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CURRENT INVENTORY OF ANTHROPOGENIC CARBON DIOXIDE
IN THE NORTH PACIFIC SUBARCTIC GYRE
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### 1.0 SUMMARY

The most significant environmental issue of the next century will be systematic changes in the earth's climate due to increases in the atmospheric burden of carbon dioxide. This secular increase is the result of the burning of fossil fuels and massive deforestation currently underway. Since 1958, the atmospheric $\mathrm{CO}_{2}$ concentration has risen from about 315 ppm to about 343 ppm ; an average rate of $0.4 \% / \mathrm{yr}$. Current wisdom places the preindustrial atmosphere at $270 \pm 10 \mathrm{ppm}$.

The major repositories for anthropogenic $\mathrm{CO}_{2}$ are the oceans and the atmosphere. Of the total that has been released, approximately $50 \%$ resides in each of these reservoirs. Recent calculations suggest that the terrestrial biosphere has been a source, approximately equal in magnitude to the cummulative fossil fuel input during the past 150 years. Potentially the oceans represent a large reservoir for $\mathrm{CO}_{2}$ because of the carbonate equilibria. However, only the surface layers are in equilibrium with the atmosphere, the remainder will be slow to come to equilibrium because most of the oceanic reservior is isolated from the atmosphere. The uptake of $\mathrm{CO}_{2}$ by the oceans ultimately depends on the rate of vertical convection and mixing within the ocean thermocline, which in turn is coupled to large scale wind-driven and thermohaline circulation. Because the ocean thermocline is not stirred uniformly, we believe that the assimilation rate of $\mathrm{CO}_{2}$ will be temporally and spatially variable. Thus, model predictions of the current $\mathrm{CO}_{2}$ inventory as well as the uptake rate depend critically on the details of near-surface ocean circulation.

The distributions of freon-11, as a surogate tracer, have been combined with precise measurements of total carbon dioxide, total alkalinity, oxygen, nutrient and hydrography in order to estimate the amount of excess
$\mathrm{CO}_{2}$ in the subarctic waters of the North Pacific gyre. The approach we employed utilizes the $\mathrm{F}-11$ profiles to determine apparent vertical mixing parameters. These parameters were input into a horizontally averaged, one-dimensional vertical diffusion model along with a carbon dioxide source function to provide model predictions of anthropogenic (excess) $\mathrm{CO}_{2}$ concentrations. These predictions were compared with observed estimates of excess $\mathrm{CO}_{2}$, based on the back-calculation method using station data. The results show very good agreement between the modeled profiles and the calculated data for all stations north of the subartic front. In the region of the front, the model assumptions are apparently not applicable due to the significance of lateral mixing. Our calculations indicate that approximately $4 \times 10^{15} 8$ of excess carbon, or about $2 \%$ of the total estimated fossil-fuel-derived carbon input now resides in the mixed layer and thermocline waters of the North Pacific gyre.

### 2.0 INTRODUCTION

The most significant environmental issue of the next century will be systematic changes in the earth's climate due to increases in the atmospheric burden of carbon dioxide (NRC, 1979; 1982). This secular increase is the result of the burning of fossil fuels and massive deforestation currently underway (Broecker and Peng, 1982). Since 1958, the atmospheric $\mathrm{CO}_{2}$ concentration has risen from about 315 ppm to current levels of 343 ppm , or an average rate of $0.4 \% / \mathrm{yr}$. Present day estimates place the preindustrial atmosphere at between $260-280 \mathrm{ppm}(\mathrm{v})$ (DOE, 1983).

The major repositories for anthropogenic $\mathrm{CO}_{2}$ are the oceans and the atmosphere. Of the total that has been released, it is believed that approximately $50 \%$ resides in each of these reservoirs (Broecker et al., 1979). Current wisdom suggests that the terrestrial biosphere was a significant source, approximately equal in magnitude to the fossil fuel input (Broecker and Peng, 1982), but the major contribution now is the burning of fossil fuels. Potentially the oceans represent a large reservoir for anthropogenic $\mathrm{CO}_{2}$ because molecular $\mathrm{CO}_{2}$ reacts with dissolved carbonate ions according to the reaction,

$$
\begin{equation*}
\mathrm{CO}_{2}+\mathrm{CO}_{3}^{2-}+\mathrm{H}_{2} \mathrm{O}=2 \mathrm{HCO}_{3}^{-} \tag{1}
\end{equation*}
$$

However, only the immediate surface layers are in equilibrium with the atmosphere (Broecker et al., 1979). The oceans as a whole will be slow to come to equilibrium because most of the oceanic reservior is isolated from the atmosphere (Bolin, 1960; Keeling, 1973; Broecker et al., 1971). The uptake of $\mathrm{CO}_{2}$ by the oceans ultimately depends on the rate of vertical convection and mixing within the ocean thermocline, which in turn is coupled to large scale wind-driven and thermohaline circulation (Sverdrup
et al., 1942). Because the ocean thermocline is not stirred uniformly, we believe that the assimilation rate of $\mathrm{CO}_{2}$ will be temporally and spatially variable. Thus, model predictions of the current $\mathrm{CO}_{2}$ inventory as well as the uptake rate will depend critically on the details of thermocline circulation.

The atmospheric concentration of $\mathrm{CO}_{2}$ is a function of the rate of release of $\mathrm{CO}_{2}$ to the atmosphere and its subsequent uptake by the oceans, assuming that the terrestrial biosphere is a source. Since the ocean, potentially, represents the largest repository for $\mathrm{CO}_{2}$, the question becomes two-fold. The first is how much anthropogenic $\mathrm{CO}_{2}$ is now in the oceans and secondly, where and at what rate is $\mathrm{CO}_{2}$ being transported into the ocean? Because of complications in ocean circulation, the former may be easier to answer than the latter. In lieu of direct measurements of excess $\mathrm{CO}_{2}$, the current inventory has been estimated separately from the distributions of various transient tracers (Oeschgar et al., 1975; Broecker et al., 1980). The tracers commonly applied to this problem are the traditional bomb transients (e.g., ${ }^{3} \mathrm{H},{ }^{14} \mathrm{C}$ ), but ${ }^{85} \mathrm{Kr}$ and chlorofluoromethanes may also be appropriate (Broecker et al., 1980; Gammon et al., 1982). The usefulness of these various tracers lies in their known source functions and predictable behavior in the oceans. Using very simple models (e.g., box and continuous), these tracers are capable of defining one or two dimensional mixing characteristics that are needed to predict $\mathrm{CO}_{2}$ coupling between the ocean and atmosphere (Bolin, 1960; Craig, 1957; Broecker et al., 1971; Keeling, 1973; Oeschger et al., 1975; and references contained therein). None of these models attempts to explain the physics of mixing, but is used diagnostically to predict $\mathrm{CO}_{2}$ inventories and uptake rates based on parameterized transport coefficients.

It is important to note that none of the studies to date has attempted to correlate model predictions with excess $\mathrm{CO}_{2}$ concentrations. The principal reason that this has not been done is the difficulty in reliably measuring the anthropogenic $\mathrm{CO}_{2}$ signal in the oceans. However, some progress has been made in recent years on the precise measurement of total $\mathrm{CO}_{2}$ and it is now possible to make estimates of excess $\mathrm{CO}_{2}$ (Brewer, 1978; Chen and Millero, 1979).

In this report we summarize our investigations of the distribution of excess $\mathrm{CO}_{2}$ in the subarctic gyre of the North Pacific. The approach we used is to estimate the concentration of excess $\mathrm{CO}_{2}$ from precise measurements of total dissolved inorganic carbon, total alkalinity and nutrient concentrations, followed by the determination of apparent vertical mixing parameters from the distributions of $\mathrm{F}-11$. This information is then combined iteratively to predict the excess $\mathrm{CO}_{2}$ concentration in the main thermocline over the North Pacific (> $40^{\circ} \mathrm{N}$ ).
3.0 METHODS
3.1 Analysis of $\mathrm{F}-11$

Water samples were collected in rosette-mounted syringes (Cline et al., 1982), fitted with Ni plated brass stopcocks and 13 ga. needles. The syringe was partially filled with seawater purged of freons to reduce the blank. Prior to lowering the rosette, the stopcocks were opened and the "zero" water forced from the sampler. On completion of the cast, the stopcocks were closed, needles removed, and samplers placed in a stainless steel tank filled with fresh seawater. The samples remained in the holding tank until analysis was complete, typically six hours.

The analytical system is similar to that described by Gammon et al. (1982). Dissolved gases were purged from 30 ml aliquots of the sample with purified nitrogen gas (Swinnerton and Linnenbom, 1967). The purged gases were dried by passage through $\mathrm{K}_{2} \mathrm{CO}_{3}$ and concentrated in a "U" trap ( $0.32 \mathrm{~cm} 0 . \mathrm{d}$. dia. stainless steel tubing) packed with Porasil C and maintained at $-80^{\circ} \mathrm{C}$. The trap was heated to approximately $85^{\circ} \mathrm{C}$ to release the freons for subsequent GC-EC analysis.

An initial separation of sample gases was accomplished with a short ( $\sim 10 \mathrm{~cm}$ ) precolumn of Porasil $\mathrm{B}\left(50^{\circ} \mathrm{C}\right)$. The primary function of this first precolumn was to partition the chlorofluoromethanes from the more slowly eluting compounds. This also permitted the quantitative retention of $\mathrm{F}-12$ and $\mathrm{N}_{2} \mathrm{O}$ on a 10 cm column of Molecular Sieve $5 \mathrm{~A}\left(130^{\circ} \mathrm{C}\right)$ isolated by a four port valve, before F -11 had passed through the first precolumn. Once the F-11 had reached the detector, the column was opened to carrier flow and the separation of $\mathrm{F}-12$ and $\mathrm{N}_{2} \mathrm{O}$ was completed.

Final separation and detection of the freons were carried out on a Hewlett Packard 5730A gas chromatograph equipped with a constant current electron capture detector ( $15 \mu \mathrm{C}{ }^{63} \mathrm{Ni}$ ) and a 3 m column of Porasil B. Detector response was quantified on a Hewlett Packard 3388A integrator. Standard gases and atmospheric samples were analyzed in the same manner.

The primary standard gas was calibrated by R. Rasmussen (Oregon Graduate Center) and Paul Goldan (NOAA Aeronomy Laboratory, Boulder). Cryo-pumped whole air samples were periodically collected at sea and used as secondary standards.

An examination of more than 100 duplicate analyses indicates a precision of $\pm 0.02 \mathrm{pM} / \mathrm{L}$ for $\mathrm{F}-11$ and $\mathrm{F}-12$.

### 3.2 Analysis for Total Carbon Dioxide, Total Alkalinity and Nutrients

Total carbon dioxide $\left(\mathrm{TCO}_{2}\right)$ and total alkalinity ( $\mathrm{A}_{\mathrm{T}}$ ) were determined from discrete water samples employing the potentiometric titration procedure described by Bos and Williams (1982). The method is based upon techniques developed by Gran (1952) and later modified by Dyrssen and Sillen (1967) and Edmond (1970). The titrations were performed with 0.25 N Baker analytical grade HCl standardized against gravimetrically prepared sodium borate decahydrate solutions.

Water samples were collected in 30-L Niskin bottles and immediately transferred into $1-\mathrm{L}$ glass stoppered bottles to which 1.0 mL of a saturated solution of $\mathrm{HgCl}_{2}$ had been added to retard bacterial oxidation of organic matter prior to analysis. The samples were stored in a dark, cold-storage room at $4^{\circ} \mathrm{C}$ for as much as 12 hours. The samples were analyzed by the potentiometric method described above using a Brinkman E636 Titroprocessor linked to a Hewlett-Packard 85 computer. The data from the titroprocessor were automatically fed into the computer and processed using the modified Gran equations described in Bradshaw et al. (1981). Alkalinity contributions from boric, silicic and phosphoric acid were computed from equations similar to those presented by Takahasi et al. (1982) in the GEOSECS Pacific Expedition Report. Total borate concentration was computed using the relation of Culkin (1965). The first and second dissociation constants of carbonic acid and the first apparent dissociation constant of boric acid are from Almgren et al. (1977). Potassium chloride was used to adjust the ionic strength of the sodium tetraborate decahydrate standards to 0.7. At each station a blank was determined by titrating aliquots of a KCl solution containing no borate. The average blank was $4 \mu e q / L$.

Figure 3.1 shows the station locations and Appendix 1 gives listings of the station number, depth, salinity, temperature, oxygen, nutrients, $A_{T}$ and $\mathrm{TCO}_{2}$ for the NOAA data from the western, central and eastern North Pacific cruises. For the eastern North Pacific $\mathrm{TCO}_{2}$ and $\mathrm{A}_{\mathrm{T}}$ data the analytical procedures are described fully in Chen (1982).

Samples for nitrate, phosphate and silicate were collected in 250 ml amber Nalgene bottles and immediately frozen for subsequent colorimetric analysis by the methods of Strickland and Parsons (1972) employing a Technicon Autoanalyzer.

### 4.0 MODELS

### 4.1 Vertical Diffusion-Advection Model

The distribution of a time dependent, non-conservative, chemical tracer is given by the equation (Sverdrup et al., 1942),

$$
\begin{equation*}
C_{t}=K_{H}\left\{C_{x x}+C_{y y}\right\}+K_{v} C_{z z}-u C_{x}-v C_{y}-w C_{z}-R, \tag{2}
\end{equation*}
$$

where the subscripts indicate the first and second derivatives with respect to the space variables. The mean velocities in the $x, y, z$ directions are $u, v$, and $w$; the horizontal and vertical eddy diffusivities are given by $K_{H}$ and $K_{V}$. Any internal source or sink term is represented by $R$. Equation (2) is rarely solved in the above form because of insufficient temporal and spatial data, therefore simplifications are required.

The principal objective in the study is to predict the inventory of excess $\mathrm{CO}_{2}$, using the simplest possible model. The first assumption is that the downward migration of $\mathrm{CO}_{2}$ or freon-11 can be treated as a diapycnal process in the subarctic gyre. This is a reasonable assumption since deep

isopycnal outcropping is not prevalent anywhere in the North Pacific (Reid, 1973), nor is there deep convection. This is not to say that vertical diffusion is the most significant process, but rather that the net effect of all transport terms can be parameterized in terms of a simple, one-dimensional vertical diffusion model (Broecker and Peng, 1982). In reality, gaseous tracers such as freon-11 and $\mathrm{CO}_{2}$ are probably responsive to winter mixing in the western North Pacific. Once injected below the seasonal thermocline, the tracers then can be recirculated in the subarctic cyclone (Cline et al., 1984). There also may be lateral transport of freons at depth from the northern part of the subtropical gyre, but we cannot evaluate the significance of this process at the present time. The net result is that the one-dimensional model overwhelmingly simplifies the physics of mixing and transport, but retains its diagnostic value.

With the assumption that the horizontal terms are either zero or they uniquely cancel each other, and that freons are conservative, eqn. (2) reduces to

$$
\begin{equation*}
C_{t}=K_{v} C_{z z}-w C_{z} \tag{3}
\end{equation*}
$$

where $C$ is the concentration of $F-11$. The solution to equation (3) for constant $K_{v}$ and $w$ is
where

$$
\begin{align*}
C(z, t) & =\exp \left(-w z / 2 K_{v}\right) \int_{0}^{t} F\left(t^{\prime}\right) G\left(z, t-t^{\prime}\right) d t^{\prime}  \tag{4}\\
G\left(z, t-t^{\prime}\right) & =\frac{z}{2 \sqrt{\pi K_{v}}\left(t-t^{\prime}\right)^{3}} \exp \left\{-z^{2} / 4 K_{v}\left(t-t^{\prime}\right)-w^{2}(t-t) / 4 K_{v}\right\}
\end{align*}
$$

The initial condition is that $C(0, t)=F\left(t^{\prime}\right)$ and boundary conditions are the $C(z, 0)=0$ and $C\left(\infty, t^{\prime}\right)=0$. These initial and boundary conditions are appropriate, since $F-11$ has no known natural source in the ocean and its
history in the atmosphere is short compared to the ventilation time of the deep sea (Gammon et al., 1982). To evaluate the integral given in (4) the source function for F-11 must be known.

Our best estimate of the historical growth of F-11 in the atmoshpere is that derived from industrial release data (McCarthy ot al., 1977) and the recent measurements of Khalil and Rasmussen (1981). By correcting the release rate for stratospheric loss, the industrial releases can be made to coincide with observations made subsequent to 1975 (Gammon et al., 1982). These results are shown in Fig. 4.1 and are applicable to $45^{\circ} \mathrm{N}$ latitude in the eastern North Pacific.

The surface concentration of F-11 is directly proportional to its atmospheric partial pressure, $C^{\prime}=\beta$, where $\beta$ is the Bunsen solubility coefficient and $p$ is the atmospheric mixing ratio. The Bunsen coefficients, a function of salinity and temperature, were calculated from the measurements of Wisegarver and Cline (1984). Although the solubility dependence on salinity was not specifically determined, this error is estimated to be less that $3 \%$ for the range of salinities encountered in the North Pacific. The source function, $F\left(t^{\prime}\right)$, is the product of the atmospheric mixing ratio (Fig. 4.1) and the Bunsen coefficient. The Bunsen coefficient is largely a function of temperature, which was chosen at each station from the mean annual value at the base of the winter mixed layer (Robinson and Bauer, 1976; Levitus, 1982). In reality, gas exchange and vertical transport are enhanced winter by winter cooling and deep wind mixing, hence our choice of the mean annual temperature at the base of the winter mixed layer is an attempt to average a seasonal process.


### 4.2 Vertical Mixing Parameters Derived from the Distribution of F-11

The distribution of $\mathrm{F}-11$ is used as a diagnostic scaler to determine the apparent vertical eddy diffusivity. This parameter is then used in conjunction with an estimate of the anthropogenic $\mathrm{CO}_{2}$ source function to determine vertical profiles of excess $\mathrm{CO}_{2}$. To demonstrate how this is accomplished, we will calculate $K_{v}$ for station $P^{\prime}$ located in the eastern North Pacific.

Station $P^{\prime}$ was sampled repeatedly between 2-10 December 1980 for the distribution of F-11 and F-12. The model fit to these observations are shown in Fig. 4.2. The solid line indicates the best model fit (eqn. 4) to these data for $K_{v}=-9.4 \times 10^{+3} w+0.35\left(\mathrm{~cm}^{2} / \mathrm{s}\right)$, where $w$ is the apparent vertical velocity (w < 0 upwelling). Unfortunately, the distribution of freon-11 is not particularily sensitive to specific values of $K_{v}$ and $w$, but rather to their ratio or the scale height. The introduction of additional tracers not linearly dependent on F-11 might be useful in determining individual values of $K_{v}$ and $w$, but clearly $F-12$ will not serve this purpose at $P^{\prime}$ (see inset Fig. 4.2). However, our intention is not to detail the physics of mixing, but rather to predict the net effect of vertical transport. To accomplish this end we ignore the convective term (i.e., w = 0) and simply describe the vertical distribution of $\mathrm{F}-11$ with the flux divergence, which at this station is $0.35 \mathrm{~cm}^{2} / \mathrm{s}$.

Using the simple one-dimensional model described above, we fit the observed distributions of $\mathrm{F}-11$ at the stations shown in Fig. 3.1. The results of these calculations are shown in Table 4.1. In general, apparent vertical eddy diffusivities increase toward the south, with the smallest value ( $0.04 \mathrm{~cm}^{2} / \mathrm{s}, \mathrm{Sta}$. WNP-20) found along the southern boundary of the Alaskan stream. This trend is expected from a one-dimensional model


Figure 4.2 Freon-11 distribution at station $P^{\prime}$ in the North Pacific gyre. The inset shows a plot of freon-11 versus freon-12 concentrations at this station.

Table 4.1. Vertical mixing parameters in the North Pacific. The apparent vertical eddy diffusivity ( $K_{\mathrm{v}}$ ) and velocity ( $w$ ) were obtained from a one-dimensional analysis of $\mathrm{F}-11$. This tracer predicts the relationship $K_{v}=a \cdot w+K_{v}^{\prime}$, where $a$ is the scale height. Setting $w=0$, the distribution is uniquely determined by the apparent vertical eddy diffusivity, $\mathrm{K}_{\mathrm{v}}^{\prime}$.

| Sta. No. | Lat <br> ${ }^{\circ} \mathrm{N}$ | Long. <br> ${ }^{\circ} \mathrm{E} / \mathrm{W}$ | $\mathrm{K}_{\mathrm{v}}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | a•w | $\mathrm{K}_{\mathrm{V}}^{\prime}$ |
| ENP |  |  |  |  |
| NP-40 | $40^{\circ} 01^{\prime}$ | 134057'W | $-9.7 \times 10^{3}$ w | 0.70 |
| NP-41 | $42^{\circ} 02^{\prime}$ | $129^{\circ} 55^{\prime} \mathrm{W}$ | --- | 0.28 |
| $\mathrm{P}^{\prime}$ | $50^{\circ} 10^{\prime}$ | $140^{\circ} 15^{\prime} \mathrm{W}$ | $-9.4 \times 10^{3}$ w | 0.35 |
| CNP |  |  |  |  |
| CNP-1 | $50^{\circ} 00^{\prime}$ | 169059'W | $-9.5 \times 10^{3} \mathrm{w}$ | 0.19 |
| CNP-2 | $47^{\circ} 00^{\prime}$ | $169^{\circ} 59^{\prime} \mathrm{W}$ | $-1.2 \times 10^{4} \mathrm{w}$ | 0.33 |
| CNP-4 | $42^{\circ} 00^{\prime}$ | $170^{\circ} 03^{\prime} \mathrm{W}$ | $-1.4 \times 10^{4} \mathrm{w}$ | 0.58 |
| CNP-5 | 40 ${ }^{\circ} 5{ }^{\prime}$ | $170^{\circ} 01$ W | $-2.7 \times 10^{4} \mathrm{w}$ | 1.9 |
| CNP-6 | $40^{\circ} 01^{\prime}$ | $170^{\circ} 10^{\prime} \mathrm{W}$ | $-2.8 \times 10^{4} \mathrm{w}$ | 1.9 |
| WNP |  |  |  |  |
| WNP-16 | $41^{\circ} 59^{\prime}$ | $165^{\circ} 03^{\prime} \mathrm{E}$ | --- | --- |
| WNP-18 | $45^{\circ} 19^{\prime}$ | $167^{\circ} 17^{\prime} \mathrm{E}$ | $-1.4 \times 10^{4} \mathrm{w}$ | 0.54 |
| WNP-20 | $49^{\circ} 57^{\prime}$ | $175{ }^{\circ} 00^{\prime} \mathrm{E}$ | $-4.8 \times 10^{3} \mathrm{w}$ | 0.04 |


Figure 4.3 Streamlines showing major current systems in the North Pacific gyre (after Dodimead
because diapycnal processes are relatively more important within the subarctic gyre, whereas to the south near the subarctic front downwelling and isopycnal mixing become more significant (Roden, 1981). Because the latter processes are more energetic, $K_{v}$ must be scaled upward to account for deeper penetration of the tracers. An apparent increase in $K_{v}$ toward the south is expected, based on circulation and salt budget considerations within the North Pacific Gyre (Reid, 1965). There, the freshening of the surface layers from surface precipitation and runoff must be balanced by the vertical transport of salt if the salinity field is to remain stationary. Salt is also transported laterally into the upper thermocline from the subtropical gyre via the west wind drift and its northern extension, the Alaska stream (Fig. 4.3).

## 4.3 $\mathrm{CO}_{2}$ Source Function

The uptake of $\mathrm{CO}_{2}$ by the oceans is more complex than that of freons. This complexity arises because gaseous $\mathrm{CO}_{2}$ reacts with water to form the aqueous species $\mathrm{H}_{2} \mathrm{CO}_{3}, \mathrm{HCO}_{3}^{-}, \mathrm{CO}_{3}^{-}$, and dissolved $\mathrm{CO}_{2}$, or $\left(\mathrm{pCO}_{2}\right)$ aq. The relative proportions of each are functions of the carbon dioxide and borate equilibria (Mehrbach et al., 1973; Lyman, 1956; Millero, 1979; Almgren et al., 1977). In practice, the concentration of each species can be estimated from measurements of total carbon dioxide $\left(\mathrm{TCO}_{2}\right)$ and alkalinity and, of course, the equilbrium constants (Bradshaw et al., 1981). We are principally interested in the partial pressure difference in $\mathrm{CO}_{2}$ (i.e., $\Delta \mathrm{pCO}_{2}$ ) across the air-sea interface, because it is this quantity that determines the flux.

Seasonally and spatially, the magnitude and direction of the flux of $\mathrm{CO}_{2}$ is highly variable. This is due to local biological effects and to
surface warming and cooling, both of which influences the flux of gaseous $\mathrm{CO}_{2}$. Thus, calculating a mean ocean flux of $\mathrm{CO}_{2}$, even locally, would require a large data base. A more tractable approach is to assume that the ocean surface is near equilibrium with the atmosphere, so long as a suitable time average is taken. For our purposes here, that time need not be less than one year, since shorter term changes could not be tested observationally (see below). In essence then, if the atmospheric growth of $\mathrm{CO}_{2}$ is known, then the partitioning of that $\mathrm{CO}_{2}$ between the atmosphere and the ocean can be calculated from known thermodynamic quantities (Takahashi et al., 1980).

Partitioning of $\mathrm{CO}_{2}$ (equilibrium) between the ocean and the atmosphere is given in terms of the Revelle factor, $R$, where,

$$
\begin{equation*}
\frac{1}{\mathrm{R}} \frac{\mathrm{~d}\left\{\mathrm{pCO}_{2}\right\}}{\left\{\mathrm{pCO}_{2}\right\}}=\frac{\mathrm{d}\left\{\mathrm{TCO}_{2}\right\}}{\left\{\mathrm{TCO}_{2}\right\}} \tag{5}
\end{equation*}
$$

In this expression, $\mathrm{TCO}_{2}$ is the sum of all carbon dioxide components. Although $R$ is a function of temperature and the carbon dioxide components, we can assume that it has been relativley constant since pre-industrial times for water masses of constant temperature. Under these conditions, eqn (5) can be integrated over the interval of interest and yields the expression
where the subscript ' $o$ ' reflects the initial boundary conditions, i.e., the value of $\mathrm{pCO}_{2}$ and $\mathrm{TCO}_{2}$ in 1825. However, what we are actually interested in is the change in fossil fuel $\mathrm{CO}_{2}$ in the atmosphere since 1825 , rather than the whole of the $\mathrm{CO}_{2}$ signal. Changing to a $\Delta$-notation requires that we substitute the following relationships into eqn (6)

$$
\begin{align*}
& \left\{\mathrm{peO}_{2}\right\}=\left\{\mathrm{pCO}_{2}\right\}-\left\{\mathrm{pCO}_{2}\right\}_{0}  \tag{7}\\
& \left\{\mathrm{TCO}_{2}\right\}=\left\{\mathrm{TCO}_{2}\right\}-\left\{\mathrm{TCO}_{2}\right\}_{0} . \tag{8}
\end{align*}
$$

We obtain after simplification and approximation the following:

$$
\begin{equation*}
\Delta \mathrm{TCO}_{2}=\frac{1}{R} \frac{\left\{\mathrm{TCO}_{2}\right\}_{0}}{\left\{\mathrm{pCO}_{2}\right\}_{0}} \Delta \mathrm{pCO} \tag{9}
\end{equation*}
$$

This equation predicts a linear relationship between the incremental increase in atmospheric $\mathrm{pCO}_{2}$ and dissolved $\mathrm{TCO}_{2}$ in the ocean. As more and more $\mathrm{CO}_{2}$ is added to the atmosphere, R increases and the ocean's ability to assimilate $\mathrm{CO}_{2}$ is diminished. It should be emphasized that the relationship depicted in eqn. 9 holds only for a constant R.

Armed with the $\mathrm{CO}_{2}$ source function and estimates of the vertical mixing parameters, we are now in a position to calculate $\Delta T \mathrm{CO}_{2}$ profiles for the North Pacific ( $840^{\circ} \mathrm{N}$ ) and compare them to observations derived from $\mathrm{TCO}_{2}$ and total alkalinity measurements. First, however, we describe the method by which excess $\mathrm{TCO}_{2}\left(\Delta \mathrm{TCO}_{2}\right)$ concentrations are determined.

### 4.4 Back-Calculation Method for Excess $\mathrm{CO}_{2}$

Over the past few years several authors have employed a variety of different techniques to directly measure or estimate the oceanic $\mathrm{CO}_{2}$ increase (Brewer, 1978; Chen and Millero, 1979; Chen and Pytkowicz, 1979; Takahashi et al., 1983). The methods fall into two distinct categories. The first method involves direct measurements of $\mathrm{CO}_{2}$ increases in surface waters from $\mathrm{pCO}_{2}$ measurements made over time spans of several years to tens of years (i.e., Takahashi et al., 1983). This method requires that accurate and precise $\mathrm{pCO}_{2}$ measurements be made at the same location over

long time intervals which, with the possible exception of the data for the North Atlantic, are not available in sufficient quantities to be useful for this purpose. The second less direct method involves a back-calculation of the $\mathrm{CO}_{2}$ concentration of a parcel of water to its initial concentration at the sea surface after corrections have been made for changes due to biological decomposition of organic matter and dissolution of carbonate tests (i.e. Brewer, 1978). Specifically, the method assumes that a water parcel maintains a fixed degree of saturation with respect to atmospheric $\mathrm{CO}_{2}$ at the sea surface. When the water parcel sinks, total $\mathrm{CO}_{2}\left(\mathrm{TCO}_{2}\right)$ is added by respiration and carbonate dissolution. The respiration-induced change in $\mathrm{CO}_{2}$ can be calculated from the oxygen data employing the wellknown Redfield ratios (Redfield et al., 1963). The changes due to carbonate dissolution are calculated from the alkalinity changes. By correcting the data for these changes as well as for the preformed values of $\mathrm{TCO}_{2}$ and total alkalinity, estimates can be made of the $\mathrm{CO}_{2}$ concentration of the water parcel when it was last in contact with the atmosphere. These back-calculated $\mathrm{CO}_{2}$ concentrations are then compared to obtain the oceanic $\mathrm{CO}_{2}$ increase.

Both measurements suffer from relatively large uncertainties associated with the quality of the data and, in the case of the back-calculation method, natural deviations from the Redfield ratios (Shiller, 1981). However, it is possible to combine models of atmospheric input along with the direct measurement methods to make reasonable estimates of the fossil $\mathrm{CO}_{2}$ inventory in the oceans.

The method for back-calculating the excess $\mathrm{CO}_{2}$ signal is similar to the method reported by Chen (1982) and is summarized as follows:

$$
\begin{align*}
& \Delta \mathrm{TCO}_{2}^{\circ}(\mu \mathrm{mol} / \mathrm{kg})=\mathrm{TCO}_{2}^{\circ} \text { (present) }-\mathrm{TCO}_{2}^{\circ} \text { (old) } \\
& =\mathrm{TCO}_{2}^{\circ} \text { (present) }-\left[\mathrm{TCO}_{2} \text { (measured) }-0.5 \mathrm{TA}\right. \text { (measured) } \\
& \left.-\alpha \mathrm{AOU}+0.5 \mathrm{TA}^{\circ} \text { (present) }\right] \tag{10}
\end{align*}
$$

where all quantities except AOU (Apparent Oxygen Utilization) are normalized to $35 \% \mathrm{~S} ; \Delta \mathrm{TCO}_{2}{ }^{\circ}$ is a measure of the excess $\mathrm{CO}_{2}$ signal; $\mathrm{TCO}_{2}{ }^{\circ}$ (old) and $\mathrm{TCO}_{2}{ }^{\circ}$ (present) are, respectively, the preformed total $\mathrm{CO}_{2}$ values for a parcel of water formed sometime ago and for a water parcel formed at present; $\mathrm{TCO}_{2}$ (measured) and TA (measured) are the measured concentrations of total $\mathrm{CO}_{2}$ and titration alkalinity, respectively; $T A^{\circ}$ (present) is the present day preformed TA value; $\alpha$ is derived from the carbon-oxygen relationship for the data set presented in the manner prescribed by Chen and Pytkowitz (1979). The calculation of $\Delta \mathrm{TCO}_{2}$ using the equation above is subject to large uncertainties (Chen and Millero, 1979; Chen and Pytkowicz, 1979; Shiller, 1981; Chen et al., 1982). The largest uncertainty is in the calculation of the $\mathrm{TA}^{\circ}$ (present) and $\mathrm{TCO}_{2}{ }^{\circ}$ (present) values. The data from ENP, CNP, WNP (Appendix 1) indicate that $T A^{\circ}$ and $\mathrm{TCO}_{2}{ }^{\circ}$ can be represented by the following equations:

$$
\begin{equation*}
\mathrm{TA} A^{\circ}(\mu \mathrm{gg} / \mathrm{kg})=2361-1.2 \theta( \pm 10) \quad \theta \leq 25^{\circ} \mathrm{C} \tag{11}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{TCO}_{2}^{\circ}(\mu \mathrm{mol} / \mathrm{kg})=2246-11 \theta( \pm 10) \quad \theta \leq 24^{\circ} \mathrm{C} \tag{12}
\end{equation*}
$$

where $\theta$ is the potential temperature and the numbers in parentheses give one standard deviation of the least-squares fit for the above equations. These equations are valid only for the North Pacific gyre.

### 4.5 Excess $\mathrm{TCO}_{2}$ Model and Source Function

The one-dimensional model used to describe the vertical distribution of freon-11 is simplistic and is not intended to describe the actual mechanisms of vertical transport. At best, the model simply decribes the sum total of all processes leading to the vertical propagation of freon-11 in terms of an apparent eddy diffusivity (Broecker and Peng, 1982). This simple goal is, however, what we desire to accomplish, because our purpose here is to predict how much excess $\mathrm{TCO}_{2}$ is in the North Pacific, not precisely how it got there. A much more elaborate model would be needed to accomplish that purpose.

The model we will use to predict the vertical distribution of excess $\mathrm{TCO}_{2}$ is the same as that adopted for $\mathrm{F}-11$, except the atmospheric source function is different. The assumption is that freons and $\Delta \mathrm{TCO}_{2}$ are conservative tracers, and that their respective source functions are spatially uniform between $40-55^{\circ} \mathrm{N}$. This provides the freons with a unique characteristic because both bomb transients were not introduced into the North Pacific in a uniform way. This means that the source function for bomb-derived ${ }^{3} \mathrm{H}$ and ${ }^{14} \mathrm{C}$ are both space and time dependent, whereas those for freons and $\Delta \mathrm{TCO}_{2}$ are only time dependent, and better known.

To estimate the $\Delta \mathrm{TCO}_{2}$ profile for any specific location we need to have an estimate of the amount of anthropogenic $\mathrm{CO}_{2}$ added since pre-industrial times as well as the rate at which it was added. The first of these can be derived from an estimate of the pre-industrial $\mathrm{pCO}_{2}$ concentration and the Revelle factor, while the second is obtained by an iterative procedure until a match between the model curves and the observed $\Delta T \mathrm{TCO}_{2}$ profiles are obtained. We begin by calculating the amount of excess $\mathrm{TCO}_{2}$ present in the surface layers of the North Pacific subarctic gyre in 1980. This
quantity is independent of biological cycling, although to determine it analytically, one must account for seasonal changes in the $\mathrm{TCO}_{2}$ pool.

We assume that the pre-industrial (1820) concentration of atmospheric $\mathrm{CO}_{2}$ was 270 ppm . In 1980 it was 340 ppm , hence the change has been about 70 ppm . The fraction of this $\mathrm{CO}_{2}$ that now resides in the ocean can be calculated from the equation (9) (Broecker et al., 1971). Setting $R=$ $11.5\left(5^{\circ} \mathrm{C} \leq \mathrm{T} \leq 10^{\circ} \mathrm{C}\right), \Delta \mathrm{pCO} 2=70 \mathrm{ppm},\left[\mathrm{pCO}_{2}\right]^{\circ}=270 \mathrm{ppm}$, and $\left[\mathrm{TCO}_{2}\right]^{\circ}=$ $2010 \mu \mathrm{~m} / \mathrm{kg}$ (see below), the concentration of excess $\mathrm{CO}_{2}$ in the North Pacific gyre is about $45 \mu \mathrm{~m} / \mathrm{kg}$. Having established theoretically and observationally the present day concentration of $\Delta T \mathrm{CO}_{2}$, we now only need to determine how $\mathrm{pCO}_{2}$ has changed historically to calculate the inventory of excess $\mathrm{CO}_{2}$ in the North Pacific gyre.

The time-dependent source function for $\mathrm{pCO}_{2}$ is not known precisely and must be estimated from other tracer data. Broecker and Peng (1982) used a modified Oeschger model to determine the separate contributions from fossil fuel and forest and soil as a function of time. Their prediction results in a near-linear increase in $\mathrm{pCO}_{2}$ since 1825 after combining the terrestrial and fossil fuel sources.

In this study we tested the $\mathrm{pCO}_{2}$ curve postulated by Broecker and Peng (1982) by fitting model $\Delta \mathrm{TCO} 2$ profiles to the measured distributions. The source function we used is shown in Fig. 4.4 and is similar in shape to that proposed by Broecker and Peng. The only difference is the pre-industrial intercept, which we set to 270 ppm instead of 250 ppm . Raising the pre-industrial value to 270 ppm together with an assumed Revelle factor of 11.5 gives a better fit to the observed excess $\mathrm{CO}_{2}$ concentrations in the mixed layer. However, uncertainties in observed
quantities as well as model assumptions do not permit us to be precise about the pre-industrial $\mathrm{pCO}_{2}$ concentration.

### 5.0 RESULTS AND DISCUSSION

### 5.1 Excess $\mathrm{CO}_{2}$ Model Predictions

Comparisons were made between the amount of excess $\mathrm{CO}_{2}\left(\Delta \mathrm{TCO}_{2}\right)$ measured and the concentration predicted from the one-dimensional, time dependent diffusion model (see eqn. 3) at six stations in the subarctic gyre for the North Pacific. These are the only stations for which both excess $\mathrm{CO}_{2}$ and freon observations were made simultaneously.

The results of the comparisons are shown in Fig. 5.1 for the $\Delta \mathrm{TCO}_{2}$ sources function given in Fig. 4.4. To make the correlation, we used the average mixed layer depth defined by the near-surface maximum in the observed $\Delta \mathrm{TCO}_{2}$, but relied on the model calculation (eqn. 9) to estimate the present day anomaly. As shown above, the calculated $\Delta \mathrm{TCO}_{2}$ concentration is about $45 \mu \mathrm{M} / \mathrm{kg}$. The average of the observed mixed layer concentrations (see Fig. 5.1) is about $38 \mu \mathrm{M} / \mathrm{kg}$, although the uncertainty is large. Photosynthesis and respiration in the mixed layer complicate an accurate measure of the present day surface $\Delta T C O_{2}^{\circ}$ concentration, hence we used the calculated value of $45 \mu \mathrm{M} / \mathrm{kg}$ as the mixed layer value.

Given that the concentration of excess $\mathrm{CO}_{2}$ and the mixed layer depth appropriate to the total $\mathrm{CO}_{2}$ concentration are not known precisely, the model fits to the observations shown in Fig. 4.1 are quite good. This is particularly surprising in view of the fact that the vertical eddy diffusivity varied from $0.04 \mathrm{~cm}^{2} / \mathrm{s}$ to $1.2 \mathrm{~cm}^{2} / \mathrm{s}$. The profiles of $\Delta \mathrm{TCO}_{2}$, shown in Fig. 5.1, indicate a slight deepening of the profiles from north to south, which corresponds with the increase in apparent vertical mixing towards


Figure 5.1 Comparison of the predicted excess $\mathrm{TCO}_{2}$ profiles in the North Pacific gyre based on modeled parameters derived from the freon-11 distribution and $\mathrm{CO}_{2}$ source function with the calculated values of excess $\mathrm{CO}_{2}$ using the back-calculation method.
the subarctic boundary (Table 4.1). Station WNP-16 notwithstanding, the model profiles were similar in shape to the observed profiles. By increasing the surface concentration of excess $\mathrm{CO}_{2}$ or by increasing the $\mathrm{TCO} \mathbf{2}_{2}$ mixed layer depth, or both the model fits could be improved at most stations. There also may be a bias in the way in which the $\Delta \mathrm{TCO}_{2}$ was calculated because they are not seasonally averaged, consequently further tinkering with model parameters would be non-productive.

The poorest fit was obtained at $\mathrm{WNP}-16$, where the $\Delta T \mathrm{TCO}_{2}$ concentration was observed to decrease more rapidly with depth than predicted by the model. We ascribe this to complex mixing along the northern boundary of the Kuroshio Extention, which precludes either a simple explanation or accurate calculation of the excess $\mathrm{CO}_{2}$ profiles. Salinity, temperature and freon-11 all suggest deep ventilation along the front in winter, hence the lack of agreement shown in Fig. 5.1 indicates that the back-calculation method may not be accurate in frontal regimes where complex water mass interactions occur.

The excess $\mathrm{CO}_{2}$ source function and atmospheric $\mathrm{pCO}_{2}$ curve are shown in Fig. 4.4. A pre-industrial value of 270 ppm was assumed and a smooth curve was arbitrarily drawn that passes through the observations since 1958 (Keeling, 1980). Minor changes in the source function prior to 1958 were tried, but none made any significant changes in the model profiles. Specifically, we imposed arbitrarily a $5 \mu \mathrm{M} / \mathrm{kg} \mathrm{TCO}_{2}$ change in 1920 to mimic the terrestrial contribution shown by Broecker and Peng (1982) with no significant change in any of the vertical profiles. We conclude that the model profiles are relatively insensitive to minor changes in the $\mathrm{pCO}_{2}$ source function, and that the function derived by Broecker and Peng (1982) gives an adequate fit to the observations, the preindustrial intercept
notwithstanding. Subtle changes in the $\mathrm{pCO}_{2}$ source function, such as those depicted by Broecker and Peng (1982), could not be discerned by our procedure unless significant improvements were made in the $\Delta \mathrm{TCO}_{2}$ calculation.

### 5.2 Model Predictions of Excess $\mathrm{CO}_{2}$ in the North Pacific Gyre

The curves shown in Fig. 5.1 were integrated from the surface to about 1000 m to calculate the water column inventory of excess $\mathrm{CO}_{2}$. The area of interest lies between $40^{\circ} \mathrm{N}$ and $57^{\circ} \mathrm{N}\left(16.5 \times 10^{6} \mathrm{~km}^{2}\right.$; Levitus, 1982). The mixed layer, assumed here to be the upper 150 m on the average, contained about $1.1 \times 10^{14}$ moles of excess $\mathrm{CO}_{2}$, whereas below 150 m the amount was $1.9 \times 10^{14}$ moles. The total amount of excess $\mathrm{CO}_{2}$ in the North Pacific subarctic gyre is therefore about $3.0 \times 10^{14}$ moles or about 18.2 moles/m ${ }^{2}$.

How do these estimates compare to the total amount of $\mathrm{CO}_{2}$ released? Broecker and Peng (1982) give an integrated $\mathrm{CO}_{2}$ production of $33 \times 10^{15}$ moles since 1825. If our estimate of the $\mathrm{CO}_{2}$ uptake in the North Pacific subarctic gyre were representative of the global ocean, which it is not, we would predict an oceanic uptake of $6.7 \times 10^{15}$ moles, or about $20 \%$ of the total. The North Pacific subarctic gyre is only about 4.5\% of the total ocean surface. In all likelihood, the above percentage is small because the North Pacific is not characterized by deep convection mixing as is the case in the North Atlantic and the Southern Ocean. Moreover, we have not included the subtropical gyres, which are apt to contain larger amounts of excess $\mathrm{CO}_{2}$ because lateral mixing brings $\mathrm{CO}_{2}$ saturated water into the main thermocline.

The effect of downward transport along isopycnal outcrops is clearly shown by the inventories of bomb-derived ${ }^{3} \mathrm{H}$ and ${ }^{14} \mathrm{C}$ (Broecker and Peng,
1982). Comparing the north temperate ocean with the North Atlantic and Pacific, after adjusting for area, it is seen that about $34 \%$ more ${ }^{14} \mathbf{C}$ resides in the subtropical gyres. This percentage would be even larger if the comparison was made for the North Pacific, because there is not deep water mass formation, which tends to increase the North Atlantic inventory of bomb carbon, and by analogy the amount of excess $\mathrm{CO}_{2}$ as well.

The relatively small amount of excess $\mathrm{CO}_{2}$ found in the North Pacific is due largely to the small apparent diffusion coefficient derived from the distribution of F-11. The global model used by Broecker and Peng (1982) and others assumed a mean diffusion coefficient of about $1.6 \mathrm{~cm} / \mathrm{s}$ compared to a mean value assumed here of $0.7 \mathrm{~cm}^{2} / \mathrm{s}$. Since the vertical inventory of excess $\mathrm{CO}_{2}$ is proportional to the $\sqrt{\mathrm{K}_{\mathrm{v}}}$ in the $1-\mathrm{D}$ model, our prediction is about $50 \%$ less than would have been predicted from the global averaged model. However, fine structure and vertical heat transfer measurements suggest that $K_{v}$ is indeed small for the North Pacific subarctic gyre (Gargett, 1984) and further indicates the need for regional modeling of excess $\mathrm{CO}_{2}$ rather than using a global-averaged $1-\mathrm{D}$ model. In this regard, the next step to be taken to improve the estimate of excess $\mathrm{CO}_{2}$ in the oceans is to increase the precision and accuracy of the excess $\mathrm{CO}_{2}$ calculation and to test it against the predictions of other tracers (e.g. freons, ${ }^{3} \mathrm{H},{ }^{14} \mathrm{C}$, and ${ }^{85} \mathrm{Kr}$ ). The permanent thermocline of the subtropical gyre of the North Pacific should be the region examined.

### 6.0 CONCLUSIONS

The distributions of freon-11 were combined with precise total carbon dioxide, total alkalinity, oxygen, nutrient and hydrographic measurements to estimate the amount of excess $\mathrm{CO}_{2}$ in the subarctic waters of the

North Pacific gyre. The approach we employed utilizes the F-11 profiles to determine the apparent vertical eddy diffusivity. These parameters were input into a zonally averaged, one-dimensional vertical diffusion model along with a carbon dioxide source function to provide vertical profiles of anthropogenic $\mathrm{CO}_{2}$ concentrations. The model predictions were then compared with estimates of excess $\mathrm{CO}_{2}$ based on the back-calculation method, which relies on precise measurements of $\mathrm{TCO}_{2}$, alkalinity, $\mathrm{O}_{2}$, and nutrients.

The results generally show good agreement between the model profiles and the calculated data for all stations north of the subarctic front. In the region of the front, the model assumptions are apparently not applicable due to the complexity of water mass interactions. Our estimate indicates that approximately $3 \times 10^{14}$ Moles ( $3.6 \times 10^{15} \mathrm{~g} \mathrm{C}$ ) of excess carbon has been assimilated by the mixed layer and thermocline waters of the North Pacific gyre. Of the total amount released (about $33 \times 10^{15}$ Moles or $4 \times 10^{17} \mathrm{~g}$ C), the North Pacific gyre only harbors about $1 \%$ of it, although the study area was $4.5 \%$ of the total surface area of the ocean. This is equivalent to about $2 \%$ of the fossil-fuel-derived carbon input to the atmosphere. The distributions of the bomb transients (e.g. ${ }^{3} \mathrm{H},{ }^{14} \mathrm{C}$ ) also suggests that the North Pacific subarctic gyre is a relatively small reservoir of excess $\mathrm{CO}_{2}$ and that the temperate ocean ( $15^{\circ}$ to $40^{\circ}$ ) will be a more significant reservoir.

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## APPENDIX 1

Chemical and Hydrographic Data for the North Pacific Gyre




 웅
Salinity Sigma-t

Theta
Deg $C$


 3吴
NNONNNNNNNNNNNNNNN



$\underset{\text { pmol / } 1}{ }$

| 3 | 5.910 | 32.66 | 25.717 | 4.141 | 1.805 |
| ---: | :---: | :---: | :---: | :---: | :---: |
| 47 | 5.370 | 32.67 | 25.789 | 4.210 | 1.834 |
| 100 | 3.620 | 33.14 | 26.327 | 3.261 |  |
| 151 | 3.650 | 33.82 | 26.884 | 0.859 | 0.399 |
| 200 | 3.620 | 33.94 | 26.983 | 0.523 | 0.377 |
| 297 | 3.560 | 34.06 | 27.084 | 0.215 | 0.158 |
| 348 | 3.510 | 34.11 | 27.129 | 0.147 | 0.111 |
| 396 | 3.450 | 34.13 | 277.151 | 0.154 | 0.077 |
| 497 | 3.320 | 34.21 | 27.227 | 0.094 | 0.058 |
| 598 | 3.187 | 34.27 | 27.287 |  |  |
| 698 | 3.030 | 34.31 | 27.333 | 0.046 | - |
| 786 |  |  |  |  |  |
| 117 | 3.720 | 33.62 | 26.718 | 2.095 | 1.053 |
| 143 | 3.640 | 33.82 | 26.885 | - |  |
| 243 | 3.600 | 34.02 | 27.049 | 0.492 | 0.290 |
| 786 | 2.910 | -- |  | 0.047 | 0.046 |
|  |  |  |  |  |  |
| 44 | 5.790 | 32.68 | 25.748 | 4.136 | 1.812 |
| 69 | 4.490 | 32.83 | 266012 | 3.910 | 1.669 |
| 95 | 3.950 | 33.22 | 26.377 | 3.153 | 1.823 |
| 143 | 3.670 | 33.81 | 26.875 | 1.007 | 0.497 |
| 190 | 3.620 | 33.94 | 26.983 | 0.436 | -- |


| Depth <br> m | Temp． $\operatorname{Deg} \mathrm{C}$ | Theta Deg C | WNP 18 LAT Salinity \％ 0 | $\begin{aligned} & 4517.4 \mathrm{~N} \\ & \text { Sigma-t } \end{aligned}$ | $\begin{gathered} \text { LONG } 167 \\ \text { D.O. } \\ \mu M / \mathrm{kg} \end{gathered}$ | $\begin{gathered} 15.9 \mathrm{E} \\ \mathrm{AOU} \\ \mu \mathrm{M} / \mathrm{kg} \end{gathered}$ | $\begin{aligned} & \text { DATE: } \\ & \text { SIO }_{4} \\ & \mu \mathrm{M} / \mathrm{kg} \end{aligned}$ | $\begin{gathered} 17 \text { JUNE } \\ \mathrm{PO}_{4} \\ \mu \mathrm{M} / \mathrm{kg} \end{gathered}$ | $\begin{gathered} \mathrm{NO}_{3} \\ \mu \mathrm{M} / \mathrm{kg} \end{gathered}$ | $\begin{gathered} \text { Alk } \\ \mathrm{meq} / \mathrm{kg} \end{gathered}$ | $\begin{aligned} & \mathrm{TCO}_{2} \\ & \mathrm{mM} / \mathrm{kg} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 5.62 | 5.62 | 32.903 | 25.944 | 335 | －27 | 32.5 | 1.51 | 17.8 | 2.226 | 2.064 |
| 73 | 2.13 | 2.13 | 33.108 | 26.447 | 336 | －1 | 42.1 | 1.73 | 23.9 | 2.243 | 2.118 |
| 143 | 2.58 | 2.57 | 33.403 | 26.648 | 265 | 65 | 43.8 | 1.81 | 24.5 | 2.258 | 2.151 |
| 243 | 3.11 | 3.10 | 33.698 | 26.838 | 136 | 190 | 76.7 | 2.53 | 34.7 | 2.286 | 2.255 |
| 344 | 3.76 | 3.74 | 33.968 | 26.992 | 87 | 233 | 87.3 | 2.67 | 37.3 | 2.312 | 2.288 |
| 443 | 3.15 | 3.13 | 34.000 | 27.075 | 54 | 271 | 112.0 | 2.91 | 41.5 | 2.324 | 2.327 |
| 542 | 3.32 | 3.23 | 34.149 | 27.178 | 42 | 281 | 108.1 | 2.85 | 38.7 | 2.342 | 2.336 |
| 642 | 3.33 | 3.29 | 34.229 | 27.241 | 38 | 285 | 117.8 | 2.93 | 40.4 | 2.344 | 2.340 |
| 742 | 3.08 | 3.04 | 34.274 | 27.300 | 35 | 290 | 123.6 | 2.96 | 40.8 | 2.362 | 2.356 |
| 842 | 2.90 | 2.85 | 34.322 | 27.355 | 28 | 298 | 141.1 | 2.94 | 41.9 | 2.371 | 2.370 |
| 1040 | 2.69 | 2.63 | 34.410 | 27.444 | 37 | 291 | 147.0 | 2.87 | 40.6 | 2.388 | 2.378 |
| 1291 | 2.35 | 2.26 | 34.476 | 27.525 | 40 | 291 | －－ | 2.93 | 40.6 | 2.402 | 2.374 |
| 1540 | 2.15 | 2.07 | 34.535 | 27.569 | 49 | 283 | 157.7 | 2.91 | 40.5 | 2.395 | 2.374 |
| 2040 | 1.85 | 1.74 | 34.613 | 27.675 | 78 | 256 | 161.5 | 2.74 | 38.0 | 2.411 | 2.368 |
| 2209 | 1.76 | 1.64 | 34.617 | 27.685 | 90 | 245 | 159.6 | 2.74 | 38.8 | 2.413 | 2.363 |
| 2538 | 1.62 | 1.46 | 34.639 | 27.713 | 110 | 226 | －－ | 2.61 | －－ | 2.412 | 2.347 |
| 3038 | 1.51 | 1.33 | 34.664 | 27.741 | 132 | 205 | 164.4 | 2.53 | 38.2 | 2.412 | 2.338 |

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33
n WNP18

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\text { WNP1 } 8
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\begin{array}{cl}
\text { CAST: } & 125 \\
\text { Depth } & \text { Temp. } \\
m & \text { Deg } \mathbf{C}
\end{array}
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\begin{aligned}
& \text { LAT } 4515.9 \\
& \text { Salinity }
\end{aligned}
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\begin{aligned}
& \text { N LONG } \\
& \text { Sigma-t }
\end{aligned}
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9 \text { N LONG } 167
$$

Salinity Sigma-t
26.236
26.488
26.767
27.075
27.125
27.223
26.236
26.488
26.767
27.075
27.125
27.223







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| Depth m | $\underset{\text { Deg }}{\text { Temp．}}$ | $\begin{aligned} & \text { Theta } \\ & \text { Deg C } \end{aligned}$ | $\begin{gathered} \text { Salinity } \\ 0 / 00 \end{gathered}$ | Sigma－t | $\begin{aligned} & \text { D. } 0 . \\ & \mu M / \mathrm{kg} \end{aligned}$ | $\begin{gathered} \text { AOU } \\ \mu M / \mathbf{k g} \end{gathered}$ | $\underset{\mu \mathrm{M} / \mathrm{kg}}{\mathrm{SIO}_{4}}$ | $\begin{gathered} \mathrm{PO}_{4} \\ \mu \mathrm{M} / \mathrm{kg} \end{gathered}$ | $\underset{\mu \mathrm{M} / \mathrm{kg}}{\mathrm{NO}_{3}}$ | Alk meq／kg | $\begin{aligned} & \mathrm{TCO}_{2} \\ & \mathrm{mM} / \mathrm{kg} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 2.840 | 2.84 | 32.837 | 26.174 |  |  | 24.6 | 1.29 | 15.4 | 2.202 | 2.081 |
| 9 | 2.830 | 2.83 | 32.750 | 26.328 | 320 | 11 | 25.9 | 1.28 | 14.7 | 2.214 | 2.084 |
| 49 | 2.820 | 2.82 | 32.674 | 26.045 | 320 | 10 | 15.5 | 1.02 | 6.8 | 2.211 | 2.081 |
| 98 | 2.880 | 2.87 | 32.844 | 26.176 | 280 | 30 | 27.4 | 1.37 | 15.2 | 2.213 | 2.087 |
| 148 | 3.230 | 3.22 | 33.660 | 26.797 | 140 | 184 | 71.8 | 2.46 | 36.2 | 2.281 | 2.263 |
| 197 | 3.270 | 3.26 | 33.809 | 26.912 | 80 | 244 | 89.0 | 2.73 | 40.7 | 2.294 | 2.302 |
| 296 | 3.510 | 3.49 | 34.004 | 27.045 | 30 | 292 | 108.5 | 2.93 | 45.1 | 2.310 | 2.339 |
| 395 | 3.480 | 3.45 | 34.102 | 27.126 | 35 | 286 | 115.4 | 2.93 | 44.1 | 2.320 | 2.345 |
| 593 | 3.170 | 3.13 | 34.245 | 27.269 | 24 | 300 | 137.0 | 2.91 | 44.3 | 2.364 | 2.364 |
| 692 | 3.030 | 2.98 | 34.295 | 27.321 | 26 | 299 | 140.9 | 2.86 | 44.1 | 2.366 | 2.372 |
| 791 | 2.880 | 2.83 | 34.343 | 27.373 | －－ | －－ | 145.9 |  | 44.3 | 2.369 | 2.377 |
| 989 | 2.690 | 2.63 | 34.404 | 27.439 | 27 | 300 | 160.0 | 2.88 | 44.3 | 2.380 | 2.383 |
| 1483 | 2.170 | 2.07 | 34.522 | 27.577 | 45 | 286 | 179.4 | 2.90 | 44.1 | 2.391 | 2.392 |
| 1978 | 1.870 | 1.74 | 34.606 | 27.668 | 71 | 263 | 181.1 | 2.72 | 42.3 | 2.411 | 2.383 |
| 2472 | 1.670 | 1.50 | 34.633 | 27.704 | 98 | 238 | 181.1 | 2.61 | 40.5 | 2.418 | 2.379 |
| 2967 | 1.580 | 1.36 | 34.658 | 27.731 | －－ | －－ | 173.1 | 2.48 | 39.2 | 2.414 | 2.359 |
| 3610 | 1.465 | 1.19 | 34.676 | 27.754 | 144 | 193 | 167.4 | 2.45 | 37.9 | 2.411 | 2.341 |
| 3857 | 1.465 | 1.16 | 34.682 | 27.759 | 183 | 154 | 170.1 | 2.32 | 37.3 | 2.421 | 2.340 |






32.837
32.750
32.674
32.844
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CNP 2

| Depth $\mathbf{m}$ | Temp. Deg C | Salinity | Sigma-t | $\underset{\text { pmol/1 }}{\text { F11 }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 8 | 3.894 | 32.983 | 26.194 | 4.52 |
| 23 | 3.895 | 32.975 | 26.188 | 4.82 |
| 50 | 3.895 | 32.981 | 26.193 | 4.65 |
| 103 | 3.895 | 32.994 | 26.203 | - |
| 121 | 3.913 | 32.967 | 26.180 | 4.43 |
| 152 | 3.967 | 33.468 | 26.573 | 3.44 |
| 179 | 3.895 | 33.629 | 26.708 | 2.73 |
| 195 | 3.859 | 33.679 | 26.752 | 2.22 |
| 225 | 3.877 | 33.738 | 26.797 | 1.82 |
| 252 | 3.895 | 33.775 | 26.824 | 1.52 |
| 305 | 3.806 | 33.821 | 26.870 | 1.10 |
| 351 | 3.788 | 33.896 | 26.931 | -- |
| 397 | 3.770 | 33.952 | 26.978 | 0.60 |
| 503 | 3.609 | 34.064 | 27.083 | 0.57 |
| 598 | 3.466 | 34.143 | 27.160 | 0.34 |

Depth
m
0.58
0.78
0.83
0.81
0.74
0.81
1.36
1.34
0.98
2.05
2.47
2.41
2.82
2.80
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\begin{gathered}
\mathrm{NO}_{3} \\
\mu \mathrm{M} / \mathrm{kg}
\end{gathered}
$$

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### 26.35

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 Depth
26.353
$\begin{array}{ll}26.355 & 3.46 \\ 26.353 & 3.56\end{array}$


|  | $\overbrace{i}^{\sim} \underset{\sim}{\sim}$ |  |  |  |  <br>  <br>  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |
| － | $0_{z}^{m} \sum_{i}^{\infty}$ |  चNNmvさ寸vmmm | $\stackrel{-1}{\infty}$ | $\underbrace{\infty}_{i}$ | かめのがNのMのロのに <br>  －TNmmmmymmmm |
| $\begin{aligned} & \stackrel{9}{2} \\ & \stackrel{2}{2} \\ & \sim \end{aligned}$ | 足 |  －்ーiNiNNiNiN |  |  |  －ウーiNNiNNiNNN |
|  |  | Noのの00000 00 <br>  <br>  | $\begin{aligned} & \ddot{9} \\ & \stackrel{y}{\|c\|} \\ & \end{aligned}$ |  | 0－N000000000 <br>  |
| 3 |  |  | 3 |  |  |
| $$ |  |  | $\begin{gathered} \text { N } \\ \text { in } \end{gathered}$ | 定童 |  |
| $\underset{\sim}{n}$ |  |  | $\begin{aligned} & \text { o } \\ & \underset{\sim}{1} \end{aligned}$ |  |  |
| $\begin{aligned} & 0 \\ & 2 \\ & \hline \end{aligned}$ | $\dot{0} \dot{0}-\stackrel{00}{x}$ |  NNN゙ | $\begin{aligned} & \text { U } \\ & \text { O } \\ & \end{aligned}$ | $\stackrel{\bullet 0}{\stackrel{\infty}{x}}$ |  mलNन |
| 2 |  |  | $z$ |  |  |
| $\begin{aligned} & 0 \\ & 0 \\ & \text { ou } \\ & \text { N } \end{aligned}$ |  |  <br>  <br>  | $\begin{aligned} & \text { n } \\ & \text { N } \\ & 0 \\ & i n \end{aligned}$ | $\begin{gathered} \dot{1} \\ \text { 置 } \\ .0 \\ .0 \end{gathered}$ |  NNOTOHनNmษすにn <br>  |
| $\underset{4}{\mathbb{E}}$ |  |  | $\stackrel{\mathrm{E}}{\underset{G}{3}}$ |  |  |
| N品 |  |  <br>  <br>  <br>  लmmmmmmmmmmmm | $\begin{aligned} & \text { v } \\ & \text { v } \\ & \text { 只 } \end{aligned}$ |  | oamanounnonon <br>  <br>  |
|  |  | ㅇㅇㅇㅇㅇㅇㅇㅇㅇㅇ은 <br>  のヘロホMmmのNNNーH |  |  |  <br>  |
|  |  |  <br>  |  |  |  <br>  |
|  | $\begin{aligned} & \text { 돌 } \\ & \stackrel{0}{0} \text { E } \\ & \text { ( } \end{aligned}$ |  |  |  |  |




| $\underset{\mathrm{m}}{\text { Depth }}$ | Temp. Deg C | $\begin{gathered} \text { Salinity } \\ \% / \infty 0 \end{gathered}$ | STR $P^{-}$ <br> Sigma-t | $\begin{gathered} \text { CAST: } 41 \\ \text { F11 } \\ \text { pmol } / 1 \end{gathered}$ | $\begin{array}{cc} \text { LAT } 50 \quad 14.5 \\ \begin{array}{c} \text { F12 } \\ 1 \end{array} \\ \text { prool } / 1 \end{array}$ | $\begin{gathered} \text { LONG } 140 \\ \text { Depth } \\ \mathrm{m} \end{gathered}$ | 15.0 W Temp. Deg C | DATE: <br> Salinity | $2 \underset{\text { SEC } 80}{\text { Sigma-t }}$ | $\begin{gathered} \text { Fl1 } \\ \text { pmol } / 1 \end{gathered}$ | $\begin{gathered} \text { F12 } \\ \text { pmol / } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 19 | 8.20 | 32.49 | 25.276 | 2.76 | 1.25 | 20 | 7.97 | 32.49 | 25.310 | 3.47 | 1.36 |
| 41 | 8.20 | 32.48 | 25.269 | 2.87 | 1.41 | 63 | 7.98 | 32.48 | 25.301 | 3.39 | 1.40 |
| 82 | 8.20 | 32.48 | 25.269 | 3.25 |  | 99 | 6.29 | 32.63 | 25.647 | 3.68 | 1.32 |
| 99 | 5.89 | 32.68 | 25.736 | 3.49 | 1.35 | 125 | 5.49 | 33.23 | 26.218 | 2.84 | 1.10 |
| 149 | 5.28 | 33.61 | 26.544 | 2.16 | 0.92 | 152 | 5.29 | 33.58 | 26.519 | 2.12 | 0.90 |
| 198 | 5.05 | 33.79 | 26.713 | 1.16 | 0.44 | 174 | 5.24 | 33.69 | 26.612 | 1.82 | 0.75 |
| 301 | 4.33 | 33.84 | 26.831 | 0.69 | 0.26 | 228 | 4.96 | 33.80 | 26.731 | 1.26 | 0.62 |
| 396 | 4.12 | 33.91 | 26.909 | 0.40 | 0.13 | 299 | 4.40 | 33.82 | 26.808 | 0.85 | 0.37 |
| 601 | 3.69 | 34.04 | 27.056 | 0.06 |  | 401 | 4.12 | 33.91 | 26.909 | 0.37 | 0.22 |
| 798 | 3.29 | 34.11 | 27.150 | 0.08 |  | 614 | 3.69 | 34.05 | 27.064 | 0.14 | 0.05 |
| 1004 | 2.94 | 34.15 | 27.214 | 0.04 |  | 811 | 3.25 | 34.12 | 27.162 | 0.16 |  |
| 20 | 8.04 | 32.50 | 25.308 | 3.06 | 1.30 | 20 | 7.95 | 32.49 | 25.313 | 3.27 | 1.54 |
| 40 | 8.04 | 32.49 | 25.300 | 2.72 | 1.21 | 50 | 7.95 | 32.48 | 25.305 | 3.35 | 1.61 |
| 80 | 8.04 | 32.48 | 25.292 | 2.92 | 1.28 | 101 | 6.25 | 32.70 | 25.707 | 3.49 | 1.75 |
| 100 | 5.87 | 32.80 | 25.833 | 2.77 | 1.26 | 111 | 5.76 | 32.82 | 25.862 | 3.37 | 1.58 |
| 125 | 5.45 | 33.24 | 26.231 | 2.28 | 1.01 | 126 | 5.67 | 33.02 | 26.031 | 3.05 | 1.57 |
| 173 | 5.16 | 33.75 | 26.668 | 1.26 | 0.53 | 154 | 5.31 | 33.47 | 26.429 | 2.30 | 1.05 |
| 227 | 4.75 | 33.81 | 26.762 | 0.86 | 0.42 | 203 | 5.13 | 33.75 | 26.672 | 1.45 | 0.78 |
| 299 | 4.35 | 33.84 | 26.829 | 0.52 | 0.25 | 304 | 4.43 | 33.83 | 26.813 | 0.66 | 0.37 |
| 401 | 4.10 | 33.92 | 26.919 | 0.26 | 0.16 | 403 | 4.12 | 33.91 | 26.909 | 0.29 | 0.20 |
| 600 | 3.67 | 34.04 | 27.058 | 0.08 | 0.02 | 607 | 3.67 | 34.04 | 27.058 | 0.14 | 0.07 |
| 804 | 3.26 | 34.12 | 27.161 | 0.05 | 0.02 | 809 | 3.29 | 34.12 | 27.158 | 0.05 |  |
| 19 | 7.99 | 32.49 | 25.307 | 3.46 | 1.32 |  |  |  |  |  |  |
| 40 | 7.99 | 32.49 | 25.307 | 3.59 | 1.32 |  |  |  |  |  |  |
| 77 | 7.99 | 32.48 | 25.299 | 3.11 | 1.45 |  |  |  |  |  |  |
| 99 | 5.79 | 32.75 | 25.803 | 3.64 | 1.47 |  |  |  |  |  |  |
| 125 | 5.38 | 33.40 | 26.366 | 2.32 | 1.12 |  |  |  |  |  |  |
| 176 | 5.15 | 33.76 | 26.677 | 1.42 | 0.65 |  |  |  |  |  |  |
| 223 | 4.85 | 33.82 | 26.759 | 0.83 | 0.45 |  |  |  |  |  |  |
| 302 | 4.37 | 33.83 | 26.819 | 0.59 | 0.32 |  |  |  |  |  |  |
| 399 | 4.15 | 33.90 | 26.898 | 0.29 | 0.16 |  |  |  |  |  |  |
| 595 | 3.71 | 34.03 | 27.046 | 0.10 | 0.07 |  |  |  |  |  |  |
| 796 | 3.29 | 34.11 | 27.150 | 0.06 | 0.06 |  |  |  |  |  |  |
| 19 | 7.99 | 32.49 | 25.307 | 3.46 | 1.32 |  |  |  |  |  |  |
| 40 | 7.99 | 32.49 | 25.307 | 3.59 | 1.32 |  |  |  |  |  |  |
| 77 | 7.99 | 32.48 | 25.299 | 3.11 | 1.45 |  |  |  |  |  |  |
| 99 | 5.79 | 32.75 | 25.803 | 3.64 | 1.47 |  |  |  |  |  |  |
| 125 | 5.38 | 33.40 | 26.366 | 2.32 | 1.12 |  |  |  |  |  |  |
| 176 | 5.15 | 33.76 | 26.677 | 1.42 | 0.65 |  |  |  |  |  |  |
| 223 | 4.85 | 33.82 | 26.759 | 0.83 | 0.45 |  |  |  |  |  |  |
| 302 | 4.37 | 33.83 | 26.819 | 0.59 | 0.32 |  |  |  |  |  |  |
| 399 | 4.15 | 33.90 | 26.898 | 0.29 | 0.16 |  |  |  |  |  |  |
| 595 | 3.71 | 34.03 | 27.046 | 0.10 | 0.07 |  |  |  |  |  |  |
| 796 | 3.29 | 34.11 | 27.150 | 0.06 | 0.06 |  |  |  |  |  |  |

