Anthropogenic CO₂ invasion into the northeast Pacific based on concurrent δ¹³C_{DIC} and nutrient profiles from the California Current

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Abstract. The stable isotopic signature of dissolved inorganic carbon (δ¹³C_{DIC}) in the northeast Pacific Ocean is lower in near-surface waters by 1.1‰ relative to values predicted from global oceanic trends of δ¹³C_{DIC} versus nutrients. A combination of anthropogenic carbon uptake from the atmosphere and thermodynamic, air-sea gas exchange processes in different water mass source areas account for the isotopic depletion. Here we evaluate the efficacy of using a concurrent nutrient-δ¹³C strategy to separate these two effects, with the goal of improving estimates of anthropogenic carbon uptake over the course of the Industrial Revolution. In depth profiles from the sea surface to 2500 m at four stations across the California Current (42°N), nitrate, rather than phosphate, is best correlated to δ¹³C_{IC} providing the best choice for this experiment. On the basis of an assumption of no anthropogenic carbon in North Pacific Deep Waters between 1000-2500 m depth (potential densities, σ_θ ~ 27.3-27.7), the “anthropogenic – preanthropogenic” carbon isotope shift (Δδ¹³C_{IC, a-p}) in near-surface waters of the northeast Pacific is inferred to be -0.62 ± 0.17‰, while the thermodynamic air-sea gas exchange signature is estimated at -0.48 ± 0.17‰. Values of Δδ¹³C_{IC, a-p} (similar to the regional patterns of Δ¹⁴C and Tritium penetration) approach zero for σ_θ > 26.8, indicating little penetration of anthropogenic carbon into the North Pacific Intermediate Water or the upper North Pacific Deep Water. Our results suggest an upper North Pacific sink of anthropogenic carbon over the past ~200 years that is ~40% greater than that estimated for the interval between ~1970 and ~1990 by Quay et al., [1992]. Our estimate of the North Pacific inventory of anthropogenic carbon, added to published estimates from the North Atlantic and Indian Ocean, is smaller than model predictions of the total carbon sink, suggesting that a significant portion of anthropogenic carbon enters the deep sea via the Southern Ocean.

1. Introduction

Variations of the stable isotopes of carbon in sea water provide a means of assessing the effect of anthropogenic activity on the global carbon cycle. The isotopic composition of anthropogenic carbon (expressed using the customary isotopic delta notation: δ¹³C = 1000[(¹³C_{sample}/¹²C_{standard})/(¹³C/¹²C_{standard})-1], where standard is CO₂ gas with the isotopic composition of the Pee Dee Belemnite (PDB) standard) released into the atmosphere by fossil fuel burning and deforestation is lower in δ¹³C than preanthropogenic carbon [Broecker and Peng, 1982]. Release of this ¹³C-depleted carbon since the beginning of the Industrial Revolution has steadily decreased the carbon isotopic composition of atmospheric CO₂ [Friedli et al., 1986]. Air-sea gas exchange has in turn reduced the carbon isotopic composition of dissolved inorganic carbon (δ¹³C_{DIC}) of seawater in contact with the atmosphere [Quay et al., 1992]. Exposure to the atmosphere thus offsets δ¹³C_{DIC} of near-surface waters relative to deep waters. Estimates of the magnitude of the near-surface water anthropogenic δ¹³C_{DIC} decrease vary from ~0.4 to ~1.0‰ (see review by Beveridge and Shackleton [1994] for further details). This range of variability results from a mixture of sampling errors as well as regional and temporal structures in oceanic uptake of anthropogenic CO₂ [see, e.g., Böhm et al., 1996].

Many methods have been used to estimate the magnitude of the anthropogenic carbon shift either directly or indirectly. These include (1) carbonate chemistry-based methods [Chen and Millero, 1979; Brewer, 1978; Gruber et al., 1996], (2) time-course measurement of the oceanic δ¹³C_{DIC} change [Quay et al., 1992; McNi-
col and Druffel, 1992; Bacastow et al., 1996), (3) estimation of the air-sea $^{13}$C disequilibrium [Tans et al., 1993], (4) proxy measurement of $^{13}$C$_{DIC}$ history recorded in the $^{13}$C of biogenic carbonates [Nozaki et al., 1978; Druffel and Benavides, 1986; Beveridge and Shackleton, 1994; Böhm et al., 1996], (5) use of a “dynamical constraint” linking the oceanic uptake of $^{14}$CO$_2$ and CO$_2$ [Heimann and Maier-Reimer, 1996], and (6) concurrent $^{13}$C$_{DIC}$-nutrient comparisons [Broecker and Peng, 1982; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995; Keir et al., 1998]. Each of these methods has merits and pitfalls, which we summarize briefly below.

Carbontate chemistry methods, which assess the temporal change in the balance of dissolved CO$_2$, HCO$_3^-$, and CO$_3^{2-}$, are relatively direct but rely on measuring small differences through time superimposed on the much larger oceanic total CO$_2$ signal. These methods are also dependent on knowledge of the preanthropogenic boundary conditions.

All of the $^{13}$C$_{DIC}$-based methods must specify a means of scaling the $^{13}$C shift into an associated change in DIC concentration. Time-course measurements of the oceanic $^{13}$C$_{DIC}$ change (i.e., assessing changes in $^{13}$C$_{DIC}$ at the same sites at different times) are complicated by seasonal and spatial sampling errors, temporal variations in instrument precision and accuracy, and the difficulty of reidentifying a water mass whose physical properties (i.e., $T$ and $S$) may drift along with its carbonate chemistry and carbon isotopic composition [Bindoff and McDougall, 1994]. The air-sea disequilibrium method (which is based on the $^{12}$C to $^{18}$C balance of the atmosphere and the associated disequilibrium relative to the ocean) is subject to sampling uncertainties and potential systematic bias associated with the selected wind speed gas transfer dependence.

Proxy measurements that rely on biogenic carbonates must assume no changes in biological or climatic overprints on the preserved isotopic record. However, among asymbiotic species of planktonic foraminifera, the carbon isotopic composition of the shell is a function of both the $^{13}$C$_{DIC}$ and the temperature at which the shell is calcified [Ortiz et al., 1996]. The isotopic composition of foraminiferal calcite is also influenced by carbonate chemistry related isotope effects [Spero et al., 1997], and symbiont-driven variations in calcite precipitation may also influence $^{13}$C and $^{18}$O disequilibrium [McConnaughey, 1989a, b]. Druffel and Benavides [1986] and Böhm et al. [1996] demonstrate the utility of slowly calcifying demosponges as recorders of the temporal shift in surface water $^{13}$C$_{DIC}$. While these organisms appear to calcify close to isotopic equilibrium, their restricted distribution limits their utility at assessing regional differences in anthropogenic CO$_2$ uptake.

Because of these sources of uncertainty, the various methods have reached considerably different conclusions regarding the overall importance of the ocean as a reservoir for sequestration of the anthropogenic CO$_2$ signal (Table 1). For example, Tans et al. [1993] concluded that the oceanic anthropogenic uptake rate was considerably less than that suggested by Quay et al. [1992]. In contrast, Heimann and Maier-Reimer [1996] arrived at essentially the same result as Quay et al. [1992] and concluded the discrepancy between the earlier studies was due to the propagation of uncertainties in the carbonate chemistry parameters needed to estimate the magnitude of the anthropogenic uptake. Using a statistical least squares method (“total inversion”), Heimann and Maier-Reimer [1996] proposed an optimized carbonate chemistry parameterization that reconciles their own approach with that of Tans et al. [1993] and Quay et al. [1992].

Here we return to the concurrent $^{13}$C$_{DIC}$-nutrient method pioneered by Broecker and Peng [1982]. This method takes full advantage of improvements in measurement techniques and avoids the difficulties of repeated measurements because analyses are conducted on temporally concurrent samples. The primary limitations of the method arise from the quality of the correlation between $^{13}$C$_{DIC}$ and a particular nutrient and from the assumptions used to partition the anthropogenic uptake signature from the effect of different preformed $^{13}$C$_{DIC}$ values in water masses at different depths. For our study sites we minimize the first of these problems by focusing on nitrate (rather than phosphate) which exhibits a superior correlation to $^{13}$C$_{DIC}$. The improvement in correlation helps us to assess water mass-dependent variations in the magnitude of the anthropogenic invasion in terms of well-established, physical mechanisms.

### 2. Methods

In September 1991, concurrent measurements of water column $^{13}$C$_{DIC}$ and nutrient content were conducted at four sites in the California Current system at ~42°N during cruise W9109B aboard R/V Wecoma (Figure 1). The stations, located ~20, 121, 289, and 650 km offshore are referred to here as the Inshore, Nearshore, Midway, and Gyre sites. Waters as deep as 2500 m were sampled during conductivity-temperature-depth (CTD) casts using 5-L Niskin bottles. CTD measurements of temperature and salinity were used to calculate sigma theta ($\sigma_\theta$), the potential density of a

<table>
<thead>
<tr>
<th>Source</th>
<th>Approach</th>
<th>Global Uptake Rate, Gt C yr$^{-1}$</th>
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<tr>
<td>Tans et al. [1993]</td>
<td>air-sea $^{13}$C$_{DIC}$ disequilibrium</td>
<td>0.6 ± 1.6</td>
</tr>
<tr>
<td>Francey et al. [1995]</td>
<td>modification of method of Tans et al. [1993]</td>
<td>1.1 ± 1.5*</td>
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<tr>
<td>Bacastow et al. [1996]</td>
<td>modeling of mixed layer $^{13}$C$_{DIC}$ time series</td>
<td>1-4</td>
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<tr>
<td>Quay et al. [1992]</td>
<td>time course change in $^{13}$C$_{DIC}$ pro files</td>
<td>2.3 ± 1.2</td>
</tr>
<tr>
<td>Heimann and Maier-Reimer [1996]</td>
<td>optimization of carbonate chemistry parameterization by “total inversion”</td>
<td>2.1 ± 0.9</td>
</tr>
<tr>
<td>Heimann and Maier-Reimer [1996]</td>
<td>“dynamical $^{14}$CO$_2$ versus CO$_2$ Constraint”</td>
<td>3.1 ± 1.6</td>
</tr>
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* Temporal average and standard deviation derived from 1982 to 1992 annual average estimates.
Figure 1. Locations of the northeast Pacific conductivity-temperature-depth (CTD) stations used in this study superimposed on local bathymetry contours (0, 200, 500, 1000-4000 m levels). These include World Ocean Circulation Experiment (WOCE) stations from the P17C and P17N lines, Multitracers (MT) sites at ~42°N, and GEOSECS station 201 (GEO-201).

water parcel, as a water mass tracer. Potential density will allow us to differentiate samples collected in near-surface waters (σθ < 25.1), from those collected in the shallow salinity minimum (SSM) (σθ < 25.1 - 26.7), North Pacific Intermediate Water (NPIW) (σθ < 26.7 - 26.9), or North Pacific Deep Water (NPDW) (σθ > 26.9).

Samples for measurement of nitrate (NO₃⁻) and phosphate (PO₄³⁻) concentration were taken from the Niskin bottles and stored in acid-washed 125-mL polyethylene bottles that were first rinsed with sample water. Frozen samples were thawed overnight prior to analysis on an Alpkern RFA autoanalyzer using standard wet chemistry techniques [Gordon et al., 1994]. The samples were run in three sets. For each set, concentrations of three to four standards were analyzed at the beginning and end of each run. The precision of the average calibration slope for the standard regressions were 1.5% for [NO₃⁻] and 5.0% for [PO₄³⁻]. The mean external precision of nine sets of triplicate surface water samples were 0.8% for [NO₃⁻] and 2.4% for [PO₄³⁻].

Water samples for carbon isotopic analysis were taken from the same Niskin bottles used for nutrient samples and stored (after overflowing using a bubble-free flow tube) in brown, 50-cc, reagent grade, prebaked septum-sealed vials. Samples were poisoned with mercuric chloride (HgCl₂) immediately after filling, stored under refrigeration in the dark, and returned to the OSU mass-spectrometer laboratory by surface freight immediately following the cruise. In the OSU mass-spectrometer laboratory, water samples were analyzed using a procedure similar to that of Kroopnick [1974]. Twenty (20) mL from each water sample were injected into a glass stripping line and acidified with 95% H₃PO₄. Total dissolved inorganic carbon (TIC) was evolved as CO₂ gas by stripping with high-purity He flowing through a glass frit. Water vapor and other easily condensable gases were frozen onto a three-loop glass trap filled with clean 2-mm glass balls (to maximize surface area) at -60°C. CO₂ gas was condensed on a one-loop cold trap containing similar glass balls at liquid nitrogen temperatures. Following stripping and trapping, the He flow was turned off, the CO₂ trap and an additional cold finger were isolated and evacuated, and trapped CO₂ was warmed and transferred to a 6-mm glass finger using liquid nitrogen. The 6-mm glass finger was then torch sealed, and the isolated CO₂ gas sample was transferred to a Finnigan/MAT-251 mass-spectrometer using a multiport/tube cracker system. External precision for the δ^{13}C of measurements based on replicate CO₂ gas samples extracted from an internal laboratory water standard following these methods was
3. Results

Southward advection, upwelling, and variations in biological activity result in systematic changes in the depth of the observed $\delta^{13}$C enrichment and nutrient depletion in upper waters of the California Current at 42°N (Figure 2). The $\delta^{13}$C in shallow waters (<50 m) ranges from 0.67‰ near the coast to 1.74‰ at the site farthest offshore. Surface water nutrient concentrations are greatest near the coast and decrease offshore from 14.36 to 0.74 mmol kg$^{-1}$ for [NO$_3^-$] and from 0.97 to 0.59 mmol kg$^{-1}$ for [PO$_4^{3-}$]. At all of the sites studied, mid-depth maxima for [NO$_3^-$] and [PO$_4^{3-}$] occur between 600-1000 m (Figure 2). The minimum in $\delta^{13}$C occurred near 600 m, with little variation at greater depth.

Figure 3. The surface [PO$_4^{3-}$] enrichment across the Multitracers transect. Concentrations of [NO$_3^-$] are stripped to near zero within the mixed layer which increases in depth from 20 m near the coast to 70 m offshore. Nutrient concentrations below the surface [PO$_4^{3-}$] enrichment layer follow Redfield scaling relationships. Nutrient axes are scaled by the Redfield AP/AN ratio of 1/16 to demonstrate this relationship.
At these sites, high-resolution shallow water casts (0-110 m) show that surface waters within the mixed layer contained more [PO₄³⁻] than [NO₃⁻] relative to the typical ΔP/ΔN Redfield ratio of 1/16 (Figure 3). The depth of the [PO₄³⁻] enrichment increased from 20 m near the coast to 75 m at the site farthest offshore, corresponding to the systematic increase in the depth of the mixed layer. This depth pattern also closely follows the distribution of biomass in these waters [Ortiz et al., 1995]. Waters below the [PO₄³⁻] enriched mixed layer had an ΔP/ΔN ratio consistent with Redfield scaling (Figure 3). We refer to these deeper waters as the "Redfield Zone." Surface nutrient enrichments such as these for [PO₄³⁻] are relatively common but seldom discussed because they are poorly understood [Haury et al., 1994]. Explanations for these features include atmospheric deposition, bubble scavenging, Langmuir circulation, and variations in nutrient cycling (see references cited by Haury et al. [1994]). The surface enrichments in [PO₄³⁻], which are not present in the [NO₃⁻] or in the δ¹³CDic data, point out the advantage of comparing δ¹³CDic with [NO₃⁻] at these California Current and similarly affected sites.

There is a strong linear relationship between [NO₃⁻] and δ¹³CDic (Figure 4) for shallow depths (<200 m) where [NO₃⁻] is <30 μmol kg⁻¹ (r² = 0.96, n = 28, significant at p<0.01). The slope of this shallow relationship is identical (with 95% confidence [Snedecor and Cochran, 1989]) to the δ¹³CDic to [PO₄³⁻] slope of Broecker and Maier-Reimer [1992] scaled to nitrate using a Redfield Ratio of 1/16:

\[
\delta^{13}\text{C}_{\text{DIC}} = -0.06(±0.006)\ [\text{NO}_3^-] + 1.6. \tag{1}
\]

In contrast to the upper water column, [NO₃⁻] and δ¹³CDic measurements from >200 m follow a considerably smaller slope (Figure 4):

\[
\delta^{13}\text{C}_{\text{DIC}} = -0.02(±0.01)\ [\text{NO}_3^-] + 0.6. \tag{2}
\]

The RMS errors on δ¹³C predicted from nitrate, on the basis of these linear regressions, are essentially identical: ±0.12‰ for the shallow (<200 m) water column and ±0.09‰ for the deep (>200 m) water column. With 95% confidence the shallow and deep slopes are statistically different from each other and from zero [Snedecor and Cochran, 1989].

The relationships between δ¹³Cdic and [PO₄³⁻] for the shallow and deep water column are consistent with those observed for δ¹³CDic and [NO₃⁻]. The shallow water δ¹³Cdic slope relative to [PO₄³⁻] is -0.96 (r² = 0.80, n = 28), while the deep slope is -0.30. As discussed above, the precision of the shallow water phosphate relationship is considerably worse than that for nitrate. We thus focus on the nitrate relationship for further analysis.

4. Discussion
4.1. Physical and Biological Factors Influencing δ¹³CDic

The δ¹³C composition of DIC arises from the interplay of several physical and biological processes. These include equilibrium and kinetic isotopic fractionation of the carbonate species in the ocean and atmosphere (e.g., H₂CO₃, HCO₃⁻, and CO₂⁻ and CO₃²⁻), biological fractionation during photosynthesis, and the mixing of water masses with different isotopic signatures. Thermodynamic equilibrium of the oceanic carbonate species with respect to carbon is temperature dependent, following a slope of -0.1‰ °C⁻¹ [Mook et al., 1974; Zhang et al., 1995]. Superimposed on the thermodynamic signature is the kinetic fractionation associated with the invasion and evasion of CO₂ across the air-sea interface. Net CO₂ invasion is greatest in the North Atlantic due to the northward advection of nutrient and CO₂-depleted surface waters to cooler high latitudes, while net evasion is greatest in regions of upwelling and subsequent warming of CO₂-rich subsurface waters such as the equatorial Pacific and eastern boundary current regions [Broecker and Peng, 1992].

Were thermodynamic equilibration the only factor influencing δ¹³CDic, average surface values would be depleted by some 3‰ relative to the deep ocean due to the large surface to deep water thermal gradient [Broecker and Maier-Reimer, 1992]. This is not observed because the timescale for isotopic equilibration of the dissolved carbon species is an order of magnitude longer than that...
for chemical equilibration. Instead, the effects of biological fractionation (which favors the fixation of $^{13}$C relative to $^{12}$C in organic matter), the export of organic carbon to the deep sea as raining particles, and water mass mixing dominate the $\delta^{13}$C signal. In response the surface waters of the modern ocean are enriched in $^{13}$C by up to 3% relative to deep waters.

As a result of the dominant biological effects, oceanic $\delta^{13}$C$_{\text{DIC}}$ varies inversely with water column nutrient content (i.e., the relationship has a negative slope). This slope varies on a regional basis due to the influence of exchange factors and mixing [Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995]. On a global scale, the utilization of carbon, nitrogen, phosphorous and other biological substrates follow set proportions as noted by Redfield et al. [1963] and revised by Anderson and Sarmiento [1994], Broecker et al. [1995], and Takahashi et al. [1995]. Similar arguments were used by Broecker and Peng [1982] and later Broecker and Maier-Reimer [1992] to estimate a "Redfield" slope for the relationship between $\delta^{13}$C$_{\text{DIC}}$ and $[\text{PO}_4^{3-}]$:

$$\delta^{13}C_p = \left(\frac{\epsilon_p}{\epsilon_{\text{CO}_2}}\frac{\Delta C}{\Delta P}\right)[\text{PO}_4^{3-}] + 2.7. \tag{3}$$

The quantity $\delta^{13}$C$_p$ thus represents the biological influence on the $\delta^{13}$C$_{\text{DIC}}$. The slope of this relationship (i.e., $\left(\frac{\epsilon_p}{\epsilon_{\text{CO}_2}}\frac{\Delta C}{\Delta P}\right)$) depends on the mean ocean photosynthetic $^{13}$C/$^{12}$C fractionation rate ($\epsilon_p$ = about -19%), the carbon to phosphorus Redfield ratio of marine organic matter ($\Delta C/\Delta P = 128$), and the mean ocean inorganic carbon concentration ($\text{ECO}_2 = 2200$ $\mu$mol kg$^{-1}$). The intercept of the relationship is determined by the mean ocean $\delta^{13}$C$_{\text{DIC}} = 0.5\%$ and the mean ocean $[\text{PO}_4^{3-}] = 2.2$ $\mu$mol kg$^{-1}$. Broecker and Maier-Reimer [1992] estimated the slope as -1.1% (\mu mol kg$^{-1}$)$^{-1}$. This value is slightly steeper than the -0.93% (\mu mol kg$^{-1}$)$^{-1}$ estimate of Broecker and Peng [1982] due to improved mass balance constrains and better estimates of the magnitude of the individual terms. The theoretical $\delta^{13}$C$_{\text{DIC}}$ to $[\text{PO}_4^{3-}]$ slope of -1.1% (\mu mol kg$^{-1}$)$^{-1}$ can be scaled relative to nitrogen using the Redfield $\Delta C/\Delta N$ ratio (= 1/16). This yields a $\delta^{13}$C$_{\text{DIC}}$ to $[\text{NO}_3^-]$ slope of -0.07% (\mu mol kg$^{-1}$)$^{-1}$.

The magnitude of the thermodynamic effects, often referred to as $\delta^{13}$C$_{\text{therm.}}$, the thermodynamically "air-sea gas exchange" component of the $\delta^{13}$C$_{\text{DIC}}$ signal, has been estimated by subtracting the mean ocean biological trend ($\delta^{13}$C$_b$) from measured $\delta^{13}$C$_{\text{DIC}}$ values [Broecker and Maier-Reimer, 1992; Charles et al., 1993; Lynch-Stieglitz et al., 1995]. Using this methodology, modern Circumpolar Deep Water has $\delta^{13}$C$_{\text{therm.}} = 0\%$ and North Atlantic Deep Water (NADW) exhibits $\delta^{13}$C$_{\text{therm.}} = -0.5\%$, while Weddell Sea Bottom Waters (WSBW) have $\delta^{13}$C$_{\text{therm.}} = +0.5\%$ due to the cold surface water temperatures. This approach can only be applied along isopycnal surfaces that do not contain a significant component of anthropogenic CO$_2$, i.e., at depths that have not exchanged carbon significantly within the time of the industrial revolution. Including the $^{13}$C-depleted anthropogenic signature prevalent in near-surface waters in this calculation would lead to an overestimate of $\delta^{13}$C$_a$ in NADW and an underestimate of $\delta^{13}$C$_{\text{therm.}}$ in WSBW.

At our study sites in the California Current, direct measurements of $\delta^{13}$C$_{\text{DIC}}$ and nutrients exhibit an inverse correlation, suggesting a dominant influence from biological processes (Figure 4). Surface $\delta^{13}$C$_{\text{DIC}}$ versus nutrient values in the upper 200 m have a lower intercept than expected relative to the deeper values (200-2500 m), however. The $\delta^{13}$C$_{\text{DIC}}$ versus $[\text{NO}_3^-]$ relationship for samples below 600 m lie on the mean ocean biological $\delta^{13}$C versus nutrient trend line of Broecker and Maier-Reimer [1992], converted from phosphate to nitrate values. Apparent depletion of $\delta^{13}$C$_{\text{DIC}}$ in shallow waters results in a "kink" in the $\delta^{13}$C$_{\text{DIC}}$ versus $[\text{NO}_3^-]$ relationship between 200 and 600 m depth at these sites. We argue that this kink arises from the combined effects of air-sea gas exchange and the uptake of anthropogenic CO$_2$. In sections 4.2-4.4, we attempt to partition the anthropogenic uptake signature for the thermodynamic air-sea gas exchange overprint.

4.2. Estimating the $\delta^{13}$C Anthropogenic and Air-Sea Gas Exchange Effects in Near-Surface Waters

To assess the anthropogenic carbon contribution to $\delta^{13}$C$_{\text{DIC}}$, we choose to estimate a preanthropogenic $\delta^{13}$C$_{\text{DIC}}$ value for near-surface waters. This will allow us to estimate the magnitude of both the anthropogenic uptake and the thermodynamic air-sea gas exchange signatures at our locations. To do this, we compare the well-constrained relationship between $\delta^{13}$C$_{\text{DIC}}$ and $[\text{NO}_3^-]$ observed in this region, with the mean ocean $\delta^{13}$C biological trend line inferred by Broecker and Maier-Reimer [1992]. It is important to note that both of these slopes contain effects due to biology and gas exchange. Keir et al. [1998] used a similar nutrient-$\delta$ approach in a North Atlantic study, although their analysis was based on comparison of $\delta^{13}$C$_{\text{DIC}}$ to $[\text{PO}_4^{3-}]$ and they assume a surface-water anthropogenic shift in order to calculate the depth of the anthropogenic carbon penetration.

To develop a model of the preanthropogenic $\delta^{13}$C$_{\text{DIC}}$ versus $[\text{NO}_3^-]$ at our sites, we assume first that nonoutcropping, North Pacific Deep Water between 1000-2500 m contains no anthropogenic carbon. This assumption is based on the fact that North Pacific water on isopycnals in this depth range ($\rho_9 \sim 27.3 - 27.7$) do not outcrop at or near the sea surface. The second assumption is that the preanthropogenic slope of the $\delta^{13}$C$_{\text{DIC}}$ to $[\text{NO}_3^-]$ relationship in this region was similar to its current near-surface value of -0.06. Our first assumption does not imply a lack of anthropogenic carbon at depths > 2500 m which could be ventilated from the south. The second assumption implies that there have been no significant, uncoupled temporal shifts in either gas exchange effects or biological fractionation of carbon isotopes on shallow isopycnals in this region (we evaluate these assumptions later). Together, the two assumptions yield $\delta^{13}$C$_p$, a preanthropogenic $\delta^{13}$C$_{\text{DIC}}$ to $[\text{NO}_3^-]$ relationship for this region (Figure 5):

$$\delta^{13}C_p = -0.06 \pm 0.006 \times [\text{NO}_3^-] + 2.2. \tag{4}$$

The offset between this pre-anthropogenic model and measured (anthropogenic) values is $\Delta\delta^{13}$C$_{\text{a,p}}$, the anthropogenic $\delta^{13}$C offset or $\delta^{13}$C Suess effect:

$$\Delta\delta^{13}C_{\text{a,p}} = \Delta\delta^{13}C_a - \Delta\delta^{13}C_p. \tag{5}$$

The mean value of $\Delta\delta^{13}$C$_{\text{a,p}}$ in the near-surface mixed layer at these locations is -0.62%. Uncertainty in $\Delta\delta^{13}$C$_{\text{a,p}}$ (which varies with depth) is estimated by propagating the regression errors for (1) (±0.12%) and (4) (±0.12%) for samples from 0-200 m and (2) (±0.09%) and (4) (±0.12%) for samples below 200 m. This yields errors that range from a maximum of ±0.17% at the surface to a minimum of ±0.15% at depth.

As an initial check on the validity of this method for estimating $\Delta\delta^{13}$C$_{\text{a,p}}$ in this region, we can calculate the magnitude of the associated air-sea gas exchange effect. Subtracting $\delta^{13}$C$_a$ from (3),
that North Pacific Deep Water in the depth range between 1000 and 2500 m (σθ = 27.3 - 27.7) does not outcrop at or near the sea surface. Waters in this depth range constitute the "oldest" water mass in the world ocean [Stuiver et al., 1983].

Additional support for the first assumption is provided by the observation that δ13C is passes through the δ13C of the deep waters on σθ = 27.3 - 27.7 at our sites. This implies either that no anthropogenic carbon was present in the GEOSECS data used by Broecker and Maier-Reimer [1992] to develop the mean biological trend line or that no additional carbon was loaded on these isopycnals in the 20 years between the GEOSECS program and 1991 when our measurements were collected. A third line of support for the first assumption comes from the absence of CFCs and bomb radiocarbon in WOCE measurements from the northeast Pacific on isopycnal surfaces between σθ 27.3 and 27.7 [Warner et al., 1996; Aydin et al., 1998]. This later constraint however covers only the last half century, when such tracers were released. Despite all this evidence, if anthropogenic carbon was found on these isopycnal surfaces, our method would underestimate the magnitude of the anthropogenic uptake. Our estimate should thus be taken as a lower bound. We explore this possibility further in section 4.6.

The validity of the second assumption requires more careful consideration. The terms that influence the δ13C signature versus nitrate slope are εp, the ΣCO₂ of the relevant water mass, and the Redfield carbon to nitrogen ratio (ΔC/ΔN). Goericke and Fry [1994] estimate that εp decreases by -0.11 to -0.29% as [CO₂]pp increases by 1 μmol L⁻¹. It is also well established that water mass ΣCO₂ varies as a function of carbonate chemistry and circulation history [Broecker and Peng, 1982]. As a result, the ΣCO₂ of a water mass can affect the δ13C signature to nutrient relationship in two ways. Increasing ΣCO₂ lowers εp by shifting the fractionation bal-

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**Figure 5.** Measurements of δ¹³CDOC versus [NO₃⁻] in the northeast Pacific. The solid line represents the least squares fit to the 0-200 m data. The anthropogenic δ¹³CDOC shift, Δδ¹³CDOC, can be estimated from the offset between the measured δ¹³CDOC values and the preanthropogenic model (shaded region). The offset between the preanthropogenic model (shaded region) and the mean ocean biological trend line inferred by Broecker and Maier-Reimer [1992], yields a combined estimate of the anthropogenic and thermodynamic air-sea gas exchange overprint. This allows us to deconvolve the anthropogenic uptake and the thermodynamic air-sea gas exchange signatures at our locations. In the mixed layer, these two effects together reach a magnitude of ~1.1‰, which implies a thermodynamic air-sea gas exchange signature in surface waters of ~0.48‰ in the California Current at 42°N. Lynch-Stieglitz et al. [1995] obtained a similar result for the magnitude of the thermodynamic air-sea gas exchange effect in the North Pacific mixed layer in the latitude range from 40°N to 50°N using another data set and somewhat different assumptions in their numerical model-data comparison. Our method for calculating Δδ¹³CDOC and the associated air-sea gas exchange rate is thus consistent with published estimates for the magnitude of the air-sea gas exchange rate at our study sites. In section 4.3 we further evaluate the assumptions behind our method.

**4.3. Error Analysis: Sensitivity of the Preanthropogenic δ¹³CDOC Model**

Reliably deconvolving the anthropogenic uptake signature from the thermodynamic air-sea gas exchange signal depends on the plausibility of our two assumptions. The first assumption that North Pacific deep waters between 1000-2500 m contain essentially no anthropogenic carbon is plausible, on the basis of the fact

**Figure 6.** N* on isopycnal surfaces in the northeast Pacific using WOCE P17 [NO₃⁻] and [PO₄³⁻] measurements. The parameter N* = 0.87([NO₃⁻]-16[PO₄³⁻]+2.90), as defined by Gruber and Sarmiento [1997], provides a quasi-conservative tracer that identifies excesses (positive values) or deficits (negative values) of nitrate relative to phosphate. Scaling for the N* axes is based on the global range of observed values. Dashed vertical line denotes the value of N* where [NO₃⁻] and [PO₄³⁻] = 0. Water mass boundaries are indicated schematically at right.
ance between \([\text{CO}_3]_{\text{aq}}, [\text{HCO}_3^-], \) and \([\text{CO}_2]^-\). At the same time, increasing \(\Sigma\text{CO}_2\) in surface waters decreases the sensitivity to biology (the slope of \(\delta^{13}\text{C}_{\text{DIC}}\) to nutrients). The Redfield carbon to nitrogen ratio, while constant along deep isopycnal surfaces, can be altered in surface waters by changes in ecological community structure [e.g., Karl et al., 1995] or by processes such as denitrification and nitrogen fixation that can alter the local nitrogen inventory [e.g., Codispoti and Richards, 1973].

To assess the sensitivity of the \(\delta^{13}\text{C}_{\text{DIC}}\) to \([\text{NO}_3^-]\) slope to these processes, we consider a hypothetical experiment, starting with temperature (11°C), salinity (33), atmospheric \(p\text{CO}_2\) (280 ppm), and surface water total alkalinity (2300 \(\mu\text{eq L}^-1\)), values likely to occur in the northern California Current for preanthropogenic boundary conditions. In this hypothetical construct, an equilibrium response to an 80 ppm rise in atmospheric \(p\text{CO}_2\) would increase surface water \(\Sigma\text{CO}_2\) by \(\approx 45 \mu\text{mol kg}^-1\) and \([\text{CO}_2]_{\text{aq}}\) by \(\approx 5.3 \mu\text{mol kg}^-1\) (or \(\approx 3.6 \mu\text{mol L}^-1\)). The maximum attainable change in \(e_p\) predicted from the more sensitive relationship of Goerke and Fry [1994] cited above would be \(\approx 1\%\).

If we recalculate the shallow water \(\delta^{13}\text{C}_{\text{DIC}}\) to \([\text{NO}_3^-]\) slope using the inferred \(\Delta\text{CO}_2\) and \(\Delta e_p\) shifts, the anthropogenic slope changes by \(+0.003 \%\) (\(\mu\text{mol kg}^-1\)) relative to the preanthropogenic slope. The potential range in the magnitude of the preanthropogenic slope (-0.057 to -0.060%) is indicated by gray shading on Figure 5. Such bias is within the range of error (\(\pm 0.006\)) we estimate for the shallow water slope and would yield a maximum change in the \(\delta^{13}\text{C}\) intercept of the preanthropogenic model at nitrate depletion of -0.135%, which is smaller than the measurement error of the method. Thus plausible changes in \(e_p\) and associated carbonate chemistry are within the propagated errors of our calculation.

A regional change in the Redfield \(\Delta\text{C}/\Delta\text{N}\) ratio could potentially occur due to differences in denitrification (a response to \(O_2\) depletion) through time or in different water masses. We tested this possibility by calculating the quasi-conservative tracer \(N^*\) of Gruber and Sarmiento [1997]. This analysis, based on data from the WOCE P17 line, allows us to assess the regional \([\text{NO}_3^-]\) deficit (or excess) relative to \([\text{PO}_4^-]\). If variations in regional denitrification rates altered the \(\delta^{13}\text{C}_{\text{DIC}}\) to nutrient slope to cause the observed “kink” in the \(\delta^{13}\text{C}_{\text{DIC}}\) to nutrient relationship, a plot of \(N^*\) versus density should exhibit a clear offset between shallow and deep isopycnals. This is not the case. Values of \(N^*\) in the WOCE data scatter between 0 and -5 \mu mol kg^-1 at all depths. Thus regional denitrification rates have not varied systematically within these water masses during the course of the industrial revolution (Figure 6). It thus seems unlikely that significant changes in the Redfield \(\Delta\text{C}/\Delta\text{N}\) ratio occurred in this region since the onset of the Industrial Revolution.

One final physical process could affect the regional \(\delta^{13}\text{C}_{\text{DIC}}\) versus \([\text{NO}_3^-]\) slope and thus bias our preanthropogenic model. Because the anthropogenic \(\delta^{13}\text{C}_{\text{DIC}}\) forcing has an atmospheric source and is time dependent, it is reasonable to infer that shallow isopycnals should experience greater anthropogenic carbon loading than deeper ones. Because this carbon is supplied to the ocean as nutrient-free \(\text{CO}_2\), this differential ventilation process could potentially alter the regional \(\delta^{13}\text{C}_{\text{DIC}}\) versus \([\text{NO}_3^-]\) slope.

To assess the magnitude of this effect, the depth range in question at our sites is the portion of the water column from 0 to 200 m which was used to derive the \(\delta^{13}\text{C}_{\text{DIC}}\) versus \([\text{NO}_3^-]\) slope. Here a depth ~200 m corresponds roughly to \(\sigma_0\) 26.5. This isopycnal is close to the base of the shallow salinity minimum which occurs along the isopycnal surface of ~\(\sigma_0\) 26.7. On the basis of CFC data from the North Pacific published by Warner et al. [1996], the waters on the slightly shallower isopycnal surface of \(\sigma_0\) 26.4 have ages between 8 and 12 years near our study sites. The critical question thus becomes by how much does the \(\delta^{13}\text{C}_{\text{DIC}}\) in this region of the North Pacific decrease over a time span of roughly one decade due to the loading of anthropogenic carbon on isopycnal surfaces? Sonnerup et al. [1999] provide us with a means of directly addressing this question. They infer a \(\delta^{13}\text{C}\) Suess effect of -0.1% decade^-1 in subpolar oceanic regions. These two pieces of information suggest that the preanthropogenic model we have developed may underestimate the magnitude of the surface water \(\delta^{13}\text{C}\) Suess effect at our locations by +0.1% at most due to differential ventilation. Given that the reported uncertainty on our model is +/-0.17% at the surface, we conclude that this effect is comparable to the noise level of our model and thus does not significantly bias our results. Although the magnitude of this potential source of bias is small relative to the uncertainty in our model, it must be pointed out that any curvature in the true preanthropogenic \(\delta^{13}\text{C}_{\text{DIC}}\) versus \([\text{NO}_3^-]\) relationship at our location would tend to increase the slope of the relationship in the near surface waters. Because of this, our anthropogenic reconstruction should be considered a lower bound.

On the basis of these sensitivity tests, we conclude that the \(\delta^{13}\text{C}_{\text{DIC}}\) to nutrient slope in this region is relatively insensitive to anthropogenic changes in ocean chemistry and differential ventilation. Small changes in \(e_p\) and \(\Sigma\text{CO}_2\) are possible but tend to cancel each other’s effect on the \(\delta^{13}\text{C}_{\text{DIC}}\) to nutrient slope. However, we caution that variations in the \(\Delta\text{C}/\Delta\text{N}\) ratio may be more important in other regions of the ocean where denitrification is more prevalent. Application of this methodology in other ocean regions should, of course, be done with cautious attention to all processes potentially at work.

4.4. The Anthropogenic \(\delta^{13}\text{C}\) Offset, Isopycnal Ventilation, and Diffusion

The value of \(\Delta\delta^{13}\text{C}_{\text{a,p}}\) varies systematically as a function of water mass at each station in the Multitracers transect (Figure 7). Near surface water of potential density (\(\sigma_0 < 25.1\)) and those within the shallow salinity minimum (SSM) have a mean anthropogenic \(\delta^{13}\text{C}\) offset of -0.62 ± 0.17%. There are no significant differences in \(\Delta\delta^{13}\text{C}_{\text{a,p}}\) within waters of \(\sigma_0 < 25.5\). Below the SSM, \(\Delta\delta^{13}\text{C}_{\text{a,p}}\) shifts from a value of -0.62% at \(\sigma_0\) 26.5 to 0% (i.e., no apparent anthropogenic carbon) for \(\sigma_0\) 27.3. Values of \(\Delta\delta^{13}\text{C}_{\text{a,p}}\) averaging 0% below 1000 m (\(\sigma_0\) 27.3, North Pacific Deep Water) reflects our first assumption that no anthropogenic carbon is present at great depths.

The relative constancy of \(\Delta\delta^{13}\text{C}_{\text{a,p}}\) in waters of \(\sigma_0 < 25.5\) suggest that near-surface waters (\(\sigma_0 < 25.1\)) and the waters of the SSM obtain their anthropogenic signature through substantial direct contact with the atmosphere. Waters of the SSM are formed by the subduction of cold, fresh, northern surface water below the warmer, more saline (but less dense) water of the California Current and subtropical gyre [Reid, 1973; Talley, 1985].

The sharp decrease in the anthropogenic offset across the base of the SSM and into the NPIW suggests that NPIW forms with limited atmospheric exchange and is consistent with diffusive propagation of the anthropogenic signal across these density surfaces. We can calculate the apparent vertical diffusivity (\(K_z\)) that
would be needed to transmit the anthropogenic $\delta^{13}$C signal from $\sigma_0 = 26.5$ to $\sigma_0 = 27.3$ (i.e., from 200 to 800 m) by diapycnal mixing. We seek to determine whether the apparent $K_z$ we obtain is similar to observed values. We solve for $K_z$ based on the time rate of change of $\Delta \delta^{13}C_{\rho}$ at 500 m, a process which is second order in depth:

$$\frac{dC}{dt} = K_z \frac{\partial^2 C}{\partial z^2}$$  \hspace{1cm} (6)$$

or by relating the penetration rate of the volume integrated $\Delta \delta^{13}C_{\rho}$ signal, which is first order in depth, to the assumed constant surface boundary condition evaluated at 200 m:

$$\frac{dC}{dt} = -K_z \frac{\partial C}{\partial z} \bigg|_{z=200m}$$  \hspace{1cm} (7)$$

In both cases, the timescale of interest spans the last 40 years, i.e., the time of the strongest atmospheric CO$_2$ forcing which should dominate the response. This time span is also consistent with an upper limit on CFC derived ages for waters on $\sigma_0 = 27.2$ in the northeast Pacific [e.g., Warner et al., 1996; Aydin et al., 1998]. While (6) is solved numerically using values for $\Delta \delta^{13}C_{\rho}$ at 200, 500, and 800 m, (7) can be solved exactly by integration assuming a constant boundary condition for the depth integrated $\Delta \delta^{13}C_{\rho}$ signal at 200 m. When solved independently for $K_z$, the two methods agree well despite the different assumptions, yielding estimates of $K_z \approx 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. This value is similar to observational estimates of diapycnal mixing in the pycnocline (i.e., $K_z \approx 1.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$) based on Sulfur Hexafluoride (SF$_6$) tracer release studies [Ledwell et al., 1993] or high resolution microstructure profiler experiments [Polzin et al., 1997].

We conclude that it is plausible for the anthropogenic $\delta^{13}$C signal to be transmitted diffusively below the SSM. Unlike the isopycnals of the SSM, the underlying density surfaces of the NPIW, centered at $\sigma_0 = 26.8$, do not outcrop in the North Pacific except in the Sea of Okhotsk [Talley, 1991]. As a result, waters below the NPIW in the northeast Pacific retain their preanthropogenic $\delta^{13}$C value.

4.5. Local Comparison of the Oceanic Anthropogenic $\delta^{13}$C, $\Delta^{14}$C$_{\text{bomb}}$ and $^3$H$_{\text{bomb}}$ Uptake Signals

We suggest that near-surface and SSM waters of the northeast Pacific have gained their anthropogenic $\delta^{13}$C signal by direct contact with the atmosphere and subsequent subduction, primarily along isopycnal surfaces. Reasonable estimates of diapycnal mixing can account for penetration of anthropogenic CO$_2$ into NPIW. If this inference is correct, ventilation of the subtropical gyre's thermocline should leave its imprint on bomb radiocarbon ($\Delta^{14}$C$_{\text{bomb}}$) and bomb tritium ($^3$H$_{\text{bomb}}$) as well. To make this comparison, we estimated $\Delta^{14}$C$_{\text{bomb}}$ using the “silica analog” method of Broecker et al. [1995] and data from the GEOSECS and WOCE expeditions. Peng et al. [1996] demonstrate that the silica analog method provides reasonable estimates of oceanic radiocarbon uptake when applied to WOCE data in this region. For these calculations we rely on water column $\Delta^{14}$C data from GEOSECS Station 201 [Östlund and Stuiver, 1980] and WOCE stations along the P17C and P17N lines near our study site [Key et al., 1996]. The WOCE data were collected during the same year as our water column $\delta^{13}$C data along sections slightly farther south or west of our transect. The WOCE P17C stations are very close to the location of GEOSECS Station 201, which was occupied in 1973 (Figure 1).

Because the timescale and input functions for the $\Delta^{14}$C$_{\text{bomb}}$ and $^3$H$_{\text{bomb}}$ signals generated by atmospheric nuclear testing during the 1950s and 1960s differ from the input function of anthropogenic CO$_2$, we can expect some differences between the observed patterns. Nevertheless, penetration of $\Delta^{14}$C$_{\text{bomb}}$ along isopycnal surfaces in the northeast Pacific bears a striking similarity to our estimate of the anthropogenic $\delta^{13}$C uptake on the same isopycnal surfaces (Figure 8). The magnitude of the surface water $\Delta^{14}$C$_{\text{bomb}}$ signal in the northeast Pacific has decreased by radioactive decay from roughly 250% when GEOSECS Station 201 was sampled in 1973 to ~150% when the WOCE samples were collected in 1991. During the GEOSECS sampling period, only the near surface waters down to $\sigma_0 25.0$ were fully loaded with bomb radiocarbon; the $\Delta^{14}$C$_{\text{bomb}}$ signal had not penetrated as deep as into the isopycnal surfaces of the SSM as can be seen in the WOCE data. By 1991, $\Delta^{14}$C$_{\text{bomb}}$ was present on the isopycnals of the SSM down to $\sigma_0 26.2$ with little measurable difference in the concentration on shallower density layers. This same pattern of constant loading on shallow surfaces can be seen in the penetration of the $^3$H$_{\text{bomb}}$ signal. Using WOCE Tritium and Helium data from the same stations (B. Jenkins, personal communications, 1996), we calculate that isopycnal surfaces shallower than $\sigma_0 26.0$ have tritium-helium age of less than 10 years that decrease very gradually toward the surface. These comparisons give us confidence that the anthropogenic $\delta^{13}$C signal we observe provides realistic oceanographic information and is strongly influenced by the ventilation of the north Pacific.

4.6. Estimating the Total Oceanic Carbon Sink: Comparison to Other Studies

Our inference of an anthropogenic $\delta^{13}$C change in near-surface waters of $-0.62 \pm 0.17\%_o$ for the northeast Pacific, based on the concurrent nutrient-$\delta^{13}$C strategy, cannot be directly compared...
with a similar study of Keir et al. [1998] in the North Atlantic. They assumed a mixed layer value for $\Delta^{13}C_{ap}$ of -0.8% (based on measurements of biogenic carbonates from the Caribbean and Coral Sea). Their primary goal was to estimate the penetration depth of anthropogenic carbon in the Atlantic, where North Atlantic Deep Water is present. In contrast, we assumed no anthropogenic carbon in North Pacific Deep Waters between $\sigma_0$ 27.3 and 27.7 and used the modern $\delta^{13}C_{[NO_3^-]}$ slope to solve for the surface water value. If Keir et al. [1998], for example, had used a $\Delta^{13}C_{ap}$ of -0.6% (similar to ours) for the North Atlantic, their estimate of the anthropogenic carbon penetration depth would be reduced from ~4500 m to somewhere between 3000 and 3500 m. Such a penetration depth would be in better agreement with carbonate chemistry based estimates for the anthropogenic carbon penetration at their North Atlantic sites [Keir et al., 1998].

The other observational method most similar in timescale to the nutrient comparison method relies on proxy measurements of biogenic carbonates secreted prior to the advent of the historic record [e.g., Druffel and Benavides, 1986; Beveridge and Shackleton, 1994; Böhm et al., 1996]. The study of Beveridge and Shackleton [1994] based on comparison of sediment trap and nutrient comparison method relies on proxy measurements of biogenic carbonates secreted prior to the advent of the historic record. Beveridge and Shackleton [1994] based on comparison of sediment trap and biogenic carbonates secreted prior to the advent of the historic record [Böhm et al., 1996] on the sediment trap data of Beveridge and Shackleton [1994] extend only to 60 m depth, it is not possible to estimate a maximum penetration depth from their data. Despite this, they used a very simple mass balance to suggest that a 20 gigaton global anthropogenic surface ocean carbon increase (as reported by Houston et al. [1990]) should produce a $\delta^{13}C_{DIC}$ shift consistent with their estimate. Because the volume and depth range over which this global balance is applied is not given, it is difficult to assess this comparison.

Using growth history $\delta^{13}C$ measurements of demosponges living in the Coral and Caribbean Seas, Böhm et al. [1996] estimated near surface $\Delta^{13}C_{ap}$ changes of -0.7 ± 0.3% and -0.9 ± 0.2% These values are slightly lower than, but within error similar to, our value from the North Pacific. Böhm et al. [1996] suggest that the $\Delta^{13}C_{ap}$ invasion process can be thought of as a two end-member mixing model between atmospheric equilibration and ocean mixing. Given the measured atmospheric $\delta^{13}C$ decrease of ~1.4% [Friedli et al., 1986], our results imply an air-sea disequilibrium of +0.8%, which is considerably larger than the +0.4% value of Tans et al. [1993]. Although atmospheric equilibration is never reached, estimates from regions with relatively strong stratification exhibit a larger $\Delta^{13}C_{ap}$ signature than values from upwelling regions such as that off northwest Africa or our study off California and Oregon. These observational results indicate that there may be significant regional structure to the $\Delta^{13}C_{ap}$ signature, a result implied by modeling studies [Heimann and Maier-Reimer, 1996; Bacastow et al., 1996].

Time-course measurements of the $\delta^{13}C$ change over an interval of a few decades should reflect somewhat smaller changes than those over the full course of the industrial revolution. In the Pacific Ocean from 30°N to 50°S, Quay et al. [1992] measured mixed layer $\delta^{13}C$ changes averaging -0.40% between ~1970 and ~1990, with roughly similar changes in the Northern and Southern Hemispheres. To estimate the magnitude of the anthropogenic carbon sink on the basis of $\delta^{13}C$, Quay et al. [1992] first integrated changes in $\delta^{13}C_{DIC}$ between ~1970 and ~1990 over depth. For the North Pacific (20°-29°N), their depth integrated $\delta$ decrease ranges between -231 and -305% m, while their whole Pacific value was -202 to -208% m. They infer an average penetration depth of 520 m. For comparison, our sites yield a depth-integrated $\Delta^{13}C_{ap}$ signature of the North Pacific of ~293%, with a mixed layer $\Delta^{13}C_{ap}$ of -0.62%, an average penetration depth of 473 m, and a maximum penetration depth of ~600 m. Thus our estimate of the mixed layer anthropogenic $\delta^{13}C$ shift is near the lower limit of the Quay et al. [1992] North Pacific values (their highest estimate) and ~30% larger than their average Pacific value. This finding suggests that at least 70% (and perhaps almost all) of the anthropogenic carbon in the North Pacific entered the ocean between 1970 and 1990.

As discussed previously, our result is sensitive to our assumption that no anthropogenic carbon is present in North Pacific Deep Water between 1000 and 2500 m (see section 4.3). Although a plausible assumption, given the uncertainty in our deep $\delta^{13}C_{DIC}$ and $\delta^{13}C_{[NO_3^-]}$ data, -0.15% represents an upper limit on how much the $\delta^{13}C_{DIC}$ on North Pacific Deep Water isoplnals between $\sigma_0$ 27.3 and 27.7 could have shifted in response to a hypothetical in-flux of anthropogenic carbon. Because these isopycnals do not outcrop, the hypothetical anthropogenic carbon influx would have to occur by some mechanism other than ventilation (e.g., remineralization at depth of contaminated, sinking particulates).

As a sensitivity test for this or some similar process, if the true preanthropogenic deep water $\delta^{13}C_{DIC}$ value was actually ~0.35% (to account for a ~0.15% anthropogenic effect) rather than the observed value of ~0.5%, the mixed layer $\Delta^{13}C_{ap}$ would increase to...
-0.77\%o, the depth-integrated $\Delta^{13}C_{\text{a,p}}$ signal would be -668\%o \text{ m}^{-1} with an average penetration depth of 868 m and a maximum penetration in excess of 2500 m. A Pacific anthropogenic carbon inventory of this size would be roughly 3 times the magnitude of that predicted by Quay et al. [1992]. Results of this magnitude would imply that only one third of the anthropogenic carbon in the Pacific was sequestered between -1970 and -1990, and that the magnitude of the global terrestrial anthropogenic carbon sink is negligible. Such results seem implausible, suggesting our deep constraint is reasonable.

To estimate the total anthropogenic carbon concentration based on the $\delta^{13}$C data requires scaling the $\Delta^{13}C_{\text{a,p}}$ estimates to CO$_2$ uptake. The global modeling results of Heimann and Maier-Reimer [1996] suggest a scaling factor that ranges from -0.016 to -0.019\%o (\text{nmol kg}^{-1})^{-1}. Keir et al. [1998] verified this slope based on $\delta^{13}$C and carbonate chemistry data in the North Atlantic as -0.016\%o (\text{nmol kg}^{-1})^{-1}. Using the slopes from Heimann and Maier-Reimer [1996] to scale our $\Delta^{13}C_{\text{a,p}}$ estimates into anthropogenic carbon concentrations, we obtain a mixed-layer anthropogenic carbon concentration of 33-39 \text{ nmol kg}^{-1} in the northeast Pacific. This is quite similar to an estimate of 30 \pm 9.6 \text{ nmol kg}^{-1} based on the carbonate chemistry method using GEOSECS and WOCE station data along 30øN in the northeast Pacific [Ono et al., 1998]. For comparison, mixed layer anthropogenic carbon concentrations estimated from carbonate chemistry in the North Atlantic and Indian Oceans range from 20 to 60 \text{ nmol kg}^{-1} depending the regional hydrography [Gruber et al., 1996; Gruber, 1998; Keir et al., 1998; Sabine et al., 1999].

The anthropogenic carbon profile derived from the concurrent $\delta^{13}$C-nutrient method can be integrated and scaled by the North Pacific surface area (8 x 10$^{15}$ m$^2$) and density (1027.5 kg m$^{-3}$) based on data from Worthington [1981] and Menard and Smith [1966] to yield a crude estimate of the North Pacific anthropogenic carbon inventory: 15-18 Gt C in 1991. In other areas, Gruber et al. [1996] and Gruber [1998] estimate the total depth-integrated uptake for the North Atlantic is 20 \pm 4 Gt C. Sabine et al. [1999] obtained a similar estimate of 20.3 \pm 3 Gt C in 1995 for the depth-integrated Indian Ocean. These values combined (\approx55-58 Gt C) support the concept of the ocean as a large sink of carbon, consistent with the net global uptake of 42 Gt between 1970 and 1990 inferred by Quay et al. [1992]. However, this observationally derived inventory is significantly lower than current model-based estimates of the total oceanic anthropogenic carbon inventory, 123-160 Gt adjusted to 1991 values (Table 2).

If the model estimates of the total oceanic inventory of anthropogenic carbon are correct, the Southern Ocean (not included in the databased estimates above) must be the dominant sink for anthropogenic carbon. Sabine et al. [1999] found that the Princeton carbon cycle GCM underestimated anthropogenic carbon uptake in the northern Indian Ocean by 0.6-0.7 and overestimated it in the south by almost a factor of 2.6. Because the NPIW appears to provide an effective barrier to the uptake of anthropogenic carbon in the North Pacific, efforts to reconcile these estimates should focus on the Southern Hemisphere.

### 5. Conclusions

We use concurrent $^{13}$C$_{\text{DOC}}$ and nutrient measurements to evaluate the causes of the observed $\delta^{13}$C$_{\text{DOC}}$ offset at sites in the northern California Current. Here [NO$_3$] is used for the comparison and appears to give much more precise results than [PO$_4$]. Our assumption of no anthropogenic carbon in the deep North Pacific between 27.3 and 27.7, based on the lack of modern ventilation, allows us to estimate both the anthropogenic uptake and thermodynamic air-sea gas exchange signature at our locations.

We observed that in the California Current at 42øN, near-surface waters of potential density ($\sigma_0$) < 25.1 and within the shallow salinity minimum ($\sigma_0$ 25.1 to 26.7) have a mean $\Delta^{13}C_{\text{a,p}}$ offset of -0.62 \pm 0.17\%o and essentially constant fractions of anthropogenic carbon. The thermodynamic air-sea gas exchange signature at the same locations is approximately -0.48 \pm 0.17\%. These results suggest that near-surface waters of the North Pacific obtain their anthropogenic signature by direct contact with the atmosphere during winter ventilation. Below the depth of the SSM, the signal may be transmitted diffusively within the North Pacific Intermediate Water. Scaling our profiles of $\Delta^{13}C_{\text{a,p}}$ to concentrations of anthropogenic carbon, we obtain a mixed layer anthropogenic carbon value in the range of 33-39 \text{ nmol kg}^{-1}. This is in reasonably good agreement with results for the North Pacific based on carbonate chemistry. Extrapolating our estimate of anthropogenic carbon concentrations to upper ocean waters of the North Pacific implies an anthropogenic carbon inventory of 15-18 Gt C in 1991. Combining this estimate with other regional estimates of anthropogenic carbon and comparing to model-based estimates of the total carbon sink implies that a large fraction of the anthropogenic carbon must enter the ocean at high southern latitudes, mixing deep into the ocean’s interior if the global model estimates are correct.

### Table 2. Model Estimates of the Global Oceanic Anthropogenic CO$_2$ Inventory

<table>
<thead>
<tr>
<th>Source</th>
<th>Global Uptake Rate, Gt C yr$^{-1}$</th>
<th>Global Inventory, Gt C</th>
<th>Global Inventory Adjusted to 1991, Gt C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarmiento et al. [1995]</td>
<td>1.86</td>
<td>106 in 1982</td>
<td>123</td>
</tr>
<tr>
<td>Stocker et al. [1994]</td>
<td>1.99</td>
<td>113 in 1982</td>
<td>131</td>
</tr>
<tr>
<td>Sarmiento et al. [1992] as reported by Sundquist [1993]</td>
<td>n/a</td>
<td>118 in 1990</td>
<td>120 \pm 0.8*</td>
</tr>
<tr>
<td>Keeling et al. [1989] as reported by Sundquist [1993]</td>
<td>n/a</td>
<td>155 in 1990</td>
<td>157 \pm 0.8*</td>
</tr>
</tbody>
</table>

* Adjusted to inferred 1991 levels using the IPCC global uptake rate [Watson et al., 1992] as revised by Sarmiento and Sundquist [1992] (i.e., 2.0 \pm 0.8 Gt C yr$^{-1}$).
Acknowledgments. We thank the captain and crew of the RV *Vega* and our colleagues in the Multitracers project. The text was improved by comments from G. Schmidt and W. Broecker and through reviews from two anonymous reviewers. S. Sutherland provided the WOCE data used for calculation of N*. The project was supported by NSF. This is L-DEO contribution 9586.

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(Received March 10, 1999; revised February 22, 2000; accepted February 23, 2000.)