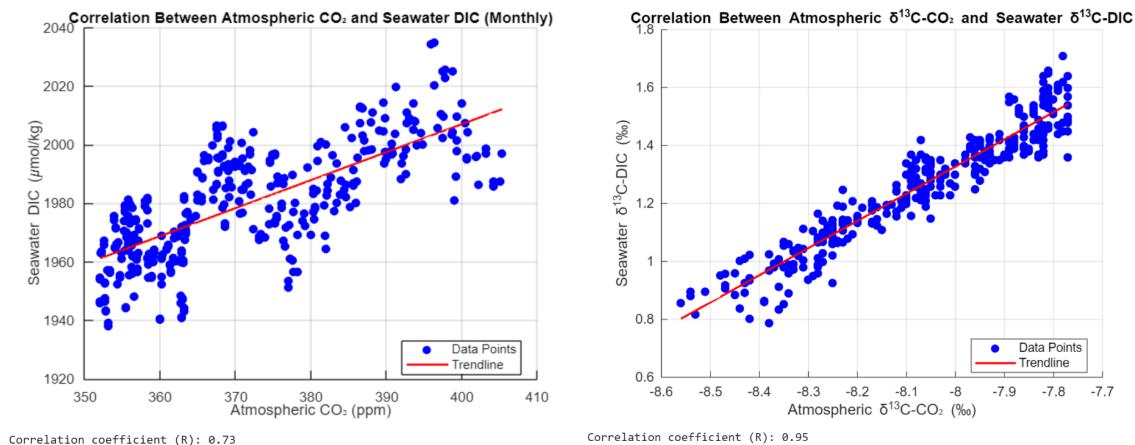
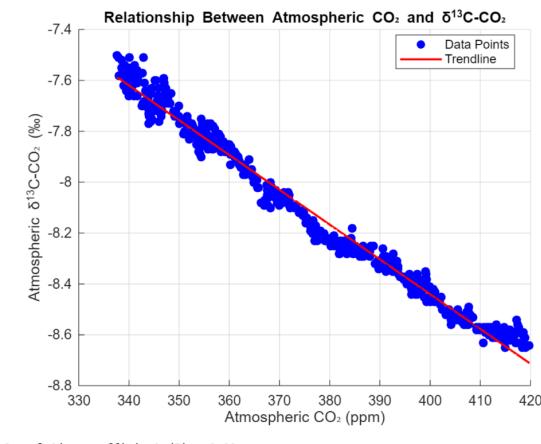


Figure 5 shows a correlation coefficient (R) of 0.73, indicating a strong positive relationship between atmospheric CO_2 and seawater DIC. As atmospheric CO_2 concentrations rise, more CO_2 dissolves into the ocean at the air-sea interface. This dissolved CO_2 reacts with water to form carbonic acid (H_2CO_3), which subsequently dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions—the primary components of DIC. This process explains the observed increase in DIC alongside rising atmospheric CO_2 . The ocean acts as a carbon sink, absorbing anthropogenic CO_2 and temporarily mitigating its buildup in the atmosphere. However, this uptake also contributes to ocean acidification, gradually altering seawater chemistry.

Figure 6 demonstrates a strong positive correlation ($R = 0.95$) between atmospheric $\delta^{13}\text{C}-\text{CO}_2$ and seawater $\delta^{13}\text{C}-\text{DIC}$, highlighting how isotopic changes in the atmosphere are mirrored in the ocean. This relationship reflects the isotopic fingerprint of anthropogenic carbon emissions. Fossil fuels are depleted in ^{13}C (containing more ^{12}C), so burning them lowers atmospheric $\delta^{13}\text{C}-\text{CO}_2$ —a phenomenon known as the Suess Effect. As the ocean absorbs this isotopically lighter CO_2 , it causes a corresponding decline in $\delta^{13}\text{C}-\text{DIC}$. Because both variables are $\delta^{13}\text{C}$ values, their comparison is isotopically meaningful and provides a powerful tracer of fossil fuel-derived carbon and air-sea carbon exchange. This strong alignment highlights the ocean's responsiveness in absorbing fossil fuel-derived CO_2 and mirroring atmospheric isotopic trends.

Fig. 7 CO₂ vs δ¹³C-CO₂



This scatterplot demonstrates a strong negative correlation ($R = -0.99$) between atmospheric CO₂ concentration (ppm) and δ¹³C-CO₂ (‰). This reflects the Suess Effect—as CO₂ increases, δ¹³C-CO₂ declines due to the rising contribution of fossil fuel emissions, which are isotopically lighter (low ¹³C/¹²C ratio). Fossil fuels—derived from ancient organic matter—are depleted in ¹³C. When burned, they release CO₂ enriched in ¹²C, lowering the δ¹³C of atmospheric CO₂.

This is not a generic chemical trend but a distinct isotopic fingerprint of anthropogenic emissions. Natural sources like volcanoes or respiration do not significantly alter δ¹³C-CO₂. This near-perfect inverse relationship confirms that the increase in atmospheric CO₂ is primarily fossil-derived, providing strong evidence of human impact on the carbon cycle.

IV. Conclusion

This study demonstrates that anthropogenic CO₂ emissions have increased over the past 40 years and have significantly altered surface seawater carbon chemistry in the Pacific Ocean near Hawaii. Analyses of CO₂, DIC, and their δ¹³C signatures reveal clear evidence of enhanced oceanic carbon uptake and isotopic shifts consistent with fossil fuel-derived CO₂. The δ¹³C-CO₂ vs. δ¹³C-DIC trend reflects isotopic fractionation driven by air-sea gas exchange and biological activity. Meanwhile, the inverse relationship between CO₂ and δ¹³C-CO₂ supports the influence of anthropogenic emissions, which are depleted in ¹³C. Together, these patterns indicate that rising CO₂ levels are altering both the quantity and isotopic composition of carbon in surface seawater, with important implications for long-term global carbon cycling.

V. Limitations

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 study only focuses on CO₂, δ¹³C-CO₂, DIC, and δ¹³C-DIC; other important variables like pH, alkalinity, temperature, and biological productivity are not included.
3. 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.

US EPA. (2017, January 23). *Climate Change Indicators: Atmospheric Concentrations of Greenhouse Gases / US EPA*. US EPA.

<https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases>.

U.S. Global Change Research Program. (2022). *Atmospheric Carbon Dioxide / GlobalChange.gov*.
[Www.globalchange.gov](http://www.globalchange.gov). <https://www.globalchange.gov/indicators/atmospheric-carbon-dioxide>