Dissolved Inorganic Carbon and $\delta^{13}C$ of the Hawaiian Ocean Time Series from 1990-2021

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2/21/2022

Abstract

As humans continue to produce large amounts of CO_2 via the burning of fossil fuels, the concentrations and isotopic signature of the ocean's dissolved inorganic carbon (DIC) is changing. Utilization of DIC and its $\delta^{13}C$ as a tracer for anthropogenic carbon at Station ALOHA has not been examined since 2017. This study modeled DIC and $\delta^{13}C$ between 1990 and 2021 and compared them to observed measurements to show that anthropogenic carbon has reached at least 200 m at Station ALOHA. Samples were collected in December of 2021 from the R/V Thomspon and analyzed in the Quay Stable Isotope Laboratory. Using historical salinity, wind, temperature, and pCO_2 data, expected DIC concentrations of the surface ocean were modeled. Over the last half decade DIC concentrations in the surface layer have increased by 20.32 μmol/kg due to anthropogenic burning of fossil fuels and the accumulation of carbon dioxide into the surface ocean at Station ALOHA has increased by 0.2 μmol/kg/yr since 2017. The average $\delta^{13}C$ values for the water column between 0 m and 1020 m have decreased by 0.63 ‰ and 0.12 ‰ on average since 1997 and 2012 respectively. The enrichment of Carbon-12 and the increase of DIC concentrations points towards increasing anthropogenic output of carbon dioxide.

Plain Language Summary

The ocean is a major sink for atmospheric carbon dioxide. As humans produce gigatons of carbon dioxide, the concentration of dissolved inorganic carbon in the ocean increases. One proxy for increased anthropogenic carbon dioxide is the relative abundance of a rare isotope of carbon known as Carbon-13. Plants prefer the much more common Carbon-12, and. since fossil fuels are fossilized plants, when fossil fuels are burned the relative abundance of Carbon-13 in the atmosphere decreases. Scientists have been tracking the relative abundance of Carbon-13 in

the ocean since 1990 at a station located 100 km of Oahu known as Station ALOHA. This study showed that not only has the abundance of Carbon-12 increased but general DIC concentrations have also increased. Not only have they increased, but the rate that they have increased is getting faster. The depth at which this anthropogenic carbon can be found has exceeded the top layer of the ocean. The consequences for this increased DIC concentrations are not entirely known, but it is known that the ocean is becoming more acidic as a side-effect of the increased DIC.

Introduction

As humans release gigatons of carbon into the atmosphere via the burning of fossil fuels, the ocean has become a sink for these emissions. Understanding the ocean's role in the global carbon cycle is key for our understanding of climate change. In order to measure the amount of anthropogenic carbon being absorbed by the ocean, the $^{13}C/^{12}C$ ratio ($\delta^{13}C$) of dissolved inorganic carbon (DIC) in the ocean could be monitored over time (Quay et al. 1992). Previous studies estimated the accumulation of anthropogenic CO_2 by measuring the increase in DIC in the ocean using measurements from the World Ocean Circulation Experiment of the 1990s and the Climate Variability and Predictability/Repeat Hydrography programs of the 2000s (Sabine and Tanhua 2010). These DIC estimates are limited by cruise tracks and therefore modeling has been used to estimate global ocean-atmosphere carbon exchange (Khatiwala et al. 2013). However, these global models still use DIC concentration to estimate anthropogenic carbon accumulation. DIC concentration estimates are limited in that they seek for small decadal variability in anthropogenic CO_2 (~10 μmol kg^{-1} decade^{-1}) in a total DIC concentration that is large and varies (~2100 μmol kg^{-1} and ~200 μmol kg^{-1}, respectively) (Quay et al. 2017). DIC concentrations can be used as an estimate of anthropogenic carbon accumulation if the seasonal variability of DIC is known for the area of interest; however, they are most effectively used in conjugation with δ^{13}C measurements (Quay et al. 1992).

As the ocean and atmosphere exchange CO_2, the ^{12}C enriched anthropogenic lowers the ocean's δ^{13}C value, this is known as the Suess effect (Körtzinger et al. 2003). The isotopic equilibrium of the ocean and atmosphere takes 10 years while CO_2 concentrations take 1 year (Körtzinger et al. 2003). The use of depth profiles allows us to consider and account for the Suess effect as deeper isopycnals will take longer to reach equilibrium than shallower ones.

δ^{13}C is an ideal tracer for anthropogenic carbon accumulation. This is due in part to the fact that δ^{13}C transport between the ocean and atmosphere ($-0.20 \pm 0.06‰\ \mathrm{decade}^{-1}$) is relatively large compared to its variability ($\pm 0.07‰$) when compared with DIC (Quay et al. 2007). This makes the δ^{13}C signal more distinct relative to seasonal changes than DIC (Quay et al. 2007) which is one major advantage over the use of DIC alone as signals often fall within the seasonal variability of DIC concentrations (Khatiwala et al. 2013). δ^{13}C is the ratio of ^{13}C/^{12}C as calculated by

$$\delta^{13}\mathrm{C} = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} - 1\right) * 1000‰$$

Fossil fuels have a depleted amount of ^{13}C due to plants' preferential use of the lighter ^{12}C (Körtzinger et al. 2003). As humans burn fossil fuels, carbon is released into the atmosphere that has a lower δ^{13}C value and eventually makes its way into the ocean

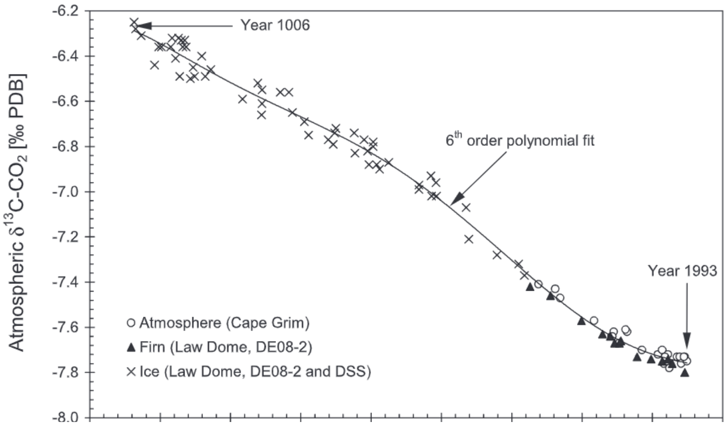

Figure 1. Atmospheric CO2 vs atmospheric δ13C (Körtzinger et al. 2003)

as DIC. The relationship between atmospheric CO_2 and atmospheric $\delta^{13}C$ (Figure 1) is preserved as CO_2 is dissolved into the ocean or eventually captured in ice (Körtzinger et al. 2003). This is important as it allows for ice cores to be used as a paleoclimate tool to determine how anthropogenic carbon has affected the isotopic signature of global carbon over time.

The Hawaii Ocean Time Series (HOT) encompasses Station ALOHA at which many surface DIC/$\delta^{13}C$ measurements have been taken overtime as well as multiple depth profiles. Since 1988, the University of Hawaii has been making monthly DIC measurements at Station ALOHA (https://hahana.soest.hawaii.edu/hot/dataaccess.html). These monthly measurements of DIC make Station ALOHA unique as perhaps the only location in the world ocean where the seasonal variability at the station is known (Keeling et al. 2004). Due to the relatively small size of the area and the known seasonal variability of the station, the commonly used multiple linear regression (MLR) (Carter et al. 2019, Quay et al. 2017) does not need to be used to estimate anthropogenic CO_2 accumulation. The MLR uses various measurements (temperature, dissolved oxygen, etc.) in conjugation with DIC and/or $\delta^{13}C$ to compensate for a lack of known seasonal variability. Instead, monthly DIC measurements haven been be used in conjugation with annual $\delta^{13}C$ measurements to provide increased confidence in results. The DIC and $\delta^{13}C$ measurements were integrated over the depth of the profiles to calculate the time rate of change. One $\delta^{13}C$ profile and one to two DIC profiles were integrated for each year from 1991-2017. After 2017, data for DIC from the Hawaii Ocean Time-series Data Organization & Graphical System (HOT-DOGS) data set is available; however, $\delta^{13}C$ data is unavailable.

Previous calculations of the time rate of change of $\delta^{13}C$ and DIC in the surface ocean of the Hawaii Ocean Time-series, using the MLR approach, found a time rate of change -0.25 ± 0.01‰ per decade for $\delta^{13}C$ (Figure 2) and +14 ± 1 $\mu mol\ kg^{-1}\ decade^{-1}$ for DIC from 1991-2014

(Quay et al. 2017). The increased time rate of change in the isotopic ratio relative to expected (−0.22‰ decade^{-1}) (Quay et al. 2007) is attributed to two factors: increased anthropogenic output of CO_2 into the atmosphere and accumulation due to horizontal transport of DIC (Quay et al. 2017). Carter et al. 2019 estimated the sourcing of anthropogenic carbon between 1991 and 2017 to be split 50/50 between horizontal transport and atmosphere-ocean interactions across the entire Pacific Ocean. To make these estimates, the total carbon flux from the atmosphere is estimated using windspeed and a simple mathematical model as outlined in Takahashi et al. (1997)

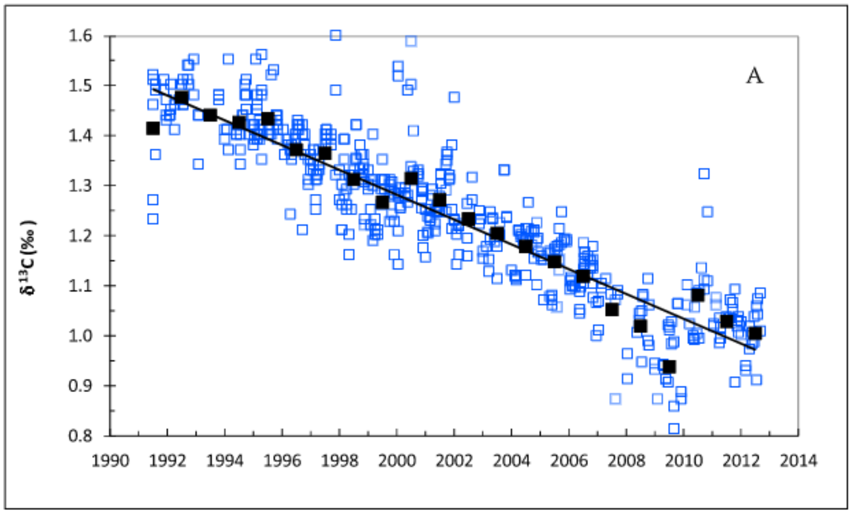

Figure 2. Surface Measurements of δ^{13}C from 1990-2014 at the Hawaii Ocean Time series. Black squares represent mean annual values, white squares represent actual measurements, black line represent linear fit to mean values (Quay et al. 2017)

This study expands on the previous estimates of anthropogenic carbon accumulation by deviating from the common practices that create uncertainties in estimation techniques. The first practice is the estimation of accumulation over a large area such as the entire Pacific Ocean (Carter et al. 2019) or entire Northern Pacific (Quay et al. 2017); this study focused solely on Station ALOHA. The second practice of using DIC alone for these estimations (Sabine and Tanhua 2010, Carter et al. 2019) is addressed by using a combination of DIC/ δ^{13}C. The last practice is the use of the MLR instead of using purely empirical data; previously the MLR was used because DIC signals were not strong enough to distinguish from the unknown seasonal variability, but, due to the known seasonal variability of Station ALOHA, DIC and $\delta^{13}C$ measurements can be corrected for seasonal sampling bias and used without the MLR.

I hypothesized, the time rate of change for the accumulation of anthropogenic carbon will have increased since its last calculation due to the increased global usage of fossil fuels; Station Aloha will have a lower measure of $\delta^{13}C$ than can be explained by ocean-atmosphere carbon flux due to horizontal transport causing increased accumulation of anthropogenic carbon. This data is significant as it uses a different methodology than *Carter et al. 2019* and not only confirmed their results but also showed how anthropogenic carbon accumulation has changed in the last half-decade.

Methods

Data

$\delta^{13}C$ measurements taken by Dr. Paul Quay's lab from 2010-2020 courtesy of samples collected during University of Hawaii cruises in the HOT region were used in combination with DIC measurements from University of Hawaii's HOT-DOGS to create depth profiles and surface time series of DIC and $\delta^{13}C$ for Station ALOHA. Dr. Quay's $\delta^{13}C$ samples were measured as outlined by the procedure in Quay et al. 1992. The 10-m wind speed data from Asia-Pacific Data-Research Center (Atlas et al. 2011) is used to estimate air-sea flux. Annual average pCO_2 for the atmosphere was sourced from NOAA's Earth System Research Laboratory at Mauna Loa (https://gml.noaa.gov/ccgg/trends/data.html, 2/21/2022). Annual average oceanic pCO_2, temperature, and salinity was sourced from HOT-DOGS (https://hahana.soest.hawaii.edu/hot/hot-dogs/, 2/21/2022).

The DIC and $\delta^{13}C$ depth profile for 2021 was collected on R/V Thompson cruise TN398 on December 19th, 2021. Samples were taken using a Sea-Bird Model SBE 9 CTD/Rossette and were subsampled into 300 mL bottles and poisoned using 1 µL of mercuric chloride. These samples were measured as outlined by the procedure in Quay et al. 1992. The following is a brief summary of the analytical process: 100 mL of seawater is acidified and then bubbled with a carrier gas (He). The carrier gas “pushes” the now extracted CO_2 through a series of water traps (dry ice slush) and two carbon traps (liquid nitrogen). After the sample is cyrofocused using liquid nitrogen, its volume is estimated using a manometric measurement which allows for the calculation of DIC. Finally, the sample is analyzed for $\delta^{13}C$ on a dual-inlet mass spectrometer.

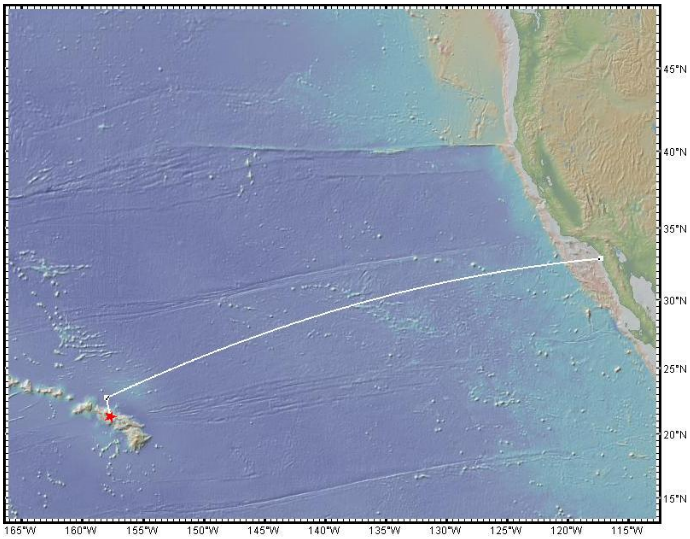

Figure 3. TN:398 Approximate Cruise Track

Analysis

DIC, oceanic pCO_2, atmospheric $pCO_{2,}$ and $\delta^{13}C$ data were averaged on an annual basis. DIC values were standardized to a salinity of 35 PSU. Due to the lack of standard sampling intervals of $\delta^{13}C$, $\delta^{13}C$ values have less temporal resolution when compared to DIC and pCO_2 values. The mean wind speed was calculated across a 5° grid centered at station ALOHA for 2000 – 2011. Salinity at the surface layer was averaged from 1998 – 2020 and a single mean valued was used. The mean annual temperature was calculated from the HOT-DOGS bottle data.

The time rate of change for DIC in the mixed layer was calculated using the differential equation:

$$Zml * \frac{\Delta DIC}{\Delta time} = k * K^0\left[pCO_2{}^{atm} - pCO_2{}^{ocean}\right] - DIC_{Export} \tag{1}$$

Where k is the transfer velocity of CO_2 and K^0 is the solubility of CO_2 calculated based on windspeed, salinity, and temperature as outlined in Wanninkhof 2014. An average net export of 0.76 $molC/m^2/day$ (Quay and Stutsman 2003) was used in the calculation. The time rate of change for DIC was calculated and plotted in Microsoft Excel.

The time rate of change for $\delta^{13}C$ was calculated using the differential equation:

$$Zml * \frac{\Delta^{13}DIC}{\Delta time} = k * K^0 * \alpha_{gas} * \alpha_{solubility}\left[pCO_2{}^{atm}(R_{atm}) - pCO_2{}^{ocean}\left(\frac{R_{atm}}{\alpha_{DIC}}\right)\right] \tag{2}$$

Where k is the transfer velocity of CO_2 and K^0 is the solubility of CO_2 calculated based on windspeed, salinity, and temperature as outlined in Wanninkhof 2014. α_{gas} is the isotopic fractionation factor for CO_2 gas transfer equal to 0.9992 (Zhang et al. 1995). $\alpha_{solubility}$ is the isotopic fractionation factor for dissolved CO_2 equal to 0.9987 (Zhang et al. 1995). α_{DIC} is the isotopic fractionation factor between DIC and dissolved CO_2 equal to 1.0081 (Zhang et al. 1995). The time rate of change for $\delta^{13}C$ was calculated and plotted in Microsoft Excel.

Results

The measurements for DIC have an average value of 2156.0 µmol/kg with a maximum value of 2349.9 µmol/kg and a minimum of 2018.1 µmol/kg. The $\delta^{13}C$ measurements have an average value of 0.147 ‰ with a minimum of -0.412 ‰ and a maximum of 0.701‰. The DIC and $\delta^{13}C$ showed inverse trends (Figure 4).

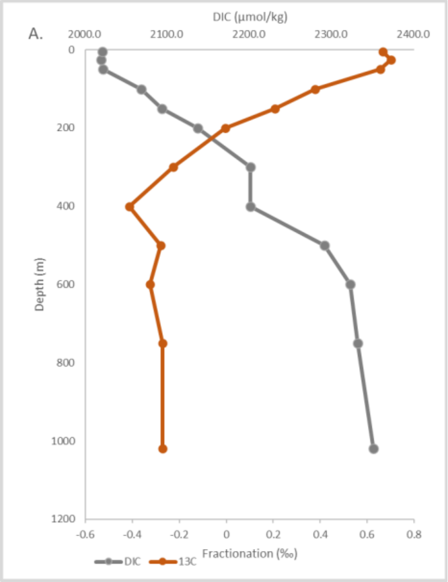

Figure 4 Depth profiles of DIC concentrations and δ13C fractionation measurements at station ALOHA for December 2021 from 0m - 1020m

The results of Equation 1 were plotted alongside the DIC time series from 1990-2021 for a mixed layer depth (Zml) of 200 m (Figure 5A). The relationship between time and projected DIC displayed a linear fit with an R^2 value of 0.9709. The relationship between observed DIC and time displayed a linear fit with an R^2 value of 0.9014. Projected values were higher than observed values except in 1999 and 2012. The mean difference between predicted and observed was 6.5 µmol/kg, the maximum difference was 17.3 µmol/kg, and the minimum was 0.4 µmol/kg. On average, the observed DIC concentration increased by 1.01 µmol/kg/yr in the surface ocean since 1990 and 0.2 µmol/kg/yr since 2017 and overall DIC concentrations in the surface ocean have increased by 15.46 µmol/kg since 2017.

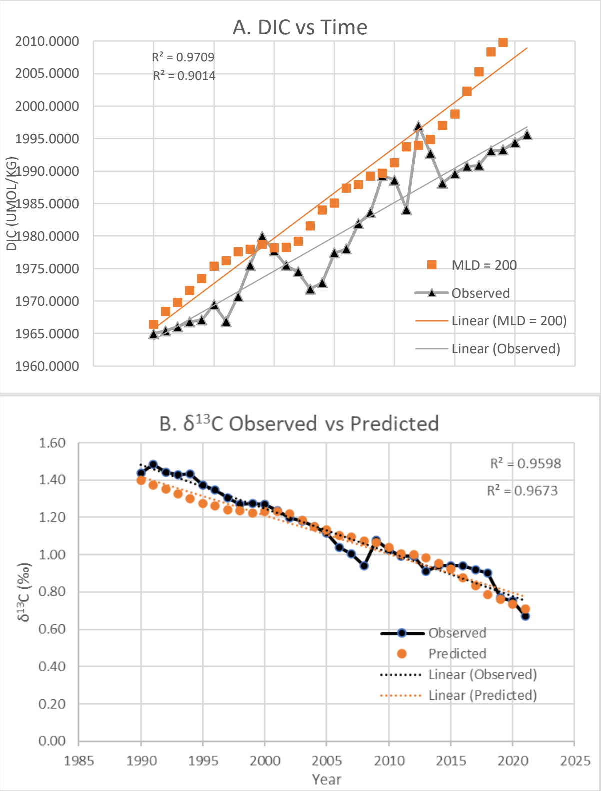

Figure 5 A. DIC observed concentrations plotted alongside predicted DIC concentrations for the surface ocean at Station ALOHA from 1990 – 2021 with Zml = 200 m. B. δ13C observed measuremnts plotted alongside predicted δ13C values for the surface ocean at Station ALOHA from 1990 – 2021.

The results of Equation 2 were plotted alongside the $\delta^{13}C$ time series from 1990-2021 with a mixed layer depth (MLD) of 200 m (Figure 5B). The relationship between time and projected $\delta^{13}C$ displayed a linear fit with an R^2 value of 0.9673. The relationship between observed $\delta^{13}C$ and time displayed a linear fit with an R^2 value of 0.9598. The mean difference between predicted and observed was 0.02 ‰, the maximum difference was 0.13 ‰, and the minimum was 0.0 ‰. On average, the observed $\delta^{13}C$ decreased by 0.02 ‰/yr.

The average concentration of DIC across a depth of 0m – 1020 m has increased by 51.8 µmol/kg and 27.8 µmol/kg since 1997 and 2012 respectively (Figure 6A). At 200 m, DIC concentrations have increased by 63.5 µmol/kg and 42.8 µmol/kg since 1997 and 2012 respectively. On average, the fractionation of δ^{13}C has decreased by 0.63 ‰ and 0.12 ‰ since 1997 and 2012 respectively (Figure 6B). The fractionation of δ^{13}C at 200m has decreased by 0.81 ‰ and 0.51 ‰ since 1997 and 2012 respectively.

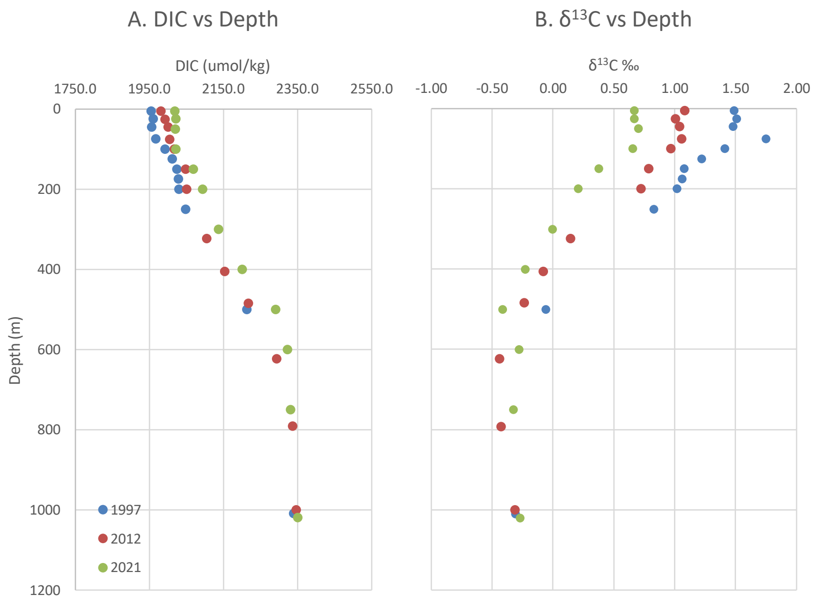

Figure 6 Depth profiles for DIC and δ13C at Station ALOHA for 1997, 2012, and 2021

Discussion

The close relationship displayed between δ^{13}C and DIC (Figure 4) points to increased concentrations of DIC (Figure 5A) being due to anthropogenic sources. The enrichment in the surface ocean with respect to Carbon-13 (Figure 5B) is consistent with previous studies (Körtzinger et al. 2003). Figure 6A displays an increase in DIC concentrations in the upper 600m of the water column likely due to anthropogenic sources. In support this idea of anthropogenic sourcing, figure 6B shows a depletion in Carbon-13 over the 600m water column consistent with Carter et al. 2019. The annual accumulation of CO_2 into the surface ocean has increased since 2017 by 0.2 µmol/kg/yr which supports the hypothesis that the time rate of change of DIC concentrations has increased likely due to anthropogenic sources.

The average mixed layer depth at Station ALOHA is ~50m and maximum is ~100m (Quay and Stutsman 2003). The projected values are based off a mixed layer depth of 200m. Other depths were tested but data most closely supported a 200 m mixed layer depth. This 200 m depth likely represents the depth that anthropogenic CO_2 has saturated. The decreased fractionation of $\delta^{13}C$ by 0.81 ‰ and 0.51 ‰ and increased DIC concentration of 63.5 µmol/kg and 42.8 µmol/kg since 1997 and 2012 respectively at 200 m support the idea that anthropogenic carbon dioxide has found its way to 200 m at Station ALOHA. Changes between 600m – 1000m are also observed, but whether these changes are due from anthropogenic sources is unclear as model output most closely supports a 200 m anthropogenic carbon signal (Figure 5).

With an increasing time rate of change of anthropogenic carbon flux into the surface ocean and anthropogenic carbon already reaching depths below the mixed layer, the depths at which anthropogenic carbon are detectable will likely increase. To test this hypothesis, future research should include more regular measurements of $\delta^{13}C$ as well as measurements below 1020 m. Increased sample resolution between 150 m and 350 m would help pinpoint an anthropogenic carbon signal. Additionally, considering data from other timeseries such as BATS and LMG would allow for a whole ocean assessment of anthropogenic carbon uptake.

Due to the lack of frequent samples, this study has some limitations. While windspeed and salinity are relatively consistent at Station ALOHA, using annual values as opposed to standardized values would likely decrease some of the noise in the projected values. $\delta^{13}C$ for years after 2017 was incredibly limited and sometimes resulted in a singular sample set being used for an entire year’s data. A constant net export rate was used, future models should incorporate some estimated annual variability in export.

Conclusion

Anthropogenic carbon is finding its way into the North Pacific Gyre at an increasing rate. Among other things, this is important as it will increase the acidity of the ocean and make it harder for calcifying organisms to survive. The change in surface DIC and δ^{13}C at Station ALOHA was known up to 2017, but not much research has been published in the last half decade. I found that the concentrations of carbon dioxide into the ocean has increased by a rate of 0.04 μmol/kg/yr and anthropogenic carbon could be consistently measured to depths 150 meters below the average mixed layer depth. This study should be followed up with a larger scale study that includes other timeseries and more frequent data collection at higher resolution.

Acknowledgments

I would like to acknowledge the crew of the R/V Thomson TN398 cruise. I would also like to acknowledge Dr. Paul Quay and Dr. Terry Rolfe for their consistent help on this project. Lastly, I would like to acknowledge Dylan Vecchione for his help sampling aboard the Thompson.

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