Rising surface ocean dissolved inorganic carbon at the Hawaii Ocean Time-series site

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Abstract

Surface ocean dissolved inorganic carbon (DIC) and titration alkalinity have been measured for 7 years as a part of the Hawaii Ocean Time-series (HOT) program. The time-series data set displays an interannual increase in the inventory of surface ocean DIC which we interpret as a response to increasing atmospheric carbon dioxide concentrations. The rate of increase in surface ocean DIC at the open ocean HOT site is approximately $1 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ with a 95% confidence interval of 0.72 to $1.37 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$. This accumulation rate is consistent with the rate of increase predicted from the rise in boundary layer p_{CO_2} . © 1998 Elsevier Science B.V.

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1. Introduction

The biogeochemical dynamics of carbon in the ocean is a subject of fundamental and long-standing interest. Recently, the role of the ocean as a sink for anthropogenic carbon dioxide has been the subject of intensive investigation and debate. Interest in the oceanic anthropogenic carbon sink is driven, at least in part, by the need to predict the rate of increase in atmospheric carbon dioxide concentrations and subsequent global environmental change. The world's oceans are believed to be taking up a significant portion of the carbon dioxide added to the atmosphere through anthropogenic activities. For exam-

ple, the oceans are believed to have taken up approximately 28% of the fossil fuel and land use carbon dioxide fluxes during the 1980's (Houghton et al., 1996). Estimates of the magnitude of the oceanic sink appear to be converging on a value of approximately 2 Gt C yr^{-1} (Keeling et al., 1989; Quay et al., 1992; Siegenthaler and Sarmiento, 1993). In addition, there is now evidence of considerable interannual variability in this rate of uptake (Fancey et al., 1995; Keeling et al., 1995). However, a detailed understanding of the temporal and spatial variability in the exchange of carbon dioxide between the ocean and the atmosphere is not available.

The chemistry of CO_2 in seawater is well understood, and the basis for modeling the carbon chemistry of the seas seems reasonably well established (Oeschger et al., 1975; Bacastow and Keeling, 1979; Takahashi et al., 1980; Brewer, 1983; Siegenthaler, 1983; Maier-Reimer and Hasselman, 1987; Bacastow

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and Maier-Reimer, 1990; Sarmiento et al., 1992; Orr, 1993). Our present understanding suggests that rising atmospheric carbon dioxide concentrations should produce a corresponding increase in surface ocean carbon dioxide partial pressure (p_{CO_2}) resulting in an increase in surface water DIC concentration of approximately $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Brewer, 1983). However, it is difficult to observe an annual increase of $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ given the seasonal and inter-annual variations observed at many oceanic locations. In addition, time-series measurements of ocean carbon chemistry to support the predicted rate of increase are scarce.

A few attempts have been made to document the rise in oceanic p_{CO_2} in response to rising atmospheric p_{CO_2} . Takahashi et al. (1983) combined data from the International Geophysical Year (IGY), Geochemical Ocean Sections (GEOSECS) and the Transient Tracers in the Ocean (TTO) expeditions from the late 1950's to the early 1980's and showed that the surface ocean p_{CO_2} in the North Atlantic was rising at about $1.5 \mu\text{atm yr}^{-1}$, as would be expected from the rate of increase in atmospheric CO_2 . It should be noted though, that the accuracy of the GEOSECS data is in doubt because of the calculation of DIC from titration data. Goyet and Peltzer (1994) have also demonstrated a rise in p_{CO_2} in the Equatorial Pacific during the 1980's by comparing the results of meridional transects occupied in 1979 and 1991. However, Goyet and Peltzer (1994) observed an increase in oceanic p_{CO_2} over only part of the latitude band they examined and concluded that variability on shorter time scales was obscuring the interannual trend over much of the transect that they studied. Inoue et al. (1995), using a large data set collected from 1984 to 1993 in the western North Pacific Ocean, showed that p_{CO_2} in the surface waters of this region of the Pacific Ocean had risen approximately $1.2 \mu\text{atm yr}^{-1}$.

A few other studies have attempted to document the anthropogenic accumulation of carbon dioxide in the oceans using direct measurements of DIC. Tsunogai et al. (1993) used direct measurements of DIC in the western North Pacific Ocean in 1991 in combination with the DIC data obtained on the GEOSECS program in 1973 to estimate the increase in DIC as a consequence of the invasion of anthropogenic carbon dioxide in the intervening 18-year

period. Their results suggest that DIC in the upper 1000 m of the water column at this location had risen at approximately $180 \pm 41 \text{ g C m}^{-2}$ over this period. Assuming an average density of 1.02 kg l^{-1} , this result suggests a rate of increase of approximately $0.85 \pm 0.19 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ in DIC in this depth interval. Interestingly, time-series measurements of DIC concentrations over an eight year period in the upper 50 m of the Sargasso Sea have not shown an increase in the DIC inventory in response to changes in atmospheric CO_2 concentrations (Keeling, 1993). However, a five year time-series of DIC measurements integrated between 0 and 250 m at the nearby Bermuda Atlantic Time-series Study (BATS) site does show an increase in DIC concentration of approximately $1.7 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. This increase has been interpreted, in part, as a response to rising atmospheric CO_2 concentrations (Bates et al., 1996). Lack of evidence for the predicted rise in upper ocean DIC concentrations in near surface waters (less than 100 m) is presumably a consequence of inadequate temporal resolution at any one location in the ocean coupled with the natural temporal variability in surface water DIC concentrations.

We have been measuring inorganic carbon system parameters in the North Pacific Subtropical Gyre (NPSG) on approximately monthly intervals since October 1988. These measurements have been made as a part of the Hawaii Ocean Time-series (HOT) program (Karl and Winn, 1991; Winn et al., 1994; Sabine et al., 1995; Karl and Lukas, 1996), which has been assessing temporal variability in the physics, chemistry and biology of the ocean at the location of the long-term time-series permanent station in the NPSG. A primary objective of this program is to document and interpret annual and interannual variability in the NPSG. In this article, we show that the surface ocean DIC concentrations at the HOT site appear to be responding to the rise in atmospheric carbon dioxide concentrations with an increase in surface water DIC concentration of approximately $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$.

We present the time-series for both DIC and alkalinity in this report. Dissolved inorganic carbon is the sum of the carbonate species in seawater (i.e., $\text{DIC} = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$) and organic decomposition where CO_2 is the sum of $\text{CO}_{2(\text{aq})}$ and H_2CO_3

Fig. 1. Location of the Hawaii Ocean Time-series station ALOHA at 22°45'N, 158°00'W and the near-shore Kahe Point sampling site at 21°20.6'N, 158°16.4'W. Also shown are the locations of NDBC buoy # 51001 about 400 km west of station ALOHA and the location of the Hawaii Mauna Loa Observatory.

(Butler, 1982). DIC concentrations are influenced by biological uptake of inorganic carbon as well as the precipitation and dissolution of CaCO_3 . In the surface water, DIC concentration is also influenced by the exchange of carbon dioxide across the air–sea interface. Alkalinity is most commonly defined as the amount of acid required to neutralize 1 kg of seawater to the endpoint corresponding to the formation of carbonic acid from bicarbonate (Dickson, 1992; Sverdrup et al., 1942). A more exact definition has recently been provided in which the alkalinity of a seawater sample is described relative to an arbitrarily defined zero level of protons (Dickson, 1981). Alkalinity is influenced by precipitation and evaporation and by the production and dissolution of CaCO_3 . Alkalinity is not changed, however, by the exchange of carbon dioxide across the air–sea interface. With the time-series of both DIC and alkalinity in the upper ocean, it is theoretically possible to evaluate whether the interannual trend in DIC is consistent with the accumulation of CO_2 in the surface ocean as a consequence of the rise in atmospheric carbon dioxide (i.e., to rule out mixing effects and/or changes in the rate of CaCO_3 precipitation as the causes of interannual variability in the DIC concentration).

2. Materials and methods

Dissolved inorganic carbon and titration alkalinity have been measured in the surface ocean and throughout the water column at station ALOHA (A Long-term Oligotrophic Habitat Assessment) since October 1988 (Fig. 1). Full water column profiles for both of these parameters are obtained at approximately monthly intervals at station ALOHA along with routine HOT program ‘core measurements’ (Karl and Winn, 1991; Karl and Lukas, 1996). These data are available via FTP on the world-wide Inter-

net system (<http://hahana.soest.hawaii.edu>). In this report, our analysis will be restricted to samples collected within the upper 50 m of the water column. The measurements of DIC and alkalinity in the upper 50 m of the water column have been averaged to yield a ‘surface ocean’ value. We have chosen to use only the upper 50 m of the water column because this region is largely within the mixed layer throughout the year (Karl and Lukas, 1996).

Water samples and hydrographic data were collected with a Seabird CTD rosette system and PVC sampling bottles. Temperature and salinity sensors were calibrated as previously described (Bingham and Lukas, 1996). The surface ocean temperature and salinity values reported here were also obtained by averaging the temperature and salinity values from the water sampling bottles used to collect the carbon samples between 0 and 50 m. In the case of temperature, the mean ‘upper ocean’ value was obtained from the CTD temperature sensor. For salinity, the ‘upper ocean’ mean value was obtained with the CTD conductivity sensor which was calibrated with discrete sample salinity measurements (Bingham and Lukas, 1996).

Our methods have evolved slightly over the past 7 years to improve the precision and accuracy of our measurements. DIC was measured via coulometry (Johnson et al., 1985, 1987). Since 1993 we have used a single operator multiparameter metabolic analyzer (SOMMA) provided by the Department of Energy (Johnson and Wallace, 1992; Johnson et al., 1993) for DIC determinations. Before 1993 a coulometric system similar to that described by Johnson et al. (1985) was used for the determination of DIC. Since 1992, the accuracy of the coulometric analysis of DIC was maintained using certified reference materials (CRMs) provided by Dr. Andrew Dickson (Dickson, 1991).

Alkalinity was determined by potentiometric titration using a modified Gran plot (Gran, 1952). As recommended by DOE (1994) for the determination

Fig. 2. Upper panel: DIC normalized to salinity 35 (NDIC) at station ALOHA versus sampling date from October 1988 to November 1995. Points represent the average value in the upper 50 m of the water column (generally 3 to 4 samples per cruise). Error bars represent ± 1 standard deviation of the measurements made in this depth interval on each cruise. Middle panel: temperature in the upper 50 m of the water column at station ALOHA versus sampling date from October 1988 to November 1995. Lower panel: boundary layer p_{CO_2} in the vicinity of station ALOHA versus sampling date from October 1988 to November 1995.

of titration alkalinity, total sulfate, fluoride and borate were computed as described by Morris and Riley (1966), Riley (1965) and Uppstrom (1974). In addition, the formulations for the equilibrium constants for sulfate, fluoride, borate, water, carbonate and bicarbonate given by Dickson (1990a), Dickson and Riley (1979), Dickson (1990b) and Roy et al. (1993), respectively, were used for these calculations. Because we were interested in measuring only total alkalinity, and in order to allow for the gravimetric determination of sample volume, titrations were performed in an open cell.

Both DIC and titration alkalinity were ‘normalized’ to a constant salinity of 35 (i.e., normalized DIC and normalized alkalinity are given as: $\text{NDIC} = \text{DIC} * 35 / S$, and $\text{NTA} = \text{alkalinity} * 35 / S$ where DIC and alkalinity are expressed in $\mu\text{mol kg}^{-1}$ and S is sample salinity). These parameters were normalized to a constant salinity in order to eliminate the effects of precipitation and evaporation on the DIC and alkalinity time-series.

The precision and accuracy of analytical techniques are an important concern for any time-series program. The precision and accuracy of our DIC analyses have been assessed with CRMs, and with deep water reference samples drawn from between 4250 and 4750 decibars on each cruise. Although our current DIC analytical precision (for the 1995 calendar year) is approximately $1 \mu\text{mol kg}^{-1}$, and the accuracy is estimated at less than $2 \mu\text{mol kg}^{-1}$, the analytical precision and accuracy for this technique over the duration of the program both average approximately $2.5 \mu\text{mol kg}^{-1}$. The standard deviation of replicates collected between 4250 and 4750 decibars over the duration of the program is $3.2 \mu\text{mol kg}^{-1}$. These deep water measurements are interpreted as conservative estimates of cumulative analytical precision because these analyses incorporate errors due to sample collection and handling. This is particularly true of the deep water DIC analyses which are affected by rapid carbon dioxide degassing during sample collection and analysis.

The precision of our alkalinity determinations is presently approximately $2 \mu\text{mol kg}^{-1}$. However, the precision of this analysis over the duration of the program is estimated to be 4 to $5 \mu\text{mol kg}^{-1}$. The standard deviation of replicates collected in the 4250 to 4750 decibar interval is $4.3 \mu\text{mol kg}^{-1}$.

Boundary layer p_{CO_2} was estimated using the Mauna Loa atmospheric CO_2 record (Keeling and Whorf, 1994) and upper ocean temperature and salinity data obtained on the time-series cruises (Fig. 2). Boundary layer p_{CO_2} was computed from the monthly dry air values using the upper ocean temperature and salinity obtained from the HOT program upper ocean measurements. A barometric pressure of one atmosphere and a saturated boundary layer was assumed for these calculations (Ambrose and Lawrenson, 1972; DOE, 1994).

3. Results

3.1. Dissolved inorganic carbon

As has been demonstrated previously (Winn et al., 1994), DIC normalized to a salinity of 35 (NDIC) in the surface ocean at station ALOHA undergoes a regular seasonal oscillation that is inversely related to surface ocean temperature. This pattern of variability predominates the NDIC data set over the length of the time-series record (Fig. 2).

3.2. Titration alkalinity

Titration alkalinity, also normalized to salinity 35 (NTA), displays no regular seasonal oscillation (Fig. 3). The time-series of titration alkalinity displays considerably more variability than the DIC time-series, at least in part, because of the relative imprecision of this analysis (Fig. 3).

Interestingly, NTA underwent what might be interpreted as a systematic oscillation in 1994. This pattern of variability was observed at both station ALOHA and at the near-shore Kahe Point station (data not shown) and was not observed in previous or subsequent years. The shift is reasonably large given the consistency of NTA that has been observed in these waters. This variability cannot easily be attributed to analytical inconsistencies in our time-series alkalinity measurements because the pattern of variability was coherent at both ALOHA and Kahe Point stations and because the analysis of CRMs run over the same time frame showed good analytical consistency.

Fig. 3. Titration alkalinity normalized to salinity 35 (NTA) at station ALOHA versus sampling data from October 1988 to November 1995. Points represent the average value in the upper 50 m of the water column. Error bars represent ± 1 standard deviation of the measurements made in this depth interval at each location.

3.3. Boundary layer p_{CO_2}

The calculated boundary layer p_{CO_2} rises over the duration of the time-series program (Fig. 2). Although there are some small changes in the annual rate of increase, the average rate of increase of p_{CO_2} in the boundary layer was $1.2 \mu\text{atm yr}^{-1}$ over the duration of the time-series record.

4. Discussion

4.1. Interannual variability in NDIC

On an annual time scale, surface ocean NDIC concentrations show a clear seasonal pattern of variability with a maximum in February through April and a minimum in September through November (Fig. 2). This pattern is inversely related to surface ocean temperature as described previously (Winn et al., 1994). It is important to note that the process of 'normalizing' DIC to a salinity of 35 removes much of the variability in the DIC time-series due to changes in upper ocean salinity as a consequence of precipitation and evaporation. When not normalized

to a constant salinity, the DIC time-series does not display an obvious seasonal oscillation (Fig. 4).

Although NDIC undergoes a very regular seasonal oscillation, there is also a significant interannual trend in these data. As a first approximation of this interannual trend, a linear least squares fit to the surface ocean NDIC time-series from station ALOHA was made (Fig. 5). Although the scatter around this linear fit is large (the standard deviation of the residuals of the fit is approximately $6 \mu\text{mol kg}^{-1}$), the fit is statistically significant (probability = 0.034) with a slope of approximately $0.8 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. The 95% confidence interval on this slope is broad though, ranging from a lower limit of $0.06 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ to an upper limit of $1.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Table 1).

In addition to the simple linear fit described above, we have also used a least squares sine fit to examine the interannual trend in DIC concentration. In this procedure, sine curves were fit to the NDIC time-series and the phase and the amplitude were chosen to minimize the least squares residuals of the fit. In one case, we also allowed the slope of the fit to vary in a linear fashion such that the residuals of the fit were minimized. Fig. 6 shows a least squares sine fit

Fig. 4. Upper panel: DIC at station ALOHA versus sampling date from October 1988 to November 1995. Values represent averages for the upper 50 m of the water column. Lower panel: salinity in the upper 50 m of the water column versus sampling date from October 1988 to November 1995. Values represent averages in the upper 50 m of the water column.

Fig. 5. Linear fit to the NDIC time-series at station ALOHA.

to the time-series which does not allow for an inter-annual increase in DIC concentration. Although the residuals of this fit are relatively small (standard deviation = $3.6 \mu\text{mol kg}^{-1}$; variance = 782.8; $n = 59$), the pattern in the residuals of this fit (Fig. 6, bottom panel) suggests that the DIC time-series contains a long-term trend. Fig. 7 shows a second least squares sine fit to the NDIC time-series in which the amplitude, phase and slope are allowed to vary in order to minimize the residuals. The residuals are minimized in this fit with a linear increase of $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ in NDIC concentration. The residuals of this second sine fit are reduced (standard deviation = $2.9 \mu\text{mol kg}^{-1} \text{yr}^{-1}$; variance = 505.5;

$n = 59$) relative to the fit which did not allow for an annual increase in NDIC concentration. In addition, a temporal pattern is not observed in the residuals to this fit (Fig. 7, bottom panel) suggesting that the addition of the interannual trend to the curve fit significantly improved the fit to the data. A simple f -test comparing the variance in the residuals of these two fits was used to examine the null hypothesis that the residuals produced by these two fits were from the same population (i.e., that the difference in the variance of the residuals of these two fits was due to chance alone). The probability that the reduction in the variance of the residuals was due to chance alone was approximately 0.048 (Table 1). We therefore

Table 1
Estimates of the rate of increase in surface ocean DIC at station ALOHA

Method	Slope ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$)	Probability	95% C.I. ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$)	Residuals ($\mu\text{mol kg}^{-1}$)
Linear fit to NDIC time-series data	0.8	0.034	0.06–1.6	6
Sine fit to NDIC time-series data	1.0	0.048	0.72–1.37	2.9

Fig. 6. Upper panel: least squares sine fit to the NDIC time-series at station ALOHA. This fit does not allow for an interannual increase in NDIC concentration. Lower panel: residuals to the least squares fit.

Fig. 7. Upper panel: least squares sine fit to the NDIC time-series at station ALOHA. This fit allows for an interannual increase in DIC concentration. Least squares fit yields an increase of $1 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$. Lower panel: residuals to the least squares fit.

reject the null hypothesis and conclude that the reduction in the variance of the residuals obtained by allowing for an increasing interannual trend was statistically significant and not due to chance alone. The 95% confidence intervals on this slope were estimated via a Monte Carlo style simulation. In this procedure, a set of random arrays, with residual errors equal to that of the least squares sine fit to the NDIC time-series, were generated in an iterative fashion and these were used to estimate the 95% confidence intervals for the slope. This analysis yielded confidence intervals at the 95% level that ranged from 0.72 to 1.37 $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Table 1).

4.2. Variability in titration alkalinity

The time-series of upper ocean NTA at station ALOHA shows no consistent pattern of annual variability and, as reported previously for station ALOHA (Winn et al., 1994), normalized alkalinity averages approximately 2305 $\mu\text{mol kg}^{-1}$. The mean value for NTA at station ALOHA is approximately 2305 $\mu\text{mol kg}^{-1}$ (standard deviation 7 $\mu\text{mol kg}^{-1}$). This value is consistent with measurements made by a variety of research programs in this region of the ocean (Millero et al., 1998). In addition, this value is in good agreement with the results of a recent transect through this region of the ocean as a part of the DOE sponsored Global CO_2 Survey of the Oceans (C.D. Winn, unpublished data). However, a significant oscillation in NTA may have been observed at station ALOHA in 1993 and 1994 (Fig. 3). This apparent annual trend in 1993 and 1994 is mostly within the envelope of variability that has been observed in upper ocean NTA over the duration of the time-series (Fig. 3). Nevertheless, within the long-term precision of the NTA time-series, there is no evidence for an interannual increase in NTA that could account for the interannual increase observed in the NDIC time-series.

4.3. Variability in upper ocean temperature

Because of the temperature dependent solubility of carbon dioxide in seawater, a 1 $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ increase in NDIC could be produced by a systematic cooling of approximately 0.1°C yr^{-1} . This calculation was done at 25°C and a salinity of 35, using the

apparent constants for K_1 and K_2 from Roy et al. (1993) and K_0 , the solubility coefficient for CO_2 , from Weiss (1974). Therefore, it is possible that the rising NDIC concentrations observed at station ALOHA could be caused by a consistent decrease in upper ocean temperature over the time-frame of our time-series measurements. However, there is no obvious evidence of a systematic cooling trend in the upper ocean temperature time-series (Fig. 2). In order to confirm that there is no statistical evidence for a cooling trend at station ALOHA, we performed the identical analysis described above for the NDIC time-series. Using this least squares approach, there was no statistical evidence for an interannual trend in upper ocean temperature.

4.4. Boundary layer p_{CO_2} and NDIC

The observed interannual increase in upper ocean NDIC of approximately 1 $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ is interpreted as a response of the upper ocean to rising atmospheric carbon dioxide concentrations. As mentioned above, this rate of increase is consistent with model predictions of the response of the ocean to rising atmospheric carbon dioxide concentrations. However, it is worthwhile to compare the estimated rate of increase over the time period of this investigation with the boundary layer p_{CO_2} time-series over the same time frame (Fig. 2). The rate of increase in atmospheric carbon dioxide concentration remained at a relatively constant proportion of the anthropogenic rate of carbon dioxide input to the atmosphere until the 1980s. In the late 1980s, the rate of increase in atmospheric CO_2 declined and in 1991 and 1992 the rate of increase dropped sharply (Keeling and Whorf, 1993; Keeling et al., 1995). This sharp decrease in the rate of atmospheric accumulation may be a consequence of the Mount Pinatubo eruption in 1991 combined with changes in the magnitude of oceanic and terrestrial sinks for carbon dioxide (Keeling et al., 1995; Ciais et al., 1995). These changes in the rate of atmospheric CO_2 accumulation are relatively small (Fig. 2), and given the uncertainties in our NDIC time-series, it is not reasonable to expect that the impact of these small perturbations would be apparent in our oceanic time-series record. Over the duration of the time-series program, however, boundary layer p_{CO_2} has

increased an average of $1.2 \mu\text{atm yr}^{-1}$ (Fig. 2). We computed the theoretical response of the oceanic concentration of upper ocean DIC to changes in atmospheric carbon dioxide using the formulations for the apparent constants K_1 and K_2 from Roy et al. (1993) and the apparent constant for K_0 from Weiss (1974), along with the average upper ocean temperature and salinity at station ALOHA (this yields a Revelle factor of approximately 9). Using this approach, and assuming that a $1.2 \mu\text{atm yr}^{-1}$ increase in atmospheric p_{CO_2} has been driving the rise in upper ocean NDIC over the time-frame of the HOT program, the rise in NDIC at the time-series site should average $0.8 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. This rate of NDIC increase is within the 95% confidence belt on the rate of increase estimated from our least squares sine fit to the NDIC time-series (Table 1).

5. Conclusions

We have used two simple approaches to estimate the interannual increase in upper ocean DIC concentrations at station ALOHA. Both of these approaches suggest that DIC concentration was rising at approximately $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ during the time period from 1989 to 1995. This rate of increase is consistent with predictions of the expected increase in surface water DIC in response to rising atmospheric carbon dioxide concentrations. In addition, this rate of increase is consistent with the few other direct measurements of the rate of increase in oceanic carbon dioxide concentrations (e.g., Takahashi et al., 1983; Tsunogai et al., 1993).

Given the relatively short oceanic DIC time-series available to date, it is not possible to rule out entirely other mechanisms that might also produce an interannual increase in upper ocean DIC concentrations. It is possible, for example, that slow changes in the gyre on decadal time scales or changes due to El Niño Southern Oscillation events (e.g., Karl et al., 1994) could also influence upper ocean DIC concentrations at station ALOHA. However, there is no evidence in our time-series of upper ocean alkalinity or temperature to suggest that the rise in DIC concentration can be attributed to anything other than the equilibration of the ocean with rising atmospheric carbon dioxide concentrations. In addition,

the observed rate of increase in upper ocean DIC is consistent with the rate of increase predicted from rising boundary layer p_{CO_2} in the vicinity of the HOT permanent station. We therefore conclude that the $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ increase in upper ocean DIC concentration observed in the HOT time-series data set is a response to rising atmospheric carbon dioxide concentrations.

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