Determination of the Change in Anthropogenic Carbon Content in the Kuroshio Extension over the past 20 years using the C* Method

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NONTECHNICAL SUMMARY

Carbon dioxide is being emitted to the atmosphere by burning gasoline in car engines, burning coal (or any other fossil fuel) in power plants, and by clear cutting forests that store large amounts of carbon. These combined inputs of carbon dioxide caused by the human race are collectively referred to as “anthropogenic carbon”. Averaged over the globe, the oceans have been observed to be passively absorbing 1/2 of the total anthropogenic CO₂ that has been emitted to the atmosphere. The goal of the research undertaken in this study is to determine how much anthropogenic carbon has dissolved into the ocean over the past 20 years in a region of the North Pacific known as the Kuroshio Extension. This region of ocean absorbs more CO₂ than anywhere else in the Pacific and it is therefore an area of intense research. To determine how much of the dissolved CO₂ in the water was of anthropogenic origin, a popular and accurate method known as the C* Method was used. The C* Method uses a series of equations to determine how much dissolved CO₂ came from biological sources, the pre-industrial era atmosphere, and the industrial era atmosphere (anthropogenic CO₂). Using this method, the dissolved anthropogenic CO₂ was calculated in the Kuroshio Extension region from publically available data for 1993 and 2005. Dissolved anthropogenic CO₂ was also calculated for 2013 using data taken on our student cruise in the Kuroshio Extension region that took place from February 24 to March 18th 2013. The results of this study provide a new anthropogenic CO₂ uptake rate in the Kuroshio Extension region of 0.936 mol C m⁻² yr⁻¹ averaged over the past 20 years. Hopefully continued research into the region will provide better estimates for future climate models as well as more compelling evidence for political action to be taken to fight human caused climate change.

ABSTRACT

In this study I have calculated the anthropogenic CO₂ inventory of the largest CO₂ sink in the North Pacific, the Kuroshio Extension region, for the years 1993, 2005, and 2013 using the C* method. The C* method is an equation for determining anthropogenic CO₂ that uses proxies to account for all sources of DIC in seawater. The largest error in the C* method is associated with estimating the effect of air-sea disequilibrium, and therefore three approaches were used for comparison. The first, the 280Eq approach, assumes equilibrium between the atmosphere and ocean. The second, the 240Eq approach, assumes that our measured disequilibrium on the cruise in the winter of 2013 has been constant over time.
The third, the CtEq approach, uses a technique from past literature to calculate the individual disequilibrium for each sample. The CtEq approach did not yield accurate results due to a combination of being unable to use CFC measurements for accurate assessment of residence times and inaccuracies in the preformed alkalinity relationship. Therefore, only in the absence of CFC data should a measured disequilibrium method be used as a next best substitute for calculating anthropogenic CO$_2$.

Anthropogenic CO$_2$ concentrations calculated with our measured air-sea disequilibrium for 1993, 2005, and 2013 averaged over the top 800 m were 24.0 µmol kg$^{-1}$, 39.2 µmol kg$^{-1}$ and 46.9 µmol kg$^{-1}$, respectively. The anthropogenic CO$_2$ surface flux necessary to account for these inventories was found to be 0.936 mol C m$^{-2}$ yr$^{-1}$ calculated using the 240Eq approach.

The ocean plays an important role in the global carbon cycle because it is a very large reservoir capable of holding much more carbon dioxide than it already does. Approximately 48% of anthropogenic carbon dioxide (CO$_2$) emissions in the industrial age have already been absorbed into the ocean (Sabine et al. 2004). This has helped in reducing the warming effects of anthropogenic CO$_2$ forcing on the planet, but has also contributed to a decrease in ocean pH known as ocean acidification.

The waters of the Kuroshio Extension region absorb more carbon dioxide from the atmosphere than anywhere else in the North Pacific [Fig. 1] (Nakano et al. 2011). Furthermore, the amplitude of seasonal anthropogenic CO$_2$ uptake has been increasing, most of which is due to increasingly high uptake in the winter (Nakano et al. 2011). Recent studies indicate maximum anthropogenic carbon uptake rates of ~0.9 mol C m$^{-2}$ yr$^{-1}$ in the Kuroshio Extension region (Nakano et al. 2011).

The Kuroshio Current is a strong northeasterly current. It is the Pacific equivalent of the Gulf Stream, and serves as a means of transporting heat from the tropics northward. The Kuroshio Extension is specifically the section of the current that breaks off towards the east off the coast of Japan (Fig. 2).

It spans a width of approximately 120 km and a depth almost to the seafloor, although its strongest currents reach down to depths of ~1000 m (Jayne et al. 2009). The high CO$_2$ uptake of the Kuroshio Extension is driven by high primary productivity, increased solubility of the current waters caused by cooling, and physical processes such as advection (Nakano et al. 2011).

The intention of this research is to determine how anthropogenic CO$_2$ penetration into the Kuroshio Extension has changed over the past 20 years in order to continue to quantify the anthropogenic CO$_2$ inventory of the region.

Figure 1: Anthropogenic CO$_2$ air-sea flux in the Kuroshio Extension region (Nakano et al. 2011).

Figure 2: Cruise track and station locations on a map of SSH contours averaged over the period of the 2013 cruise. White = 2013 Station 4, Green = 2005 Station 97, Pink = 1993 Station 77.
Anthropogenic carbon uptake can be determined using four main methods: measurement of surface CO$_2$ flux rates, computer modeling, the C* method, and $\Delta$C-13 analysis (Quay et al. 1992). The most common and accurate method is used in this study, the C* method (Gruber et al. 1996). The C* method will be applied to data from CLIVAR cruises from 1993 and 2005 and compared to our own data taken when we occupied the region in February 25 to March 18, 2013. The locations of all three stations can be seen in Fig. 2 plotted with the 2013 cruise track and the SSH contours averaged over the cruise period.

METHODS

Station Locations and Sampling Methods:

Samples were collected in February/March 2013 on an NSF (National Science Foundation) funded cruise led by Chief Scientists Steve Emerson and Steve Riser aboard the R/V Melville. I chose to use the samples taken at Station 4 on our 2013 cruise for this study because this station was the closest to previous CLIVAR stations 97 and 77 from 2005 and 1993 respectively. I then calculated dissolved anthropogenic CO$_2$ concentrations using the C* method for each of these stations in order to quantify the change in anthropogenic CO$_2$ penetration over the past 20 years.

Sampling at Station 4 along our cruise track was done with a 24-Niskin Rosette and Seabird CTD. Sampling depths were chosen with frequent sampling in the mixed layer (approximately 200 m deep) and samples taken every ~100 m past the mix layer down to a maximum depth of ~1000 m.

At each station, samples were collected from each Niskin bottle to be analyzed on the ship for DIC, salinity, temperature, dissolved oxygen, and nutrients. Sample bottles for alkalinity were sent to Seattle where Nancy Williams at PMEL labs performed alkalinity analysis using a standard method open vessel titration system (Dickson et al. 2007). Solomon Wilson and myself analyzed DIC samples on the ship with a standard method using a DIC coulometer (Dickson et al. 2007). Anton Shomshor analyzed nutrients and salinity aboard the ship using an auto-analyzer. Seth Bushinsky and Chuck Stump analyzed dissolved oxygen aboard the ship using the Winkler titration method on a dosimat analyzer (Carpenter 1965). CLIVAR cruise data were taken from publically available spreadsheets accessible at http://cdiac.ornl.gov/oceans/RepeatSections/.

Coulometric titrations measure DIC very accurately by applying a current to the solution until all of the DIC is reduced at which point a dramatic shift in the potential of the working electrode signifies the endpoint of the titration. The magnitude and duration of the current can then be used to calculate the number of moles present. Based on the density of the given sample a DIC concentration in µmol kg$^{-1}$ can then be calculated.

Calculation of Anthropogenic CO$_2$ with the C* method:

The C* Method for calculating anthropogenic CO$_2$ is a common method that uses proxies to account for all sources of DIC present in a parcel of water in order to determine the portion that is of anthropogenic origin (Sabine et al. 2002). Each of the sources of DIC are represented in the following equation:

$$Canth = Cm - \Delta C_{bio} - C_{280} - \Delta C_{diseq}$$

(1)

Where Canth = anthropogenic carbon concentration (µmol kg$^{-1}$). Cm = the measured DIC concentration in (µmol kg$^{-1}$). $\Delta C_{bio}$ = the DIC (µmol kg$^{-1}$) changes from the remineralization of organic matter and the dissolution of calcium carbonate particles and denitrification, C$_{280}$ = DIC (µmol kg$^{-1}$) of waters in equilibrium with a pre-industrial atmospheric CO$_2$ of 280ppm, and $\Delta C_{diseq}$ = air-sea CO$_2$ difference ($\Delta pCO_2$) expressed in DIC (µmol kg$^{-1}$). The first three terms on the right side of equation (1) constitute the quasiconservative tracer termed $\Delta C*$:

$$\Delta C* = Cm - \Delta C_{bio} - C_{280} = Canth + \Delta C_{diseq}$$

(2)
Cm is determined via measurements of the DIC of the sample. C280 is determined using the carbonate system of equations together with the preformed alkalinity (TA0) and pre-industrial pCO2 value of 280 ppm. TA0 was determined based on a linear regression of alkalinity in the North Pacific using the following equation (Sabine et al. 2002):

$$TA0 = 148.7 + 61.36 \times S + 0.0941 \times PO - 0.582 \times \theta$$

(3)

Where S is salinity, PO is a quasiconservative tracer ($PO = dissolved \ oxygen + 170 \times phosphate$), and $\theta$ is potential temperature. This represents the total oxygen present before removal due to respiration in organic matter remineralization. TA0 relationship can only be applied to waters with a potential density less than 26.8 kg m$^{-3}$ because waters of greater density originated outside of the Pacific basin. This means that the C* method can only be applied to the top ~800m of the water column which may not represent the entire anthropogenic region.

$\Delta$Cbio is calculated by the summing of the terms for the DIC contribution of hard parts, soft parts, and denitrification ($\Delta$Cbio = soft parts + hard parts + denitrification). The following relationships are used to determine each portion of the $\Delta$Cbio DIC change (Sabine et al. 2002):

- Soft parts: $(117/170) \times [O - Osat]$
- Hard parts: $-1/2(TA - TA0 - (16/170) \times [O - Osat])$
- Denitrification: $(106/104) \times N^*_{anom}$

$$\Delta C_{bio} = (117/170) \times [O - Osat] - 1/2(TA - TA0 - (16/170) \times [O - Osat]) + \frac{(106/104) \times N^*_{anom}}{\text{anom}}$$

(4)

Where TA and O are measured concentrations for the water sample in $\mu$mol kg$^{-1}$ and Osat is the oxygen saturation that the waters would have at their potential temperature and one atmosphere pressure (Garcia and Gordon. 1992). ($N^*_{anom}$ described later). The biological components for soft parts uses the AOU [O-Osat] and the ratio of C:O to determine the DIC change caused by remineralization of organic matter. The component for hard parts uses the difference between measured alkalinity and preformed alkalinity to estimate changes in DIC from the dissolution of calcium carbonate particles, with a small correction for the effect of proton flux release due to organic matter degradation on TA.

The denitrification term $N^*_{anom}$ is used to determine the DIC change due to denitrification with the use of the tracer $N^*$ ($N^* = N - 16P + 2.9$). $N^*$ was then averaged for the data set and the difference between each measured N* and the average was defined as the $N^*_{anom}$. The denitrification stoichiometric ratio for C:N of 106:104 was used to correct the $\Delta C^*$ term (Sabine et al. 2002).

3 approaches to $\Delta C_{diseq}$ calculations:

- The most difficult of the $C^*$ terms to calculate in this study was the $\Delta C_{diseq}$ term. The difficulty was mainly due to the fact that for the Ctieq approach we could not calculate the age of the water parcel accurately because we lacked CFC measurements for our cruise. Because CFC measurements were unavailable, three other methods of determining $\Delta C_{diseq}$ were performed for comparison.

- The first approach assumes that there was no disequilibrium ($\Delta C_{diseq} = 0$) at the time the water parcels were each last in contact with the atmosphere. This assumption of equilibrium between the atmosphere and ocean was made mainly to determine the significance of the $\Delta C_{diseq}$ term. With this approach, anthropogenic CO2 concentrations were calculated with equation (1) with the $\Delta C_{diseq}$ term omitted:

$$Canth = Cm - \Delta C_{bio} - C280$$

(5)
The next approach assumed that the average disequilibrium (-40ppm) we measured on the 2013 cruise could apply to all C* calculations. This approach will be called CtEq approach because it assumes that a -40 ppm disequilibrium can be applied to the calculation of the C280 term and that therefore the parcel actually only equilibrated to an atmospheric pCO2 value equivalent to 240 ppm. It is an unlikely assumption that every parcel equilibrated to 40 ppm less than the atmospheric pCO2 (because the air-sea disequilibrium is not constant throughout the year), but that assumption is held intentionally for this approach in order to use a ΔCdiseq value in the range of what those actually observed. This approach effectively combines the C280 term and the ΔCdiseq term into a new term that can be called C240. Dissolved anthropogenic CO2 is then determined with a modification of equation (1):

\[ C_{\text{Canth}} = C_m - \Delta C_{\text{bio}} - C_{240} \]  

(6)

C240 is calculated using the carbonate system of equations with the temperature, salinity and TA0 of the sample along with an atmospheric pCO2 value of 240ppm (which represents our measured -40ppm disequilibrium applied to the pre-industrial atmospheric pCO2 of 280ppm).

The final approach is called the CtEq approach and this approach uses CFC measurements to determine water parcel age (Sabine et al. 2002). The water parcel is then assigned an atmospheric pCO2 level corresponding to the year it was last in contact with the atmosphere (date sample was taken – CFC age = date parcel was last in contact with the atmosphere). An atmospheric pCO2 value is then assigned to the year that the water parcel was last at the surface based on publicly available atmospheric pCO2 time series data. This unique pCO2 value along with TA0, temperature, and salinity are used in the carbonate system of equations to determine an expected DIC value due to equilibration when the parcel was last in contact with the atmosphere. This DIC value in µmol kg\(^{-1}\), is called CtEq:

\[ \text{CtEq} = \text{DIC (µmol kg}^{-1}) \] calculated with carbonate system of equations using TA0, S, T, and atmospheric pCO2 of the year the parcel was last at the surface.

CtEq can be considered a combination of the C280 term and the Canth term because it represents the DIC present due to equilibration with an atmosphere that contains both the pre-industrial quantity of CO2 (280ppm) and the added anthropogenic quantity up to the point in time when the parcel equilibrated at the surface. Therefore CtEq can be represented as the sum of C280 and Canth:

\[ \text{CtEq} = C_{280} + \text{Canth} \]  

(7)

This new value CtEq is then substituted for C280 into the definition of the tracer ΔC*:

\[ \Delta C^* = C_m - \Delta C_{\text{bio}} - \text{CtEq} \]  

(8)

The original definition of the tracer ΔC* (ΔC* = C_m – ΔCbio – C280) can be rearranged with the terms in equation (1) to be written as ΔC* = Canth + ΔCdiseq. In the case of the CtEq approach since C280 and Canth are effectively combined (6), it can be said that:

\[ \Delta C^* = \Delta C_{\text{diseq}} \]  

(9)

With this approach, an individual ΔCdiseq is calculated for each sample separately and this unique ΔCdiseq is substituted in as the ΔCdiseq in equation (1) for each individual sample. This approach is considered the most precise way to calculate ΔCdiseq, but due to a lack of CFC data for our cruise water parcel age was determined in a less accurate way. For our calculation of CtEq we assume the CFC ages of the study area given by Warner et al. 1996. These ages are given by a relationship of potential density to CFC age:

- 25.4 kg m\(^{-3}\) = 1 year old
- 26.0 kg m\(^{-3}\) = 3 years old
- 26.4 kg m\(^{-3}\) = 6 years old
26.8 kg m\(^{-3}\) = 14 years old

Total anthropogenic CO\(_2\) inventories were determined for each sampling year by integrating the dissolved anthropogenic CO\(_2\) concentrations over 100 m intervals and summing all of the intervals. The total inventory was then averaged over the top 800 m of the water column because below ~800 m potential density is greater than 26.8 kg m\(^{-3}\) and the North Pacific TA0 regression cannot be applied. The difference between the averaged dissolved anthropogenic CO\(_2\) concentration (µmol kg\(^{-1}\)) in 2013 and 1993 was then divided by the period of 20 years to find the rate of anthropogenic CO\(_2\) increase. This value, in µmol kg\(^{-1}\) yr\(^{-1}\) was then converted to a surface flux by multiplying by average density, water column height, and ratio of mols per µmol. The resulting flux is in mol Anthro CO\(_2\) m\(^{-2}\) yr\(^{-1}\) and accounts for the total anthropogenic CO\(_2\) inventory change over the 20-year period.

RESULTS

The total DIC measured on our cruise in 2013 at Station 4 was higher than had been measured at Station 97 in 2005 or Station 77 in 1993. The total DIC vs. depth for the years 1993, 2005, and 2013 can be seen plotted in Fig. 3. Note the trend of increase over time as well as increase with depth, both of which are expected. Depth profiles of temperature, salinity, dissolved oxygen, DIC and alkalinity from our cruise in 2013 are plotted in Fig. 4.
DISCUSSION

The anthropogenic CO$_2$ vs. depth calculated using each of the three ΔC$_{diseq}$ approaches for 1993, 2005 and 2013 are presented in Fig. 5, 6, and 7, respectively.

**Figure 4:** Depth profiles of temperature, salinity, dissolved oxygen, DIC (blue) and total alkalinity (red) for station 97 (2005).

**Figure 5:** Dissolved anthropogenic CO$_2$ vs. depth at station 77 in 1993 using all three methods of calculating C$_{diseq}$.

**Figure 6:** Dissolved anthropogenic CO$_2$ vs. depth at station 97 in 2005 using all three methods of calculating C$_{diseq}$.
In 1993 negative dissolved anthropogenic CO₂ values are observed deeper than 300 m in the “no disequilibrium” approach ($\Delta C_{\text{diseq}} = 0$), indicating a method for calculating the air-sea disequilibrium must be included to accurately determine dissolved anthropogenic CO₂ with the C* method.

When comparing our findings using the 240Eq approach applied to the 2005 data with findings for the same region from Sabine et al. 2002, I found that the measured disequilibrium (240Eq) approach yielded anthropogenic CO₂ concentrations closer to those in Sabine et al. 2002 than the other two approaches. In the Sabine et al. (2002) study they measured anthropogenic CO₂ concentrations from approximately $45 \mu$mol kg$^{-1}$ at the surface to $10 \mu$mol kg$^{-1}$ at 800 m. Compared with data three years later (2005) in the same region I calculated (using 240Eq approach) values of $55 \mu$mol kg$^{-1}$ and $20 \mu$mol kg$^{-1}$ at the surface and 800 m respectively. These values were closer than those calculated with the other two disequilibrium approaches. Therefore, for the purposes of this study, it can be concluded that the measured disequilibrium approach yields the most accurate values.

In past literature the CtEq approach has been the preferred method for calculating the $\Delta C_{\text{diseq}}$ term (Sabine et al. 2002). This has been considered the most accurate method, but when the CtEq approach was replicated in this study, anthropogenic CO₂ values higher than other studies in the same region and time frame were calculated. This discrepancy is most likely due to a combination of underestimation of CFC age and inaccuracies of the preformed alkalinity relationship. The effect of increasing CFC age on the total calculated anthropogenic CO₂ can be seen in Fig. 8.

Note that when the age of the water is doubled, the calculated anthropogenic CO₂ decreases. This is due to the $\Delta C_{\text{diseq}}$ becoming larger, or more negative. The Warner et al. relationship (1996) used in this study to substitute for actual CFC measurements was therefore inaccurate and produced an underestimation of water age which, along with contributions due to limitations of the preformed alkalinity relationship, contributed to $\Delta C_{\text{diseq}}$ values that were too large. The larger (more negative) $\Delta C_{\text{diseq}}$ values after being inputted into equation (1) yielded anthropogenic CO₂ values that were larger than expected.
All three approaches showed a trend of increasing anthropogenic CO$_2$ over time. While we may not trust the absolute values of anthropogenic CO$_2$ calculated with CtEq approach, a rate of change over time can still be calculated with this data because the same error was propagated through all of the assessments so relative changes will still be accurate. Surface flux rates of 0.678 mol anthropogenic CO$_2$ m$^{-2}$ yr$^{-1}$ and 0.936 mol anthropogenic CO$_2$ m$^{-2}$ yr$^{-1}$ were found for the period between 1993-2013 in the Kuroshio Extension region for the CtEq and 240Eq approaches respectively. Since the 240Eq approach yielded results closest to past studies, this data will be the most trusted when calculating actual inventories and absolute concentrations. The dissolved anthropogenic CO$_2$ using the 240Eq approach averaged over the top 800 m of the water column for 1993, 2005 and 2013 are presented in Fig. 9.

![Figure 9: Total anthropogenic CO$_2$ inventory average over the top 800 m for 1993, 2005 and 2013.](image)

The calculated flux values agree with the maximum surface flux of 0.9 mol anthropogenic CO$_2$ m$^{-2}$ yr$^{-1}$ found by Nakano et al. 2011. This value also agrees with the surface flux of 0.52 mol anthropogenic CO$_2$ m$^{-2}$ yr$^{-1}$ found by Wilson (2013) for the entire p10 CLIVAR cruise track using a multiple linear regression.

CONCLUSIONS

Both approaches for calculating the disequilibrium term yield similar anthropogenic CO$_2$ flux rates that agree with values found by past studies. The CtEq approach used in this study yielded anthropogenic CO$_2$ inventories consistently larger than past studies had measured in the same region and time period. This warranted investigation into the source of the discrepancy and it was determined that it was due to both an underestimation of the water age caused by a North Pacific CFC-potential density relationship as well as inaccuracies in the preformed alkalinity relationship used. The measured disequilibrium method (240Eq) can therefore be concluded a more accurate approach in the absence of CFC measurements. It should be noted that the measured disequilibrium method assumes the value measured during this study is a constant that can be applied to all of the samples. In reality the value of disequilibrium varies throughout the year. Therefore, if true water age can be determined with CFC data the calculated disequilibrium (CtEq approach) should be used for more accurate ΔC diseq values.

Anthropogenic CO$_2$ inventories in the Kuroshio Extension have increased consistently over the past twenty years. This region will continue to be a large CO$_2$ sink and it is therefore important for the scientific community to conduct future studies more frequently and across a larger area of the Kuroshio Extension region to improve the pool of data that can be incorporated in to climate modeling simulations.

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REFERENCE LIST


