GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 8, NO. 2, PAGES 157-163, JUNE 1994

Air-sea carbon dioxide exchange in the North Pacific Subtropical Gyre: Implications for the global carbon budget

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Abstract. The role of the ocean as a sink for anthropogenic carbon dioxide is a subject of intensive investigation and debate. Interest in this process is driven by the need to predict the rate of future increase of atmospheric carbon dioxide and subsequent global climatic change. Although estimates of the magnitude of the oceanic sink for carbon dioxide appear to be converging on a value of ~2 (Gt) C yr^{-1} for the 1980s, a detailed understanding of the temporal and spatial variability in the rate of exchange of carbon dioxide between the ocean and the atmosphere is not available. For example, recent modeling work and direct measurements of air-sea carbon dioxide flux produce very different estimates of the air-sea flux in the northern hemisphere. As a consequence, it has been suggested that a large unidentified oceanic carbon dioxide sink may exist in the North Pacific. As a part of our time series observations in the North Pacific Subtropical Gyre, we have measured dissolved inorganic carbon and titration alkalinity over a four-year period. These measurements constitute the most extensive set of observations of carbon system parameters in the surface waters of the central Pacific Ocean. Our results show that the ocean in the vicinity of the time series site is a sink for atmospheric carbon dioxide. On the basis of these observations, we present a mechanism by which the North Pacific Subtropical Gyre can be a potential sink for ~0.2 Gt C yr^{-1} of atmospheric carbon dioxide. Although our observations indicate that the North Pacific Subtropical Gyre is a sink for atmospheric carbon dioxide, the magnitude of this oceanic sink is relatively small. Our data and interpretations are therefore consistent with the argument for a relatively large sink during the 1980s in northern hemisphere terrestrial biomass. Another possibility is that the net release of carbon dioxide to the atmosphere owing to land use activities in tropical regions has been overestimated.

Introduction

After almost 20 years of investigation and debate, the global carbon cycle remains unbalanced. In fact, the global carbon cycle in nature is "balanced," but the scientific community has been unable to resolve the magnitudes and direction of carbon dioxide fluxes involving the oceans and terrestrial biomass. This is not surprising, given the complexity of the carbon cycle and the difficulty of accurately determining carbon fluxes on a global scale. Table 1 shows the carbon dioxide budget averaged for the 1980s. The carbon imbalance, the so-called "missing sink," is estimated as 1.8 ± 1.4 Gt of carbon per year (Gt C yr^{-1}). Of the two anthropogenic inputs, the flux of carbon dioxide to the atmosphere from the combustion of fossil fuels is a more precisely known value than that of land use activities (e.g., deforestation). Furthermore, it is known that ~57% of the anthropogenic carbon production has accumulated in the atmosphere [*Keeling et al.*, 1989]. The remaining carbon, about 43%, is either sequestered in the oceans or in terrestrial biomass.

What are the sinks for this missing carbon? Two recent detailed studies came to opposite conclusions with regard to whether the ocean or the terrestrial biosphere is the predominate sink for anthropogenic carbon dioxide [*Keeling et al.*, 1989; *Tans et al.*, 1990]. *Keeling et al.* [1989], using the historical record of atmospheric carbon dioxide accumulation and its $^{13}C/^{12}C$ isotope signature, concluded that the oceans are the major sink for carbon dioxide in the northern hemisphere. *Tans et al.* [1990], using the latitudinal gradient of atmospheric carbon dioxide and its global atmospheric accumulation rate as well as an extensive global compilation of the thermodynamic driving force for air-sea carbon dioxide exchange, concluded that a large sink for carbon dioxide must exist in terrestrial biomass in the northern hemisphere.

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Paper number 94GB00387.
0886-6236/94/94GB-00387$10.00

Table 1. Global Carbon Dioxide Budget

Source/Sink		Value
Sources to the atmosphere		
	Fossil fuel combustion	5.4 ± 0.5
	Changes in land use	1.6 ± 1.0
	Total 7.0 ± 1.2	
Sinks		
	Atmosphere	3.2 ± 0.1
	Oceans	2.0 ± 0.8
	Total	5.2 ± 0.8
Missing Sink[a]		1.8 ± 1.4

Data, averaged for the 1980s, from the Intergovernmental Panel on Climate Change [*Houghton et al.*, 1990].
[a]Carbon unaccounted for by global budget.

More recent investigations have suggested that *Tans et al.* [1990] may have underestimated the magnitude of the oceanic sink [*Enting and Mansbridge*, 1991; *Robertson and Watson*, 1992; *Sarmiento and Sundquist*, 1992]. In addition, *Quay et al.* [1992], using oceanic $^{13}C/^{12}C$ isotope ratios of dissolved inorganic carbon, have concluded that the oceans are larger carbon sinks than the data summarized by *Tans et al.* [1990] indicate. In addition, *Broecker and Peng* [1992] suggest that the North Atlantic is a large sink for carbon dioxide via the formation of carbon-rich North Atlantic Deep Water. However, the validity of the conclusions reached by *Quay et al.* [1992] have been questioned [*Broecker and Peng*, 1993], and the carbon that *Broecker and Peng* [1993] postulated is transported from the North Atlantic to the Southern Ocean via North Atlantic deep water may in fact reappear in the North Pacific Ocean [*Tans et al.*, 1994].

In a more recent article, *Tans et al.* [1994] reassess their global carbon budget. They correct their previous estimates for the effects pointed out in the studies described above as well as other work published subsequent to their original 1990 article. Although their corrections yield a sink of diminished magnitude, their global carbon budget still requires a substantial sink for carbon in northern hemisphere terrestrial biomass. However, a northern hemisphere terrestrial sink of sufficient magnitude to balance the global carbon budget has not been identified, and it has been suggested that a northern hemisphere terrestrial sink may not exist [*Houghton*, 1993].

We have been measuring inorganic carbon parameters in the North Pacific Subtropical Gyre (NPSG) for the last four years as part of the Hawaii Ocean Time-series Program (HOT). Our results suggest that the NPSG is a sink for atmospheric carbon dioxide. In this paper we present a mechanism by which the NPSG can be a net sink for atmospheric carbon dioxide, and we calculate that the magnitude of this sink may be ~0.2 Gt C yr^{-1}. Although this uptake rate is twice as large as the net flux into the entire North Pacific calculated from the data set compiled by *Tans et al.* [1990], the magnitude of this sink is still approximately an order of magnitude smaller than that needed to balance the global carbon budget.

Methodology

Monthly measurements of dissolved inorganic carbon (DIC) and titration alkalinity were made in the mixed layer of the NPSG from October 1988 to December 1992. These measurements were made within the context of a larger program designed to assess annual and interannual variability in the physics, chemistry, and biology of a site representative of the NPSG [*Karl and Winn*, 1991; *Winn et al.*, 1993]. This site is the Hawaii Ocean Time-series station ALOHA located at 22° 45'N, 158°00'W (Figure 1).

Total DIC was measured using a commercial coulometer (UIC, Inc. model 5011) modified for high-precision work [*Johnson et al.*, 1985, 1987]. Water samples were collected in clean 250-mL Pyrex reagent bottles as soon as possible after the rosette arrived on deck. The bottles were flushed with at least two volumes of sample, and the water was preserved with 100 µL of saturated $HgCl_2$. Sample bottles were sealed with apiezon grease, and a small air space was left in the bottle (1-2 cm^3) in order to maintain an effective seal. Because of the short duration of the HOT cruises, all samples were returned to the laboratory for analysis. In the laboratory, 25-30 mL seawater subsamples were delivered to our coulometer extractor with a carefully calibrated pipet bulb, or the subsamples were weighed and injected in tared syringes. The precision of this analysis on replicate subsamples from the same Niskin bottle is approximately ±2 µmol/kg.

Titration alkalinity was determined by the potentiometric titration method using a modified Gran plot which corrected for competing side reactions involving sulfate and fluoride [*Grasshoff et al.*, 1983; *Gran* 1952]. Because we were only interested in measuring total alkalinity, titrations were performed in an open cell. The precision of our gravimetric titration procedure is quite good at approximately ±2 µmol/kg. However, because of errors associated with acid standardization and electrode drift, we consider the assay to be reproducible to approximately ±5 µmol/kg on the month-to-month time frame of the HOT program.

Water column carbon dioxide fugacity (fCO_2) was calculated from DIC and alkalinity using the apparent constants of *Khoo et al.* [1977], *Dickson and Riley* [1979], *Dickson and Millero* [1987] and *Johannson and Wedburg* [1982] as recommended by *DOE* [1991]. Atmospheric carbon dioxide fugacity was computed as described by *Weiss* [1974] using the Mauna Loa atmospheric carbon dioxide record and marine boundary layer temperature and atmospheric pressure obtained from the National Data Buoy Center (NDBC) #51001 buoy (Figure 1). A saturated boundary layer was assumed for these calculations.

Results

DIC, total alkalinity, mixed layer temperature, and fCO_2 in both the ocean and the marine boundary layer are shown in Figure 2. In order to remove variability introduced by changes in salinity, both DIC and titration alkalinity are normalized to 35 parts per thousand (ppt) salinity. DIC varies by ~15 µmol kg^{-1} over the four-year measurement period and is inversely correlated with mixed layer temperature. After normalizing to 35 ppt salinity, titration alkalinity displays little temporal variability and averages ~2304 µeq kg^{-1}.

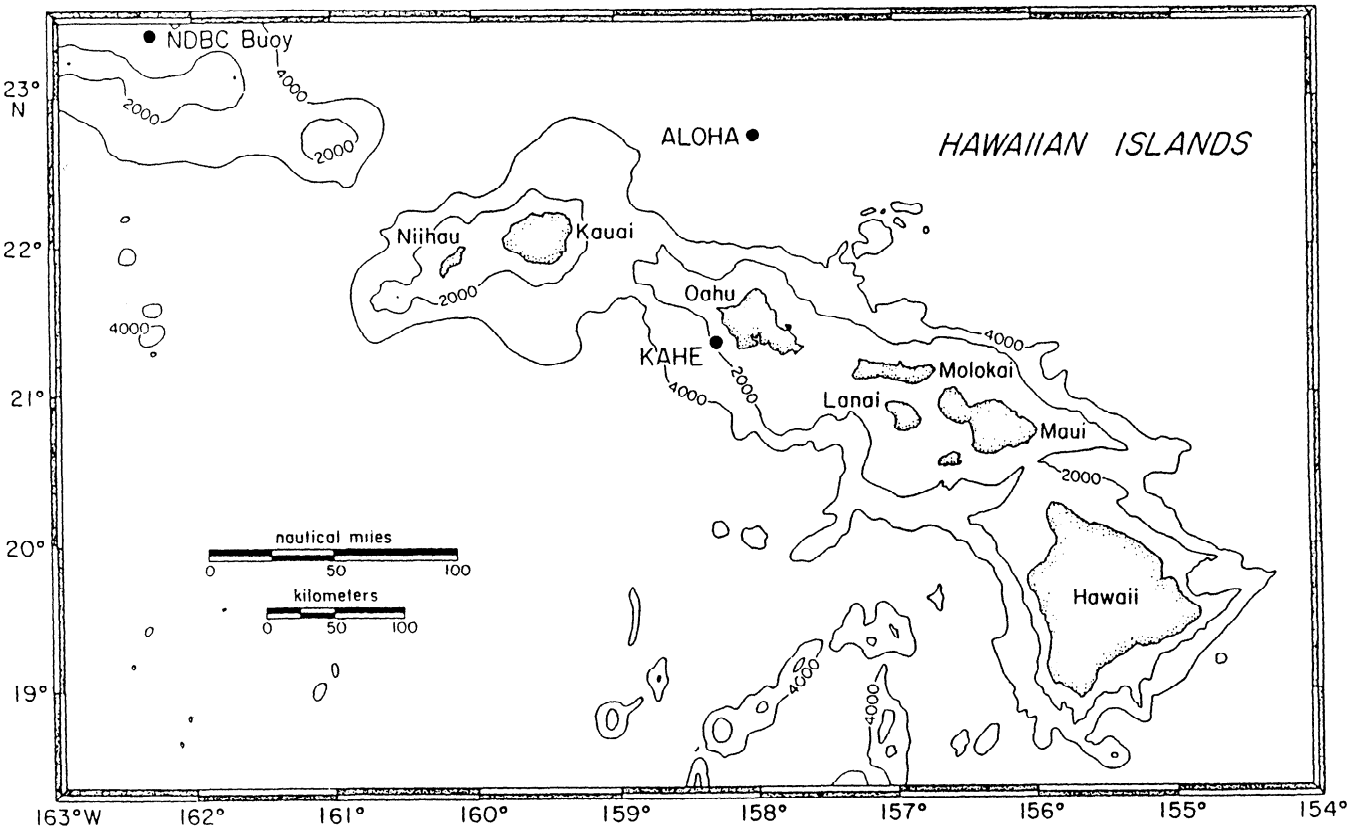


Figure 1. Location of station ALOHA, the US-JGOFS Hawaii Ocean Time-Series permanent station at 22° 45'N 158° 00'W.

Although normalized titration alkalinity varies by a little more than 5 μeq kg^{-1}, this range of variability encompasses our estimate of the reproducibility of the assay conducted over a four-year period. Within the precision of this assay therefore, titration alkalinity appears to be controlled mainly by mixing of water masses with slightly different salinities. This observation supports the prediction of *Weiss et al.* [1982] and the recent observations of *Sabine* [1992] that titration alkalinity is proportional to salinity in the tropical limb of the NPSG.

The annual variability in DIC at the HOT site is strongly correlated with mixed layer temperature. Assuming an average mixed layer depth of 60 m, the 15 μmol kg^{-1} yr^{-1} change in DIC concentration amounts to ~0.9 mol C m^{-2} yr^{-1}. This value is 15-fold larger than the estimated average rate of anthropogenic carbon dioxide increase of ~1 μmol kg^{-1} yr^{-1} in the surface waters of the world's oceans [*Brewer*, 1983]. Given this annual variability, several years of careful measurements will be required to document accurately the expected rise in upper ocean DIC owing to anthropogenic carbon dioxide accumulation.

The strong correlation between DIC and temperature can be interpreted to be a consequence of air-sea carbon dioxide exchange driven by changes in upper ocean temperature. However, the annual cycle in mixed layer temperature at the HOT site is a consequence of local heating and cooling as well as advection of water from the eastern and the tropical Pacific Ocean [*Seckel*, 1962]. In addition, the calculated fCO_2 data indicate that the ocean is a net sink for atmospheric carbon at the HOT site. Therefore we interpret the annual cycle in DIC in the upper ocean at the HOT site to be a consequence of both air-sea exchange driven by local heating and cooling as well as the advection of relatively warm, DIC-poor water to the site via Ekman transport.

Our time series data set was used to estimate the rate of carbon dioxide air-sea exchange at the HOT site. Carbon dioxide flux across the air-sea interface was estimated [*Tans et al.*, 1990] using the annual average wind speed (7 m s^{-1}) measured at NDBC buoy #51001 and the average delta fCO_2 (atmosphere minus ocean) of approximately -10 μatm (Figure 2). Using these data, a net flux of ~0.7 mol C m^{-2} yr^{-1} into the ocean is obtained.

This air-sea flux estimate is very dependent upon the fCO_2 values calculated from DIC and alkalinity, and some doubt has been expressed about the accuracy of these calculations [*Goyet et al.*, 1991]. Recently, however, good agreement between measured and calculated carbon system parameters in the tropical Pacific Ocean has been reported [*Millero et al.*, 1994]. These results indicate that when the apparent constants we have used are applied, fCO_2 can be calculated with an accuracy of ± 3 μatm or better in tropical ocean waters [*Millero et al.*, 1994]. In order to ensure the accuracy of our DIC measurements, we used reference materials provided by Andrew Dickson for the analysis of DIC. In addition, we have compared extensively our DIC and alkalinity measurements with replicate analyses provided by Charles Keeling at Scripps Institution of Oceanography over a 36-month period. This comparison demonstrated excellent agreement between these

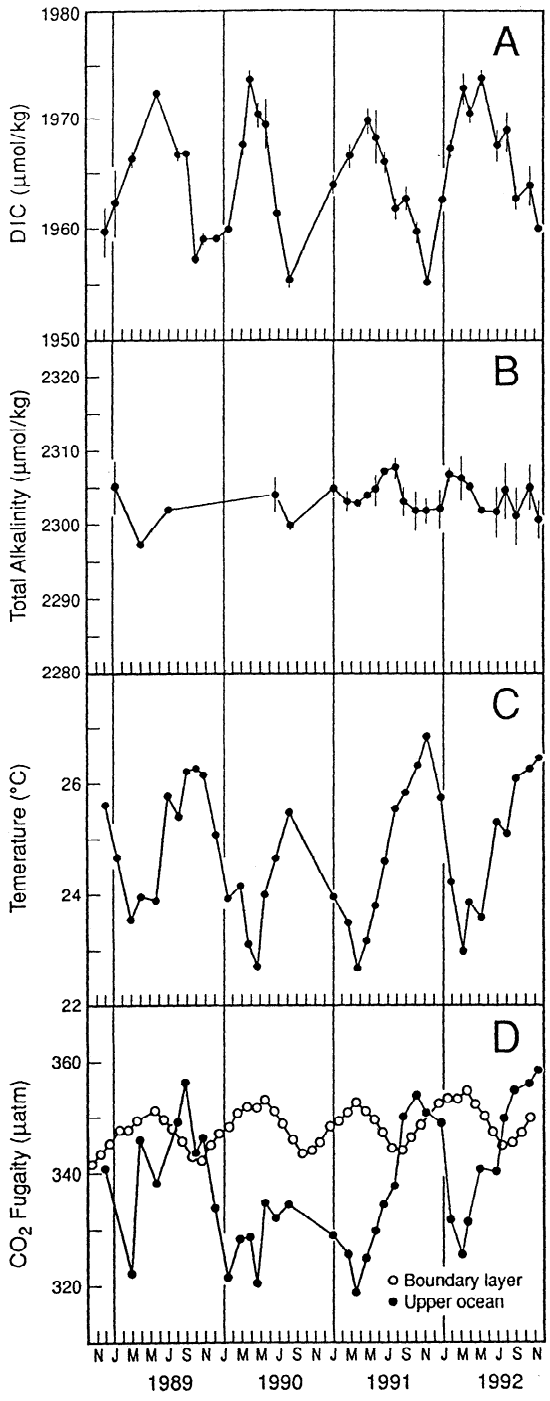


Figure 2. Carbon system parameters in the upper 60 m of the water column at the HOT site from October 1988 to December 1992. (a) DIC normalized to 35 ppt salinity (error bars represent the standard deviation of samples collected in the upper 50 m). (b) Titration alkalinity normalized to 35 ppt salinity (error bars represent the standard deviation of samples collected in the upper 60 m). (c) Mixed layer temperature in the upper 60 m of the water column. (d) Solid line shows carbon dioxide fugacity in the mixed layer at the HOT site. As a result of a five-month gap in the time series sampling program between early August 1990 and January 1991, the peak of mixed layer fugacity which would have appeared in the summer of 1990 was not observed.

independent analyses, with the mean and standard deviation of the difference between the two sets of measurements being 0.60 ± 5.0 μmol kg^{-1} and -0.31 ± 4.9 μeq kg^{-1} for DIC and alkalinity, respectively.

The observation that the ocean in the vicinity of the HOT site is a sink for atmospheric carbon dioxide is inconsistent with previous results [*Weiss et al.*, 1982], which indicated that the tropical limb of the NPSG ~10° south of the HOT site is in equilibrium with the atmosphere on an annual timescale. However, our results are consistent with the trend of delta fCO_2 becoming more negative with increasing latitude in the subtropical North Pacific [*Keeling*, 1968; *Broecker and Peng*, 1982]. Our results also suggest that the net annual flux of carbon into the ocean at our study location is reasonably similar to the annual average value per square meter of ocean surface for the entire North Pacific Ocean between 15° and 50°N as estimated in previous studies [*Tans et al.*, 1990; *Takahashi et al.*, 1991]. Assuming that the NPSG (the area between 15°N and 40°N and 120°W to 130°E) occupies ~26.3 x 10^6 km^2 and that our estimate of carbon flux (0.7 mol C m^{-2} yr^{-1}) is representative of the NPSG as a whole, we estimate that this region is a sink for ~0.2 Gt C yr^{-1}. Note that this estimate is derived from measurements at one location in the NPSG. We therefore consider this to be only an approximation of the air-sea flux in this region. It is important to point out, however, that the magnitude of this sink is small relative to the current global carbon cycle imbalance (Table 1). As a consequence, our estimation of the net air-sea CO_2 flux in the NPSG can be considerably in error without changing our conclusion that the sink for CO_2 in this region is small relative to the current imbalance in the global carbon budget.

We calculated that the annual net flux of carbon dioxide from the atmosphere to the ocean is ~0.7 mol m^{-2} yr^{-1}. If this carbon was accumulating in the upper 75 m of the water column at the HOT site, DIC concentrations would increase at a rate of ~10 μmol kg^{-1} yr^{-1}. This accumulation rate would be easily identified with our analytical techniques, but it is not observed (Figure 2). Some mechanism must remove the carbon entering the ocean at this location in the NPSG to prevent a rapid rise in carbon dioxide concentrations in surface waters.

We interpret the negative annual average delta fCO_2 and the subsequent net flux of carbon dioxide from the atmosphere to the ocean to be a consequence of the advective processes which predominate in subtropical gyres. The predominant current at this latitude is the North Equatorial Current, which moves water westward across the Pacific Ocean. One obvious scenario therefore is that DIC concentrations increase in surface waters as they move from east to west across the subtropical Pacific. However, the available data suggest that latitudinal gradients in DIC concentrations are small [*Takahashi et al.*, 1991]. In contrast, the meridional gradients in DIC concentrations at the latitude of the HOT site are relatively large. Furthermore, Ekman transport, as a consequence of the prevailing trade winds at this latitude in the North Pacific, moves surface water from the south toward the subtropical convergence. In fact, the NPSG is characterized by downwelling at a rate of ~30 m yr^{-1} as a consequence of Ekman transport toward the subtropical convergence [*Stommel*, 1979; *Roden*, 1980]. Water that is downwelled in the region of the HOT site is replaced by

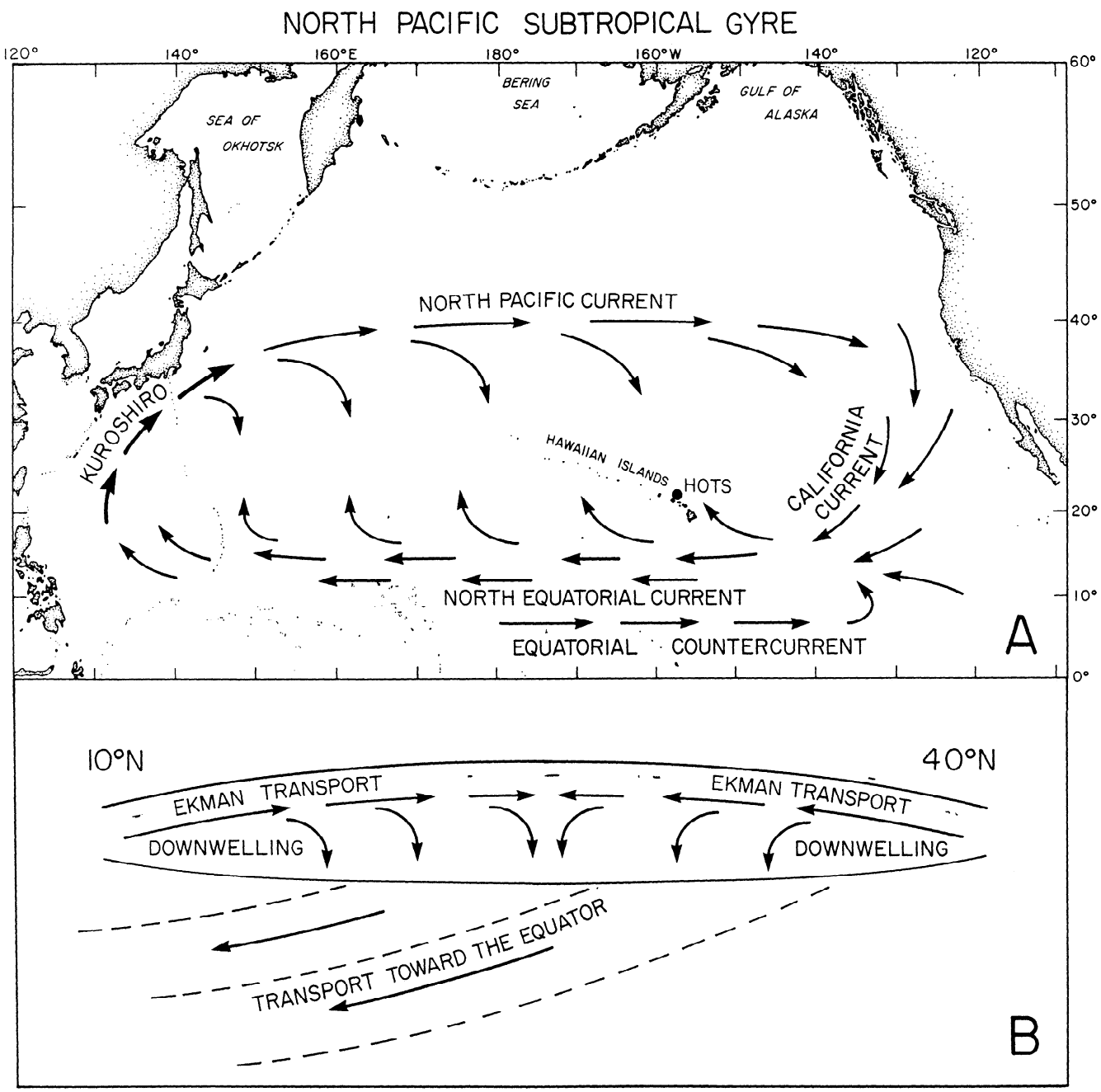


Figure 3. Major climatological currents in the NPSG. (a) Major horizontal surface flows in the NPSG relative to the Hawaiian Archipelago and the Hawaii Ocean Time-series site. (b) Schematic of the vertical flows along a north-south transect through the center of the gyre from ~10°-40° N.

surface waters originating in the equatorial ocean with a warmer temperature and lower DIC concentrations. We believe therefore that the net flux of carbon dioxide from the atmosphere to the ocean is balanced by the replacement of DIC-enriched water downwelled at the HOT site with water from the tropical Pacific. The DIC-enriched water that is downwelled as a consequence of the convergent flow in the gyre is then returned to the tropical Pacific within the upper reaches of the main thermocline (Figure 3).

A mass balance calculation indicates that the scenario described above is reasonable. Assuming that the upper 75 m of the water column is in contact with the atmosphere at the HOT site, and assuming that the water moving downward at ~30 m yr^{-1} is replaced from the southeast, we calculate that the northwest flowing water should have a DIC content of less than 1940 μmol kg^{-1} when normalized to 35 ppt salinity. The DIC content of the water at low latitudes in the eastern North Pacific (i.e., 10°N) is significantly lower than this value [*Feely et al.*, 1993].

Implications

The data set summarized here is the longest time series of observations of the inorganic carbon system in the North

Pacific Ocean. Our data indicate that the net flux of carbon from the atmosphere to the ocean in the NPSG is ~0.2 Gt C yr^{-1}. This amount is reasonably similar to previous estimates of sink for carbon dioxide in the North Pacific Ocean of 0.06 Gt C yr^{-1} [*Tans et al.*, 1990] and 0.1 Gt C yr^{-1} [*Takahashi et al.*, 1991]. Our observations are therefore consistent with the previous conclusions that the North Pacific Ocean is a relatively small sink for atmospheric carbon dioxide. The results of the JGOFS time series in the North Atlantic at the Bermuda Atlantic Time Series site (N. R. Bates, unpublished data, 1994] indicate that this gyre is also a small sink for atmospheric carbon dioxide. At the present time the global carbon cycle is out of balance by ~1-2 Gt C yr^{-1} [*Tans et al.*, 1994]. In general, our observational data and its interpretation confirm but do not prove the hypothesis that there was a relatively large terrestrial sink in the northern hemisphere during the 1980s. Another possibility is that the net flux of CO_2 to the atmosphere owing to land use activities in tropical regions has been overestimated. However, this conclusion is strongly debated by terrestrial ecologists [*Woodwell et al.*, 1983; *Houghton*, 1991; *Houghton et al.*, 1991; *Fearnside*, 1992; *Lugo*, 1992; *Lugo and Wisniewski*, 1992].

Acknowledgments. Support for this work was provided by the National Science Foundation's Chemical and Biological Oceanography Programs and by the National Ocean and Atmospheric Administration's Global Change Program.

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(Received November 4, 1993; revised January 25, 1994; accepted February 9, 1994.)