# Air-water gas exchange and the carbon cycle of Green Bay, Lake Michigan 

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# AIR-WATER GAS EXCHANGE AND THE CARBON CYCLE OF <br> GREEN BAY, LAKE MICHIGAN <br> by <br> James Touchstone Waples <br> A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of <br> Doctor of Philosophy <br> in <br> Biogeochemistry 

at

The University of Wisconsin - Milwaukee
MAY 1998

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# AIR-WATER GAS EXCHANGE AND THE CARBON CYCLE OF GREEN BAY. LAKE MICHIGAN 

by<br>James Touchstone Waples<br>The University of Wisconsin - Milwaukee. 1998<br>Under the Supervision of Dr. J. Val Klump

The purpose of this study was to constrain estimates of the kinetics of gas transfer across the air-water interface as well as quantify the net flux of carbon between southern Green Bay ( $1635 \mathrm{~km}^{2}$ ) and the atmosphere.

In 1994 and 1995. over 3500 measurements of surface water $\mathrm{CH}_{4}$ and $\mathrm{CO}_{2}$ were made using a continuous sample disk equilibrator. Estimates of $\mathrm{CH}_{4}$ flux from southern Green Bay to the atmosphere based on air-water concentration gradients, shear corrected wind speeds and the $\mathrm{U} / \mathrm{K}$ (wind speed / transfer coefficient) relationship of Broecker et al. (1978) agreed to within $\sim 10 \%$ of the estimate of $\mathrm{CH}_{4}$ influx from sediments and rivers (Klump and Fitzgerald (1998) and this study). Corrections for wind shear based on airwater temperature differences resulted in flux estimates that were $\sim 30 \%$ higher than those based on a neutral ung coefficient of $1.3 \times 10^{-3}$. The implied support for the $\mathrm{U} / \mathrm{K}$ relationship of Broecker et al. (1978) suggests that the kinetics of air-water gas exchange are $\sim 2.2$ times higher than that predicted by the frequently used $U / K$ relationship of Liss and Merlivat (1986).

Southern Green Bay exported $13 \times 10^{7}$ moles $\mathrm{CH}_{4} \mathrm{yr}^{-1}$ in 1994 and $16 \times 10^{7}$ moles $\mathrm{CH}_{4} \mathrm{yr}^{-1}$ in 1995. Inter-annual differences in $\mathrm{CH}_{4}$ flux were shown to be largely due to dramatic differences in wind direction-which altered the hydrodynamics of the bay and ultimately. sediment temperatures. In Sturgeon Bay (a shallow, isolated section of the study site). spatially weight averaged $\mathrm{CH}_{4}$ concentrations rose by a factor of 2.1 for every $10^{\circ} \mathrm{C}$ increase in water temperature $\left(\mathrm{r}^{2}=0.82\right) ; \mathrm{CH}_{4}$ flux to the atmosphere increased by a factor of $1.8\left(r^{2}=0.46\right)$.

Southern Green Bay exported $180 \times 10^{7}$ moles of $\mathrm{CO}_{2}$ to the atmosphere in 1994 and $240 \times 10^{7}$ moles of $\mathrm{CO}_{2}$ in 1995. However, the spatial and temporal direction and magnitude of flux were far from uniform. Using published rates of primary productivity, the ratio of areal primary productivity to heterotrophic respiration as a function of distance from the Fox River is presented along with a preliminary budget for allochthonous carbon inputs.


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To the hundreds that were pressed into field work (for at least one day) under the pretense that a pleasant boat-ride on Green Bay might not be so bad. my apologies and thanks. I especially thank Don Szmania and Rich MacKenzie who knew better but kept coming back. Their help, enthusiasm and humor made all the difference. I could not have done this work without them.

My field work was carried out on the R/V NEESKAY—pound for pound, the finest research vessel afloat. I thank her present and former captain and crew-Ron Smith. Clyde Winter, Greg Stamatelakys and Terry Snowball-for sailing anywhere at any time under (almost) any weather condition. Their positive attitude and ability to solve problems saved many-a-day.

I must also thank David Schink for lending me his disk equilibrator-and Chris Sabine for telling me what it did. No other tool played a greater role in this project.

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## List of Common Symbols

```
\gamma = activity coefficient
\delta}=\mathrm{ cross virial coefficient for non ideal gas mixture (Chapter 2)
b = equilibrator response constant (Chapter 4)
B = virial coefficient for non-ideal gas (Chapter 2), Revelle factor (Chapter 5)
C = concentration, degrees Celsius
CD = drag coefficient (Chapter 3)
CDN = neutral drag coefficient (Chapter 3)
D = molecular diffusion coefficient (cm}\mp@subsup{}{}{2}\mp@subsup{\textrm{sec}}{}{-1}
f(gas) = fugacity of a gas ( }\mu\textrm{atm}\mathrm{ )
I = ionic strength
J = flux (mol m
K = air-water transfer coefficient (m day }\mp@subsup{}{}{-1}\mathrm{ )
k = von Karmen's constant (Chapter 3)
L = Obukhov scale length (Chapter 3)
P = pressure (atm), primary productivity (Chapter 5)
p(gas) = partial pressure of a gas ( }\mu\textrm{atm}\mathrm{ )
R = heterotrophic respiration (Chapter 5)
Sc = Schmidt number (Chapter 3)
se = stripping efficiency (Chapter 2)
t = time
t = temperature ( }\mp@subsup{}{}{\circ}\textrm{C}
T = temperature ( }\mp@subsup{}{}{\circ}\textrm{K}
U* = friction velocity ( }\mp@subsup{\textrm{cm sec}}{}{-1}\mathrm{ )
U
x(gas) = mole fraction of a gas (ppm)
z = height above air-water interface (Chapter 3). ionic charge (Chapter 5)
zBL}=\mathrm{ boundary layer thickness ( }\mu\textrm{m}\mathrm{ )
```


## Chapter 1

## Introduction

Carbon is arguably the keystone element in an ecosystem and an understanding of the carbon cycle is essential to understanding how an ecosystem functions. However, the chemistry of both organic and inorganic carbon is complex and the flux of carbon within and between biological and non-biological compartments can be rapid.

On a global scale, many aspects of the carbon cycle are still poorly understood. Of primary concern is a better understanding of the role the ocean plays as a sink for atmospheric $\mathrm{CO}_{2}$. This is difficult not only because of the ocean's size and heterogeneity. but also because the rate of $\mathrm{CO}_{2}$ uptake is very close to the rate of $\mathrm{CO}_{2}$ release (Siegenthaler and Sarmiento 1993, Sarmiento and Sundquist 1992. Tans et el. 1990). For this reason, many process-oriented studies of the carbon cycle have been carried out in more manageable systems such as lakes.

In the Great Lakes and their estuarine-like bays, large gradients in both physical and biological forcing over small spatial and temporal scales produce disequilibria in the carbon dioxide system that are relatively easy to measure. Moreover, because these lakes are essentially closed systems, a carbon mass balance can be constrained much more easily than in an open system such as the ocean.

The task is far from simple though. Along with complex chemical and biological transformations, several carbon species- namely carbon dioxide and methane-are volatile and pass freely across the air-water interface. Resolving fluxes within the carbon
cycle and closing the carbon budget, therefore, requires an unusually large suite of measurements.

Several key components of a carbon budget for southern Green Bay have been measured by Klump and Fitzgerald (1998) (Figure 1-1). These include estimates of organic carbon sedimentation, burial and bacterial remineralization (Figure 1-2). The objective of this study was to determine the net exchange of carbon between the southern bay and atmosphere.

To estimate the flux of carbon across the air-water interface, several approaches were possible. A mass balance approach required measuring all other sources and sinks of carbon to southern Green Bay (see Eadie and Robertson 1976). The difference between the carbon sources and sinks would approximate the net flux of carbon to the atmosphere. However, due to the relatively high concentration of inorganic carbon ( $\sim 2.3 \mathrm{mM}$ ). any error in the flushing rate with northern Green Bay (past Chambers Island) would have resulted in a large error in air-water carbon exchange (see Miller and Saylor 1993).

Measuring the change in the ratio of the stable isotopes of dissolved inorganic carbon over time has also been used to estimate air-water carbon exchange, but only in lakes with low concentrations of inorganic carbon (Quay et al. 1986. Herczeg 1987). In Green Bay, the background concentration of inorganic carbon was so high-and the net isotopic fractionation of carbon so low-that this method was also of little use (see Appendix 5). Therefore, estimates of the flux of carbon across the air-water interface were determined using Fick's first law.

Fick's first law states that

Figure 1-1. a) Green Bay. Lake Michigan (from Torrey 1976). Study site includes all area south of Chambers Island to the mouth of the Fox River. b) Bathymetry of southern Green Bay.



Figure 1-2. Preliminary terms in the carbon budget for southern Green Bay as determined by Klump and Fitzgerald (1998).




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$$
J_{\mathrm{aw}}=K \Delta C,
$$

where $\mathrm{J}_{\mathrm{aw}}$ is equal to the flux of a gas across the air-water interface. K is an empirically derived transfer coefficient and $\Delta C$ is the concentration gradient of the gas across the airwater interface (Liss 1983). While measuring the concentration gradient of carbon dioxide or methane across the air-water interface was a straightforward process (see Chapter 2 for methods). measuring or estimating the transfer coefficient was not.

Estimates of K have been determined in the field as well as in wind-water tunnels and have usually been correlated with concurrently measured wind speeds (see Broecker and Peng 1984 and Liss 1983). Knowledge of the wind speed, therefore, could be used to estimate K . Unfortunately, the relationship between wind speed and K is poorly constrained. Estimates of $K$ for a given wind speed span nearly two orders of magnitude (Liss 1983, Broecker et al. 1986. Wesley 1986).

Part of the discrepancy may stem from uncertainties in the stability of the air column-resulting in uncertainties in wind shear over height. Measurements of the dependency of $K$ on the wind speed have been determined from wind speeds measured at $\sim 0.1$ to 10 meters above the air-water interface. To standardize these measurements, wind speeds have typically been scaled to a height of 10 meters by assuming wind speeds increase with height according to a classical logarithmic profile. In reality, the shear of the atmospheric surface layer depends on a variety of meteorological factors; the most significant being the air-water temperature gradient (Kraus and Businger 1994).

In Chapter 3, estimates of K are determined using several wind speed / transfer coefficient relationships and hourly wind speeds recorded at a nearby meteorological buoy. The effects of air-water temperature differences on air column stability are also explored using a computer program written by Arlindo da Silva (see Appendix 6).

To constrain the relationship between wind speed and K , an independent estimate of methane flux across the air-water interface is derived in Chapter 4. Methane flux across the air-water interface was determined as the difference between all other methane source and sink terms in southern Green Bay (i.e. a methane mass balance). The mean value of K which supported this flux based upon the observed air-water methane concentration difference $(\Delta \mathrm{C})$ could then be used to constrain estimates of K based on wind speed.

In Chapter 5, measured values of the concentration gradient of $\mathrm{CO}_{2}$ across the airwater interface and the constrained estimates of $K$ (derived in Chapters 3 and 4) are used to estimate the flux of $\mathrm{CO}_{2}$ from southern Green Bay to the atmosphere.

Finally, estimates of the ratio of areal primary production to heterotrophic respiration are calculated using published estimates of primary productivity in Green Bay (Sager and Richman 1990. 1991). Preliminary constraints on the carbon budget for southern Green Bay are discussed in light of the estimates of carbon flux across the airwater interface.

## Chapter 2

## Methods

## Sampling frequency

Gas concentrations in the surface waters of Green Bay were measured aboard the R/V NEESKAY on 13 separate cruises (31 days) from November 2. 1993 to November 9. 1995. Shipboard sampling began as early as $\sim$ two weeks after ice out and continued until icing threatened ship safety in late fall. Additional samples were taken through the ice of Green Bay in 1995. 1996. and 1997. Sampling through the ice was generally limited to the months of February and (early) March. The distribution of sampling dates during the 1994-1995 field seasons are shown in Figure 2-1. Specific sampling dates can be found in Appendix 3.

## Spatial coverage

Each cruise generally lasted three days with each day beginning and ending in either Sturgeon Bay or the Fox River. Transects for each cruise totaled approximately 250 km and covered the southern half of Green Bay from Chambers Island to the Fox River. Weather, schedule conflicts, and equipment failure occasionally abbreviated or altered the intended routes. The transects completed during the 1994-1995 field seasons are shown in Figure 2-2. Water column profiles were measured at seven stations spanning the major axis of the bay during open water transects (Figure 2-3a). The station designations are those used by Klump et al. (1997). Winter sampling sites were dictated by ice conditions (Figure 2-3b). The coordinates for all stations are given in Appendix 1.

Figure 2-1. Distribution of sampling dates during the 1994-1995 field seasons.


Figure 2-2. Transects completed during the 1994-1995 field seasons. Coordinate units. shown in the upper left hand corner, are in UTM (meters). Points reflect methane sampling coordinates only.






 reci imanty io zo

nosi iminnyte se

Figure 2-3. Distribution of profile stations visited during the a) 1994-1995 open water field seasons and b) winters of 1995-1997. Specific coordinates for each station are given in Appendix 1.

ice stations (1995-1997)


## Sample collection

Water samples were analyzed while underway and on station. The various instruments and tools were plumbed according to Figure 2-4. During a transect. water was pumped continuously from the ship's bow and split to a) a container housing an array of Sea-Bird sensors (SB) and b) a disk equilibrator (EQ). The bow pump (BP) inlet was located $\sim 2$ meters below the waterline. Measured flow rates to the Sea-Bird and equilibrator were approximately 15 and 10 liters per minute respectively. The water stream was again split just forward of the equilibrator and diverted to an inline YSI oxygen probe $(\mathrm{Y})$ and Orion pH electrode (B). The flow rate to these instruments was kept at a minimum to avoid streaming effects. Additional aliquots of water ( $<10$ milliliters per minute) where withdrawn from the disk equilibrator itself for $\mathrm{\Sigma CO}_{2}$ (flow injection) analysis. The residence time of water on board was very short. A saline spike injected at the bow pump was detected by the Sea-Bird after 20 seconds (Arthur Brooks, personal communication). The turnover time for the Sea-Bird box was approximately 2 minutes. The turnover time for the equilibrator was $\sim 1$ minute.

Data from the Sea-Bird included time and Loran (L) coordinates which were coordinated with gas measurements and stored electronically on a computer (C). The disk equilibrator was used to measure dissolved concentrations of methane. carbon dioxide. and radon. Details on its operation are discussed below. A typical view of the wetlab is shown in Figure 2-5.

On station. a submersible pump (SP) and HydroLab (HL) were lowered through the water column. The water pumped up was either sent to the disk equilibrator for

Figure 2-4. A schematic of the apparatus used on R/V NEESKAY during the 1994-1995 field seasons. Abbreviations: (SB) Sea-Bird. (BP) bowpump, (BS) bulk sample water station. (HL) HydroLab, (SP) submersible pump, (L) Loran, (C) Computer. (B) Orion pH electrode. (Y) YSI oxygen probe, (FIA) $\Sigma \mathrm{CO}_{2}$ flow injection setup, (I) Shimadzu integrator, (EQ) disk equilibrator, (OW) equilibrator out-wash effluent, (AP) air sample port. (IRGA) Li-Cor $\mathrm{CO}_{2}$ analyzer. (GC) Carle gas chromatograph. (FID) ISR flame ionization detector. (Stds) gas standards.


Figure 2-5. Dissolved gas analysis setup on the R/V NEESKAY (1994).

dissolved gas analysis or diverted to the deck where bulk water samples (BS) were collected for ${ }^{222} \mathrm{Rn}$, oxygen and $\Sigma^{13} \mathrm{CO}_{2}$ analysis. Data from the Hydrolab were viewed in real time and used to select sampling depths. Particulate carbon was collected from either the bulk sample outflow or the equilibrator outwash (OW) and size fractionated for measurement of organic ${ }^{13} \mathrm{C}$. Water samples were collected with a 5 liter Niskin bottle on several occasions to check for any systematic effects caused by the pump. None were found.

## Disk equilibrator

Concentrations of dissolved carbon dioxide. methane and radon were determined using both discrete and continuous water sample techniques. The latter employed the use of a disk equilibrator as shown in Figure 2-6. The equilibrator consists of a series of rapidly spinning disks housed within a cylinder. When a continuous stream of water is run through the cylinder. the spinning disks carry a thin film of water into the overlying headspace. Since the process of equilibration is chiefly a function of surface area and turbulence, a dissolved gas within the liquid phase rapidly equilibrates with its gas phase fugacity (see Appendix 2 for a discussion on gas concentration nomenclature). The headspace can then be sub-sampled and analyzed to obtain the gas's mole fraction. To determine its in situ (lake) concentration, the 1) pressure of the headspace. 2) equilibration temperature and 3) temperature difference between equilibration and in situ conditions must also be known. Since it is also desirable to keep a constant headspace pressure, the headspace is opened directly to the atmosphere via a long narrow tube. Mixing between the atmosphere and headspace is negligible as long as the volume of water in the

Figure 2-6. The disk equilibrator. The 60 disks are attached to a central axle and housed in an acrylic cylinder 60 cm long and 20 cm in diameter. A motor spins the axle (and disks) at approximately $120-150 \mathrm{rpm}$. A continuous stream of water runs through the equilibrator at $\sim 10$ liters per minute. At steady-state, approximately two thirds ( 9 liters) of the cylinder is filled with water. The equilibrator is normally raised at the inflow side as shown by the water line. The remaining one third contains air. The equilibrator headspace is kept at atmospheric pressure via a long tube (vent). Mixing between the equilibrator headspace and atmosphere is insignificant as long as the water volume in the equilibrator is kept constant. Air within the headspace is rapidly circulated against the flow of water with a pump. Sub-samples are drawn from a segment of line located between the pump and a flow meter. Positive pressure forces the air along a $\sim 2$ meter section of $1 / 8$ inch tubing to the instruments (flow rate: $\sim 2-10 \mathrm{ml} / \mathrm{sec}$ ).

equilibrator is kept constant. Any fluctuation in water volume can be checked by placing the end of the vent tube in a vial of water.

The equilibrator used in this study was built by D. R. Schink (see Schink et al. 1970) and based on the original designs of Williams and Miller (1962). Significant modifications were made according to the suggestions of C. L. Sabine (1994, personal communication). A brief physical description of the equilibrator is given in the caption of Figure 2-6. During transect operations, the flow of water through the equilibrator was adjusted manually with a valve at the inlet to 10 liters per minute. The water volume and flow rate could also be manipulated by raising one end of the equilibrator or changing the head of the effluent tube. At steady state, approximately two-thirds (8 to 11 liters) of the cylinder was filled with water, leaving a headspace of $\sim$ four to seven liters air. The equilibrator headspace was mixed by pumping against the flow of water at a rate of $\sim 10$ liters per minute. This arrangement, while not perfect, proved satisfactory in the field. Water levels in the equilibrator were stable while underway. A small adjustment to the flow rate typically had to be made while on station. In extremely rough weather, the heaving of the ship overwhelmed the bow pump and operations had to be canceled. Approximately 50 milliliters of headspace gas were required for methane and carbon dioxide analyses. One hundred milliliters were required for radon analysis.

## Methane analysis

Methane was measured by gas chromatography using a flame ionization detector. Gas samples were injected into a $0.412 \pm 0.001 \mathrm{ml}$ sample loop and flushed into a nitrogen carrier stream with an Altex 6-way valve. The samples were dried with a Drierite column
just prior to separation. Separation took place on a 80/100 Porapak Q column at 50 to 100 C . Voltage response from the detector was recorded with a Shimadzu C-R5A integrator. The mole fraction of methane in each gas sample was determined using onepoint calibration. Methane standards of $9.98 \mathrm{ppm} \pm 2 \%, 107 \mathrm{ppm} \pm 2 \%, 9.93 \mathrm{ppm} \pm 5 \%$. and $17.07 \mathrm{ppm} \pm 10 \%$ were obtained from Scott Specialty Gas.

For continuous sample analysis, water saturated (wet) air was sampled directly from the disk equilibrator headspace and measured for methane. The calculated mole fraction of methane $\left(\mathrm{xCH}_{4}\right)$ was multiplied by the measured atmospheric pressure to obtain the partial pressure of methane $\left(p \mathrm{CH}_{4}\right)$ inside the equilibrator headspace. The dissolved methane concentration inside of the equilibrator was calculated as:

$$
\begin{equation*}
\left[\mathrm{CH}_{4}\right]_{\mathrm{eq}}=p \mathrm{CH}_{4}(\beta / 22.414) \tag{2-1}
\end{equation*}
$$

Differences between the partial pressure and fugacity of methane were assumed to be negligible. The Bunsen solubility coefficient ( $\beta$ ) was calculated using an equation given by Yamamoto et al. (1976), where

$$
\begin{equation*}
\ln \beta=\mathrm{A}_{1}+\mathrm{A}_{2}\left(100 / \mathrm{T}_{\mathrm{eq}}\right)+\mathrm{A}_{3} \ln \left(\mathrm{~T}_{\mathrm{eq}} / 100\right)+\mathrm{S}\left[\mathrm{~B}_{1}+\mathrm{B}_{2}\left(\mathrm{~T}_{\mathrm{eq}} / 100\right)+\mathrm{B}_{3}\left(\mathrm{~T}_{\mathrm{eq}} / 100\right)^{2}\right] \tag{2-2}
\end{equation*}
$$

$\mathrm{T}_{\mathrm{eq}}$ is the equilibrator water temperature $\left({ }^{\circ} \mathrm{K}\right)$. S is salinity (\%), and A and B are the following constants
$A_{1}=-67.1962$
$A_{2}=99.1624$
$\mathrm{A}_{3}=27.9015$
$B_{1}=-0.072909$
$B_{2}=0.041674$
$B_{3}=-0.0064603$

Salinity was estimated from measured conductivity and temperature using the 1978 Practical Salinity Scale algorithms (Sea-Bird Operating Manual 1995).

An additional correction had to be made due to an apparent lag in equilibration time. While methane equilibration inside the equilibrator occurred nearly instantly, equilibration between in situ surface water methane and the equilibrator headspace was quite slow due to methane's low solubility (e-folding time $\sim 14$ minutes). Assuming nearly instantaneous equilibration within the equilibrator, in situ surface water methane concentrations were estimated with the equation:

$$
\begin{equation*}
\left[\mathrm{CH}_{4}\right]_{\text {ln stu }}=\left(\mathrm{C}_{0}+\Delta \mathrm{C}\right) /\left(1-\mathrm{e}^{-b \Delta t}\right) . \tag{2-3}
\end{equation*}
$$

where $C_{0}$ is the observed concentration of methane in the equilibrator at time $0, \Delta C$ is the observed change in concentration over time $\Delta t$ and b is equal to

$$
\begin{equation*}
b=\left(f^{*} \beta_{\mathrm{eq}}\right) / \text { vol } \mathrm{l}_{\mathrm{HS}} \tag{2-4}
\end{equation*}
$$

where $f$ is the flow rate of water entering the equilibrator, $\beta_{\mathrm{eq}}$ is the Bunsen solubility coefficient for methane at the observed equilibrator water temperature and vol ${ }_{H S}$ is the volume of the headspace.

Discrete water samples were measured using a modified method of Stainton (1973). The concentration of dissolved methane in a discrete sample of water was calculated using the equation

$$
\begin{equation*}
\left[\mathrm{CH}_{4}\right]=\left(\mathrm{xCH}_{4} * \mathrm{P} * \operatorname{vol}_{\mathrm{HS}}\right) /\left(\mathrm{R} * \mathrm{~T} * \operatorname{vol}_{\mathrm{SAM}} * \mathrm{se}\right) \tag{2-5}
\end{equation*}
$$

where $\left[\mathrm{CH}_{4}\right]$ is expressed in molarity. xCH 4 is the measured mole fraction of methane in the syringe headspace. P is the measured atmospheric pressure in atmospheres, vol ${ }_{\mathrm{Hs}}$ is the volume of the equilibration (gas phase) headspace. volsam is the volume of the discrete water sample. R is the gas constant ( 0.0821 liter $\operatorname{atm} / \mathrm{mole}{ }^{\circ} \mathrm{K}$ ), T is the temperature of equilibration in ${ }^{\circ} \mathrm{K}$. and se is the stripping efficiency which is determined empirically by repeating the entire equilibration process.

Clean air samples were drawn into a 20 ml syringe while underway and analyzed for atmospheric $\mathrm{CH}_{4}$.

A number of tests were run to determine how quickly the equilibrator responded to changing methane concentrations and whether or not the modeled corrections described above adequately corrected for the observed lag in equilibration. Discrete sample analyses were run simultaneously to check for bias between the two methods. In order to run the tests. a constant source of methane was required. Tests run in Sturgeon Bay over periods
of up to four hours showed surface water methane concentrations could vary by as much 30 nM . Since the tests were usually conducted during (windy) weather days. this is not surprising. A sufficiently stable source of methane was found in Milwaukee tap water. The results of one test are presented in Figure 2-7. The gray circles show the (raw) calculated concentrations of methane derived from the partial pressure of methane measured in the equilibrator headspace. The concentrations rise exponentially with an e-folding time of approximately 14 minutes. An exponential fit of the raw data shown by the dotted line predicted a source concentration of 53 nM CH . The black circles show the modeled concentration of methane based on equation 2-3. Excluding the one outlying point that occurred eight minutes into the test. the model predicted a similar mean concentration of $53 \pm 2 \mathrm{nM}$. At $\sim 105$ minutes into the test, the temperature suddenly dropped $0.3^{\circ} \mathrm{C}$ and the methane concentration rose $\sim 20 \%$. Discrete sample analyses (shown as triangles) gave a mean concentration of $65 \pm 2 \mathrm{nM} \mathrm{CH}$. Continuous sample (equilibrator) analyses run between the discrete samples averaged $66 \pm 3 \mathrm{nM} \mathrm{CH}_{4}$. Specific parameters used to calculate the concentrations shown in Figure 2-7 are given in Table 2-1.

A comparison of raw and modeled methane concentrations determined with the disk equilibrator on a transect of northern Green Bay on May 24, 1995 is shown in Figure 2-8. The transect began in Sturgeon Bay, ran north into Green Bay, around Chambers Island and back to Sturgeon Bay (see Chapter 4 for transect chart). In the top panel. the gray circles show the raw calculated concentrations of methane heading out of Sturgeon Bay. The open circles denote methane concentrations measured on the return leg. In the bottom panel, modeled methane concentrations are shown using the same color scheme (i.e. outbound: gray, inbound: open). The dotted line represents the raw values shown in

Figure 2-7. Methane method calibration. Continuous and discrete sample methods were compared using Milwaukee tap water. Gray circles show the calculated (equation 2-1) concentrations of methane derived from the partial pressure of methane measured in the equilibrator headspace. The dotted line shows an exponential fit of the raw data. The black circles show the modeled concentration of methane which were calculated using equation 2-3. At $\sim 105$ minutes into the test, the temperature suddenly dropped $0.3^{\circ} \mathrm{C}$ and the methane concentration rose $-20 \%$. Samples run after the concentration shift are grouped inside of the box. In the statistical table below the graph. $\left[\mathrm{CH}_{4}\right]_{\text {modt }}$ is for modeled methane concentrations (black circles) outside of the box excluding the outlying point at $\sim 8$ minutes. Exp Fit gives the predicted source concentration at $t_{\infty}$. $\left[\mathrm{CH}_{4}\right]_{\text {mod }}$ represents the modeled methane concentrations (black circles) inside the box and $\left[\mathrm{CH}_{4}\right]_{\text {discrete }}$ represents the discrete samples indicated by open triangles.


|  | [CH4]mod1 | Exp Fit | [CH4]mod2 | [CH4]discrete |
| :---: | :---: | :---: | :---: | :---: |
| Mean | 0.053 | 0.053 | 0.066 | 0.065 |
| Std Dev | 0.002 | $*$ | 0.003 | 0.002 |
| Std Err | 0.000 | $*$ | 0.002 | 0.001 |
| 95\% Conf | 0.001 | $*$ | 0.008 | 0.002 |
| 99\% Conf | 0.001 | $*$ | 0.019 | 0.004 |

Table 2-1. Parameters of the methane calibration test. The parameters needed to calculate the values shown in figure 2-7 are shown below. The $1^{\text {x }}$ column shows time of measurement in minutes. the $2^{\text {nd }}$ column denotes whether the measurement was determined using the continuous (eq) or discrete method, the $3^{\text {rd }}$ column gives the mole fraction of methane measured from either the equilibrator headspace or syringe headspace. $P_{\text {atr }}$ is the measured atmospheric pressure; $T_{\text {room }}$ is room temperature; $T_{e q}$ is the measured equilibrator water temperature; warming is the amount of warming the water experienced from the source to the equilibrator in ${ }^{\circ} \mathrm{C}$; sal is the estimated salinity in $\%$; b is the equilibrator response constant based on the Bunsen solubility coefficient (a function of temperature), a headspace volume of 6 liters and a flow rate of 11 liters $\mathrm{min}^{-1}$ : se is the stripping efficiency; vol $l_{\text {sam }}$ and vol ${ }_{\text {hs }}$ are in milliliters; $\left[\mathrm{CH}_{4}\right]$ gives the raw concentrations on the molarity scale; $\left[\mathrm{CH}_{4}\right]_{\text {mod }}$ gives the modeled concentration on the molarity scale.

| 市A NA |
| :---: |
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Figure 2-8. Raw and modeled surface water methane concentrations determined with the disk equilibrator on a transect of northern Green Bay on May 24, 1995. See Chapter 4 for transect chart.


the top panel. As expected. the raw values show a significant discrepancy south of UTM 4980000. High levels of methane in Sturgeon Bay dropped faster than the equilibrator could respond when the NEESKAY entered Green Bay. On the return trip, the raw methane values accurately marked the boundary between Green Bay and Sturgeon Bay water masses but greatly underestimated the true concentration. The modeled values on both legs of the transect agreed with each other and with the raw values when the in situ methane gradient decreased to a level the equilibrator could keep up with. It should also be noted that while it was important to use the modeled methane concentrations for comparisons with physical scalars. it made little difference whether raw or modeled values were used to determine average methane concentrations for Green Bay on the whole. Using the modeled concentration values presented in Figure 2-8. the spatially weight averaged concentration over the entire transect area bounded by the shoreline of Green Bay was 46.1 nM . The raw concentrations averaged 47.9 nM .

## Carbon dioxide analysis

During the past decade, continuous sample equilibrators have been routinely used in conjunction with infrared gas analysis to measure dissolved carbon dioxide. The equilibration methods used in this study were similar to those described by Wanninkhof and Thoning (1993), DOE (1994), and Sabine et al. (1994). $\mathrm{CO}_{2}$ equilibrium between the headspace and water sample was generally reached within several minutes with an efolding time of less than 1 minute (Sabine et al. 1994). $\mathrm{CO}_{2}$ equilibrated much faster than methane primarily due to the fact that the solubility of $\mathrm{CO}_{2}$ is $\sim 25-30$ times greater than that of methane.

The method of infrared gas analysis in this study differed significantly from the papers cited above. In Wanninkhof and Thoning (1993), for example, gas from the equilibrator headspace was allowed to flow continuously through the sample cell of a Li Cor $\mathrm{CO}_{2}$ analyzer at a rate of $\sim 75 \mathrm{ml} \mathrm{min}^{-1}$ for 23 minutes. The response from the analyzer was recorded after 3 minutes and averaged over 20 minutes. During shipboard analyses, this translated to an 8 km average while underway. While this would pose no significant problem in a relatively homogenous environment like the ocean. this can not be said for Green Bay where the fugacity of dissolved $\mathrm{CO}_{2}$ can change several hundred micro-atmospheres over the distance of a kilometer. The introduction of $\sim 1.5$ liters of (outside) ambient air into the equilibrator headspace would also have significantly altered the equilibration time for methane (which was being measured concurrently). It was decided therefore to inject a small standard volume of sample into a nitrogen carrier stream that ran continuously through the sample cell of a Li - $\mathrm{Cor} 6252 \mathrm{CO}_{2}$ analyzer. The response of the analyzer was then recorded on an integrator. Standards were run in a similar fashion and the resulting peak heights were fit to their respective mole fractions using a second order polynomial equation. Reproducibility was generally better than $1 \%$.

Both sample and reference cells of the Li-Cor analyzer were flushed continuously with $\mathrm{N}_{2}$ at a metered flow rate of 20 milliliters per minute and vented directly to the atmosphere. Samples and standards were introduced into the sample cell through a 0.326 $\pm 0.001 \mathrm{ml}$ sample loop with an Altex 6-way valve. It was assumed that gases reached room temperature before being flushed into the Li-Cor. A thermistor measuring gas temperatures inside the Li-Cor sample cell showed no systematic difference between
equilibrator and standard samples. The analyzer voltage output was recorded on a Shimadzu C-R5A integrator. Water vapor was removed prior to the sample loop by passing all samples through a Perma Pure Dryer and Drierite. At least three replicates of three standards were run every one to two hours depending on changes in room temperature or atmospheric pressure. The standard concentrations were chosen to bracket observed in situ concentrations. Standards of $100 \mathrm{ppm} .101 \mathrm{ppm}, 299 \mathrm{ppm} .501 \mathrm{ppm}$. 1011 ppm and $1.00 \%$ carbon dioxide in nitrogen were obtained from Scott Specialty Gas. Additional standards of 2023 ppm and $2710 \mathrm{ppm} \mathrm{CO}_{2}$ in $\mathrm{N}_{2}$ were obtained from Linox. All standards were rated at $\pm 2 \%$ accuracy.

An inter-lab comparison between continuous and discrete sampling methods was conducted in Egg Harbor (Green Bay) on July 12 ${ }^{\text {th }}$, 1996. The $\mathrm{CO}_{2}$ concentrations measured with the disk equilibrator were determined using a set of standards obtained from Scott Specialty Gas. The discrete sample $\mathrm{CO}_{2}$ concentrations were determined by Susan Boehme at the Lamont Doherty Earth Observatory using a set of standards calibrated to WMO (World Meteorological Organization) $\mathrm{CO}_{2}$ standards. Based on 3 surface water ( $\sim 2$ meter depth) measurements, the disk equilibrated samples had a mean wet fugacity of $486.0 \pm 0.6 \mu \mathrm{~atm}$. Only one discrete sample from a depth of $\sim 2$ meters was run with a reported wet partial pressure of $487.46 \mu \mathrm{~atm}$. Converting both sets of samples back to mole fractions in dry air (at in situ temperatures). the continuous sample mean concentration of $510.1 \pm 0.6 \mathrm{ppm}$ compared well with the discrete sample concentration of 509.94 ppm . The raw data values measured during the continuous sample analyses are presented in Table 2-2. The equations used to calculate in silu

Table 2-2. Continuous sample $f \mathrm{CO}_{2}$ calculations from Egg Harbor on July 12 ${ }^{\text {th }}, 1996$. See text for equations used to calculate each parameter. "RT" = integrator retention time in minutes. "PK HT" = integrator peak height. " $\mathrm{xCO}_{2}$ " = mole fraction of $\mathrm{CO}_{2}(\mathrm{ppm})$ in dry air. "eq temp" = the temperature $\left(\mathrm{C}^{\circ}\right)$ of water inside the equilibrator. "wat temp" = the in situ (bay) temperature $\left(\mathrm{C}^{\circ}\right)$. "warming" = eq temp - wat temp. "pressure" = atmospheric pressure in hPa . Salinity is in \%o. "Patm" = the atmospheric pressure in atmospheres. "Pw" $=$ the partial pressure of water vapor in atmospheres. " $\mathrm{B}(\mathrm{vc})=$ the virial coefficient for $\mathrm{CO}_{2} . "$ sigma(cvc)" $=$ the cross virial coefficient for $\mathrm{CO}_{2}$ and air. "eq fugacity" $=$ the fugacity of $\mathrm{CO}_{2}$ in water saturated air inside the equilibrator headspace in units of microatmospheres. "dln $\mathrm{fCO} 2 / \mathrm{dT}$ " = the natural log of the change in the fugacity of $\mathrm{CO}_{2}$ caused by the temperature change between in situ and equilibrator conditions. "in situ $\mathrm{fCO} 2 "=$ the fugacity of $\mathrm{CO}_{2}$ in water saturated air that is in equilibrium with in situ $\left[\mathrm{CO}_{2}\right]$. "in situ $\mathrm{xCO}_{2}$ " = the mole fraction of $\mathrm{CO}_{2}$ at in situ conditions in dry air. The " xCO 2 eq " values were calculated using the $2^{\text {nd }}$ order polynomial "STANDARD CURVE" which in turn was generated from the results of the 10 standard runs shown.

fugacities from $\mathrm{CO}_{2}$ mole fractions determined from the equilibrator headspace are given below.

For continuous sample analysis, the procedure for calculating in situ carbon dioxide concentrations are described at length in DOE (1994) and Murphy et al. (1995). The equations below are taken from Murphy et al. (1995).

The fugacity of carbon dioxide in the equilibrator was calculated as

$$
\begin{equation*}
f\left(\mathrm{CO}_{2}\right)_{\mathrm{eq}}=\mathrm{x}\left(\mathrm{CO}_{2}\right)_{\mathrm{eq}} *\left(\mathrm{P}_{\mathrm{atm}}-\mathrm{P}_{\mathrm{w}}\right) * \exp \left[\mathrm{P}_{\mathrm{atm}}(\mathrm{~B}+2 \delta) / \mathrm{RT}\right] \tag{2-6}
\end{equation*}
$$

where $\mathrm{x}\left(\mathrm{CO}_{2}\right)_{\mathrm{eq}}$ is the measured mole fraction of carbon dioxide in dried equilibrator air. $\mathrm{P}_{\text {atm }}$ is the total barometric pressure, $\mathrm{P}_{\mathrm{w}}$ is the partial pressure of water vapor inside the equilibrator. B is the virial coefficient for carbon dioxide (a correction for non-ideal behavior between $\mathrm{CO}_{2}$ molecules), $\delta$ is the cross virial coefficient for carbon dioxide and air (a correction for non-ideal behavior between $\mathrm{CO}_{2}$ molecules and the remaining gases found in air). R is the gas constant ( $82.056 \mathrm{~cm}^{3} \mathrm{~atm} /$ mole ${ }^{\circ} \mathrm{K}$ ), and $\mathrm{T}_{\mathrm{eq}}$ is the temperature of water in the equilibrator in ${ }^{\circ} \mathrm{K}$.
$\mathrm{T}_{\mathrm{eq}}, \mathrm{P}_{\mathrm{atm}}$, and $\mathrm{x}\left(\mathrm{CO}_{2}\right)_{\text {eq }}$ were measured directly or estimated by means described below (see barometric pressure and temperature sections). $\mathrm{P}_{\mathrm{w}}$ was calculated using an equation from Weiss and Price (1980). Assuming 100\% relative humidity:

$$
\begin{equation*}
\ln P_{w}=24.4543-67.4509\left(100 / T_{e q}\right)-4.8489 \ln \left(T_{e q} / 100\right)-0.000544 \mathrm{~S} \tag{2-7}
\end{equation*}
$$

where $\mathrm{S}=$ salinity in $\%$ and $\mathrm{T}_{\text {eq }}$ is the temperature of water inside the equilibrator in ${ }^{\circ} \mathrm{K} . \mathrm{B}$ was estimated using a power series given by Weiss (1974):
$B=-1636.75+12.0408 \mathrm{~T}_{\mathrm{eq}}-3.27957 * 10^{-2} \mathrm{~T}_{\mathrm{eq}}{ }^{2}+3.16528 * 10^{-5} \mathrm{~T}_{\mathrm{eq}}{ }^{3} \mathrm{~cm}^{3} / \mathrm{mole}$

The cross virial coefficient $\delta$ was also determined by Weiss (1974) as:

$$
\begin{equation*}
\delta=57.7-0.118 \mathrm{~T}_{\mathrm{eq}} \mathrm{~cm}^{3} / \mathrm{mole} \tag{2-9}
\end{equation*}
$$

To calculate the fugacity of carbon dioxide in equilibrium with the surface waters of Green Bay, an additional correction had to be made for any change in temperature the water experienced while in transit to the equilibrator since temperature affects not only the solubility of $\mathrm{CO}_{2}$ but also the carbonate equilibria. An equation describing the change in fugacity with respect to temperature is given by Weiss et al. (1982):

$$
\begin{equation*}
\Delta \ln f\left(\mathrm{CO}_{2}\right) / \Delta \mathrm{t}=0.03107-2.785 * 10^{-1} \mathrm{t}_{\mathrm{eq}}-1.839 * 10^{-3} \ln f\left(\mathrm{CO}_{2}\right) \tag{2-10}
\end{equation*}
$$

where $f\left(\mathrm{CO}_{2}\right)$ in this case is the fugacity of $\mathrm{CO}_{2}$ in the equilibrator headspace. $\mathrm{t}_{\text {eq }}$ is the equilibrator water temperature in ${ }^{\circ} \mathrm{C}$. and $\Delta \mathrm{t}$ is the equilibrator temperature minus the in situ water temperature in ${ }^{\circ} \mathrm{C}$. During the 1994-1995 transects, $\Delta \mathrm{t}$ was always positive and ranged from $\sim 0.0^{\circ} \mathrm{C}$ in the summer to $0.9^{\circ} \mathrm{C}$ in early spring and late fall.

The warming corrected in situ fugacity was calculated as:

$$
\begin{equation*}
f\left(\mathrm{CO}_{2}\right) \mathbf{w}=\exp \left(\ln f\left(\mathrm{CO}_{2}\right)_{\mathrm{eq}}-\Delta \ln f(\mathrm{CO})_{2}\right) \tag{2-11}
\end{equation*}
$$

The warming corrected (in situ) mole fraction of carbon dioxide in dry air was back-calculated by rearranging equation 2-6 as:

$$
\begin{equation*}
\mathrm{x}\left(\mathrm{CO}_{2}\right)_{\mathrm{w}}=f\left(\mathrm{CO}_{2}\right)_{\mathrm{w}} /\left(\left(\mathrm{P}_{\mathrm{atm}}-\mathrm{P}_{\mathrm{w}}\right)^{*} \exp \left[\mathrm{P}_{\mathrm{atm}}(\mathrm{~B}+2 \delta) / \mathrm{RT}\right]\right) \tag{2-12}
\end{equation*}
$$

where T. $\mathrm{P}_{\mathrm{w}}, \mathrm{B}$ and $\delta$ were calculated using in situ lake temperatures.
The concentration of carbon dioxide was calculated using the equilibrium constant of Weiss (1974). For

$$
\begin{gather*}
\mathrm{K}_{0}=\left[\mathrm{CO}_{2}{ }^{*}\right] / f\left(\mathrm{CO}_{2}\right),  \tag{2-13}\\
\ln \mathrm{K}_{0}=93.4517(100 / \mathrm{T})-60.2409+23.3585 \ln (\mathrm{~T} / 100)+ \\
\mathrm{S}\left[0.023517-0.023656(\mathrm{~T} / 100)+0.0047036(\mathrm{~T} / 100)^{2}\right] \tag{2-14}
\end{gather*}
$$

where T is the in situ temperature in ${ }^{\circ} \mathrm{K} . \mathrm{S}=$ salinity $(\%)$, and $\left[\mathrm{CO}_{2}{ }^{\circ}\right]$ in equation $2-13$ is expressed on the molality scale and represents the sum of $\left[\mathrm{CO}_{2}\right]+\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]$. It should be noted that $\left[\mathrm{CO}_{2}\right] \cong\left[\mathrm{CO}_{2}{ }^{*}\right]$ and the two are used interchangeably unless otherwise noted.

Discrete sample $\mathrm{CO}_{2}$ analyses were performed on only a few samples collected during the winter. Discrete samples collected from under the ice were agitated (spun) for 15 minutes at surface water temperatures (or snow) in 2 liter syringes with a gas:liquid
phase ratio of $\sim 1: 100$. Ambient air was used to displace the headspace. As the syringe plunger was free to move, it was assumed that equilibration was carried out at atmospheric pressure. The headspace was then transferred to a dry syringe for later analysis.

Rigorous calculation of $\left[\mathrm{CO}_{2}\right]$ content in a discrete sample is quite complicated (DOE 1994). In simple terms, a known volume of air is allowed to equilibrate with a known volume of water in some sort of container. As carbon dioxide equilibrates between the two phases, the total inorganic carbon content in the liquid phase changes; the alkalinity does not. This sets up a series of adjustments between the carbonate species which ultimately affects the fugacity of carbon dioxide in the headspace. The fugacity of the perturbed sample is calculated and used along with the measured $\Sigma \mathrm{CO}_{2}$ of the original sample to determine the $\Sigma \mathrm{CO}_{2}$ of the perturbed sample. The $f \mathrm{CO}_{2}$ and $\Sigma \mathrm{CO}_{2}$ of the perturbed sample are then used to calculate alkalinity using a series of equilibrium constants. Finally, the alkalinity and $\Sigma \mathrm{CO}_{2}$ of the original sample are used to backcalculate the $f \mathrm{CO}_{2}$ in equilibrium with the undisturbed sample.

DOE (1994) shows that for an air:water sample volume ratio of $\sim$ 1:9. a $\Sigma \mathrm{CO}_{2}$ concentration of $\sim 2 \mathrm{mM}$, and a measured (disturbed sample) $p \mathrm{CO}_{2}$ of $343.7 \mu \mathrm{~atm}$. the corrected partial pressure of carbon dioxide was $341.1 \mu \mathrm{~atm}$ a $0.7 \%$ decrease. Since the magnitude of the perturbation is proportional to the air:water volume ratio, the air:water sample volume ratio was increased to $\sim 1: 100$ and mass balance corrections were ignored. This resulted in a probable bias of $<0.5 \%$ above the real fugacity.

Clean air samples were drawn into a 100 ml syringe while underway and analyzed for atmospheric $\mathrm{CO}_{2}$. The samples were allowed to warm to wetlab temperatures before injection into the sample loop.

A number of discrete water and air samples were collected by Susan Boehme in 1995. Carbon dioxide analyses were run in John Goddard's laboratory at the Lamont Doherty Earth Observatory using a set of primary standards traceable to WMO (World Meteorological Organization) $\mathrm{CO}_{2}$ standards.

## $\underline{\mathrm{CO}_{2}}$ and Alkalinity

Bulk water samples for $\mathrm{\Sigma CO}_{2}$ and alkalinity analysis were collected on profile stations in accordance with the recommendations described by DOE (1994). Each sample was poisoned with 0.1 ml of a saturated mercuric chloride solution. stoppered with Apiezon $\circledR^{\circledR}$ L grease, secured and stored in a refrigerator until analysis. Coulometric analyses of $\Sigma \mathrm{CO}_{2}$ were run by Brian Eadie at the Great Lakes Environmental Research Laboratory in Ann Arbor. Michigan and Susan Boehme at Princeton University. Gran titration alkalinities were run by Susan Boehme at Princeton University.

During the second year of this study (1995). total carbon dioxide was measured while underway using a flow injection analysis method described by Hall and Aller (1988). Standard solutions were prepared from dried sodium bicarbonate (J. T. Baker Chemical Co.. $99.7 \%$ assay) and weighed out on a Mettler micro-balance. Problems associated with the ship's power supply and temperature regulation resulted in significant baseline drift in
the conductivity detector. Precision across the range of $\Sigma \mathrm{CO}_{2}$ measured (2.1-2.9 mM) was $\sim \pm 5 \%$.

Additional estimates of $\Sigma \mathrm{CO}_{2}$ were obtained manometrically during $\Sigma^{13} \mathrm{CO}_{2}$ analysis of 10 ml water samples (see Appendix 5).
pH

During the 1994 field season. surface water pH was measured with a Sea-Bird (SBE 30) pH sensor. The sensor was calibrated before each cruise with commercial buffer solutions traceable to NBS standards and stored in a KCl saturated pH 4 buffer solution when not in use. Accuracy was probably no better than $\pm 0.1 \mathrm{pH}$ units.

In 1995. an Orion semi-micro Ross combination pH electrode and thermistor were inserted into the water stream just forward of the disk equilibrator. pH values were read with a Beckman pH meter with automatic temperature compensation. Two point calibrations were performed several times each day using commercial buffer solutions traceable to NIST standards. Water flow across the probe membrane could be adjusted independently of the equilibrator flow rate. Precision across the range of temperatures measured was probably better than $\pm 0.03 \mathrm{pH}$ units.

## Stable isotope analysis

Samples for inorganic ${ }^{13} \mathrm{C}$ analysis where collected at all profile stations during the 1995 field season. A syringe was used to carefully draw 10.0 ml of bulk water flowing from the submersible pump. The sample was then gently injected into a pre-combusted 15
ml Pierce vial containing $\sim 20 \mathrm{ul}$ of saturated mercuric chloride solution and a micro stirbar. The vial was quickly sealed with a Pierce neoprene septum and crimped with an aluminum closure. All samples were refrigerated and stripped within three weeks.

Carbon dioxide was extracted and purified with phosphoric acid and a flowthrough cryogenic stripping line based on a design used by Chris Martens and coworkers (Howard Mendlovitz, personal communication). The samples were acidified and degassed in their original vials by inserting needles through the neoprene septa. The bore of the gas uptake needle was large enough so as not to cause isotopic fractionation. Leaks around the septum were checked for with a drop of Snoop $\circledR$. Samples were acidified with 1 ml of phosphoric acid that had been stripped with a steady stream of helium for $>2$ hours. Samples were mixed with a magnetic stirrer placed under the vial. Water vapor was removed through a magnesium perchlorate column. Carbon dioxide was trapped with liquid nitrogen, manometrically quantified using a 10 torr full-scale MKS pressure transducer, and sealed in borosilicate tubing. The primary standard was Solenhofen Limestone (NBS Isotope Reference Sample No. 20). A secondary calcium carbonate standard was also established (Fisher Chemical Lot No. 941480). Standards and samples were treated identically and run using the same method. Isotopic ratios were determined by Brian Eadie (NOAA GLERL) on a VG Prism Mass Spectrometer.
${ }^{222} \mathrm{Rn}$ analysis

Discrete radon samples were analyzed using the method and apparatus described by Mathieu et al. (1988). Depending on the expected activity of the sample, 2 to 20 liters of bulk water were collected in pre-evacuated containers. The samples were returned to
the laboratory and flushed with helium within a day. Radon was collected on a charcoal column trap using a dry ice/alcohol slurry then flushed with helium to a Lucas type scintillation cell for counting (see Mathieu et al. 1988 for details).

A very good estimate of in situ ${ }^{222} \mathrm{Rn}$ activity was also determined by withdrawing 100 ml of headspace from the disk equilibrator and injecting it through a Drierite column directly into a Lucas cell. Helium was added to the cell to bring the internal pressure up to 1 atmosphere. The cell was then counted immediately onboard the R/V NEESKAY.

Scintillation cell efficiencies and background counts were determined by J. Val Klump. Activities were calculated using a spreadsheet developed by George Kipphut.

## Wind measurements

Hourly wind speed and direction data were obtained from the NDBC meteorological buoy \# 45002 through the NOAA Great Lakes CoastWatch Program. The buoy is located in northern Lake Michigan (45.30 N 86.42 W ), approximately 85 km NE of Sturgeon Bay. Anemometer height was reported to be 5 meters. Wind speeds were reported in $\mathrm{m} / \mathrm{sec}$ at $0.1 \mathrm{~m} / \mathrm{sec}$ resolution. Accuracy was listed at $\pm 1 \mathrm{~m} / \mathrm{sec}$.

A similar data set from the Green Bay Austin Straubel International Airport (NOAA Station $14898,44.48 \mathrm{~N} 88.14 \mathrm{~W}$ ) was used to compare wind speed over water to that measured on land. The station is located approximately 75 km SW of Sturgeon Bay. Wind speeds were recorded at a height of 10 meters and reported in knots at 1 knot resolution.

## AVHHR data

Green Bay surface temperatures were observed using Advanced Very High Resolution Radiometers (AVHRR) aboard two polar-orbiting satellites (NOAA-12 and NOAA-14). Observations were made twice a day by each satellite (NOAA-12: 08:00. 20:00; NOAA-14: 02:00, 14:00 hrs local time). The data were processed and made available to the public on the World Wide Web through the NOAA Great Lakes Coast Watch Program. Daily estimates of surface temperature for the entire Great Lakes region were mapped to a Mercator projection and translated to a $512 \times 512$ pixel grid in GIF format. Actual temperatures were embedded at $1^{\circ} \mathrm{C}$ resolution in the pixel color codes and $0.2^{\circ} \mathrm{C}$ resolution in the color palette codes (Dave Schwab, personal communication). Cloud-free areas were updated with new AVHRR information daily. Surface temperatures for cloud-covered areas were estimated from the previous day's image using a smoothing algorithm. Pixel resolution was 2.56 km . Daily images from 1994 and 1995 were "archived" in FLC movie format. This conversion erased the color palette information.

Actual temperatures were extracted from the RGB color coded images using the following procedure. The FLC movies were downloaded and converted to individual frames using Display (a shareware program written by Jih-Shin Ho). Pixel image coordinates and RGB color codes were extracted with Image Tool (a shareware program developed at the University of Texas Health Science Center in San Antonio). Geographic (Long., Lat.) coordinates for each image pixel coordinate ( $\mathrm{x}, \mathrm{y}$ ) were provided by Dave

Schwab (NOAA GLREL. Ann Arbor. MI; personal communication). RGB color codes were converted to temperatures using the color scale included in each image.

Ice analysis

During ice season. estimates of ice on Green Bay were obtained every three days from the NOAA/NAVY Ice Center. During periods of ice growth or breakup. each of the seven study site zones were subjectively considered "iced covered" if greater than $80 \%$ of each zone was covered with ice.

## Barometric pressure

During the 1994 transects, hourly measurements of atmospheric pressure were obtained from the NDBC meteorological buoy \# 45002 through the NOAA Great Lakes Coast Watch Program. Pressures were given with 0.1 hPa resolution at a reported accuracy of $\pm 1 \mathrm{hPa}$ and corrected to apparent sea level. The real (local) barometric pressure was back-calculated using the (National Weather Service) equation

$$
\begin{equation*}
P=\left(A^{n}-b H\right)^{(1 . n)}+0.3 \tag{2-15}
\end{equation*}
$$

where P is the local pressure in millibars. A is the apparent sea level pressure in millibars. H is station elevation in meters. $\mathrm{b}=8.4288 \mathrm{e}-5$. and $\mathrm{n}=0.190284$.

In 1995. the atmospheric pressure was measured on the R/V NEESKAY at a resolution of 1 hPa . Differences between locally observed pressures and those obtained from buoy \# 45002 were generally less than 1 hPa at any given time.

## Temperature

Temperature was measured at a number of points during each transect (Figure 29). The most accurate measurements were made with the Sea-Bird thermistor located on deck. The Sea-Bird is factory calibrated each year and typical accuracy/stability specifications are rated at $\pm 0.0004 \mathrm{C}$ per year. Temperature readings from the HydroLab and YSI thermistors $\left(0.01^{\circ}\right.$ and $0.1^{\circ} \mathrm{C}$ resolutions respectively) were compared to the SeaBird thermistor in a large tank and found to differ by $\sim+0.02^{\circ} \mathrm{C}$ and $-0.1^{\circ} \mathrm{C}$ respectively. The YSI bias persisted across a range of temperatures so corrections were made accordingly.

To determine in situ (lake) gas concentrations. both equilibrator and in situ water temperatures were required. In 1994, disk equilibrator temperatures were assumed to be steadily biased to those measured by the Sea-Bird. The equilibrator effluent was measured infrequently and recorded with Sea-Bird measurements. As the seasons changed, this was found not to be the case. The temperature bias between the Sea-Bird and equilibrator changed. In 1995, disk equilibrator temperatures were more directly inferred by placing the YSI temperature probe into the water stream just prior to the equilibrator. Temperature measurements of the effluent stream agreed to $0.1^{\circ} \mathrm{C}$.

In siiu lake temperatures were more difficult to obtain. The HydroLab recorded in situ temperatures only while on station. The NEESKAY did carry a thermistor in its water coolant intake pipe, but temperatures were recorded on an analog clock-driven radial chart and difficult to interpret (later analysis showed they were accurate to $\sim \pm 0.1^{\circ} \mathrm{C}$ ).

Figure 2-9. Thermistor locations on the R/V NEESKAY. (B) $T$ and (Y) $T$ were only added in 1995. (BP) T was actually located in the water coolant intake pipe which drew water from a depth of -2 meters.
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Figure 2-10. The YSI (Y) and HydroLab (HL) thermistors were calibrated with the SeaBird (SB) thermistor and used to observe temperature differences between the water column ( 2 meters), equilibrator and open deck (Sea-Bird box) at profile stations during the entire 1995 field season. The observed differences were fit to $2^{\text {nd }}$-order polynomial equations and used to estimate the equilibrator temperature (1994) and in situ (lake) temperature (1994 and 1995).


Therefore, empirical relationships between equilibrator. lake ( 2 meter) and deck (Sea-Bird box) temperature were determined at profile stations throughout the 1995 field season. The results are shown in Figure 2-10. Equilibrator temperatures ( $E Q_{t}$ ) were estimated from Sea-Bird temperatures $\left(\mathrm{SB}_{\mathrm{r}}\right)$ with the equation:

$$
\begin{equation*}
E Q_{\mathrm{T}}=\mathrm{SB}_{\mathrm{t}}+\left(0.5599+\mathrm{SB}_{\mathrm{t}}^{*}-0.0489+\mathrm{SB}_{\mathrm{t}}{ }^{2} * 9.124 \mathrm{e}-4\right) \tag{2-16}
\end{equation*}
$$

where temperatures are in ${ }^{\circ} \mathrm{C}$. If YSI temperatures were known. in situ water temperatures ( $\mathrm{WAT}_{t}$ ) were estimated with the equation:

$$
\begin{equation*}
\mathrm{WAT}_{\mathrm{t}}=\mathrm{YSI}_{\mathrm{t}}-\left(0.7683+\mathrm{YSI}_{1}^{*} *-0.0427+\mathrm{YSI}_{\mathrm{t}}^{2} * 7.333 \mathrm{e}-4\right), \tag{2-17}
\end{equation*}
$$

where YSI' refers to the bias corrected temperature (YSI $+0.1^{\circ}$ ). In situ water temperatures were estimated from Sea-Bird data with the equation:

$$
\begin{equation*}
\mathrm{WAT}_{\mathrm{t}}=\mathrm{SB}_{\mathrm{t}}-\left(0.5135+\mathrm{SB}_{\mathrm{t}}^{*}-0.0240+\mathrm{SB}_{\mathrm{t}}{ }^{2} * 5.972 \mathrm{e}-4\right) \tag{2-18}
\end{equation*}
$$

## Geostatistics

Statistical interpolation of surface water gas concentrations. temperatures, volumes and areas were done with Surfer (Golden Software. Version 6). Calculations were simplified by converting the data coordinates from the Geographic Coordinate System to the Universal Transverse Mercator (UTM, Zone 17) Grid System using ArcInfo (a GIS software package). The chief advantage of the UTM system is that coordinates are expressed in meters. Grid interpolations were generally calculated using an exact inverse distance method. The inverse distance method was chosen over the Kriging method (linear variogram, zero smoothing) since the Kriging method tended to generate negative
methane concentrations due to very steep methane gradients (in spite of this. mass estimates determined using both interpolation methods agreed to within $10 \%$ ). The distance between grid nodes ranged from 100 to 2000 meters and depended on the resolution of the data points and/or the area under consideration. The inverse distance equation employed by Surfer to calculate the value of each grid node is given as:

$$
\begin{equation*}
z=\frac{\sum_{i=1}^{n} z_{h_{n}}^{z_{i}} \beta}{\sum_{i=1}^{n} \beta}, \tag{2-19}
\end{equation*}
$$

where $z=$ the interpolated grid node value, $z_{i}=$ the neighboring data point. $h_{y j}=$ the distance between the grid node and data point, and $\beta=$ the weighing power which was set to 2.

The interpolated surface water gas concentrations were averaged over seven sections (labeled zone 1 through zone 7) of southern Green Bay (Figure 2-11). The sections roughly correspond to the Green Bay hydrodynamic box model zones of Mortimer (1978) and effectively divide southern Green Bay into zones with distinct depth. temperature. riverine input and/or trophic structure characteristics (Sager and Richman 1991).

Figure 2-11. The seven zones of southern Green Bay. All mean depth, area. and volume calculations were determined using Surfer software. 100 meter grid intervals and NOAA bathymetry and boundary files. The seven zones compose a total volume of $22.5 \mathrm{~km}^{3}$ with a total surface area of $1635 \mathrm{~km}^{2}$.

0
0




## Chapter 3

## The Kinetics of Air-Water Gas Exchange in Green Bay

## Introduction

Estimating the rate of gas transport across the air-water interface of an aquatic system is important on a global scale because many of the gases that play a role in regulating the Earth's climate are in part controlled by processes that occur in aquatic systems. On a smaller scale. estimates of fluxes of biogenic gases across the air-water interface help to constrain the mass balance of biogeochemically important elements, which in turn. illuminate the trophic status of an aquatic system. Two models describing gas transter across the air-water interface are currently in use; they are: the thin-film (or stagnant boundary layer) model, and the surface-renewal (or film-replacement) model. Both models are derived from Fick's first law of diffusion and can be abbreviated as:

$$
\begin{equation*}
\mathrm{J}=\mathrm{K} \Delta \mathrm{C} \tag{3-1}
\end{equation*}
$$

where $J$ is equal to the flux of a gas. $K$ is an empirically derived transfer coefficient and $\Delta \mathrm{C}$ is the concentration gradient of the gas across the air water interface (Liss 1983). J is generally expressed in terms of mass area ${ }^{-1}$ time ${ }^{-1}$ (e.g. moles $\mathrm{m}^{-2}$ day $^{-1}$ ), $\Delta \mathrm{C}$ is expressed as a concentration (e.g. moles $\mathrm{m}^{-3}$ ), and the transfer coefficient is expressed as a velocity (e.g. $\mathrm{m} \mathrm{day}^{-1}$ ). The sign and magnitude of $\Delta \mathrm{C}$ determines the thermodynamic force and direction of gas flux while K describes the kinetics of the process. In the thin-film model,

$$
\begin{equation*}
\mathrm{K}=\mathrm{D} / \mathrm{z}_{\mathrm{BL}}, \tag{3-2}
\end{equation*}
$$

where $D=$ the molecular diffusion coefficient of a gas and $z_{B L}=$ the thickness of a boundary layer at the air-water interface where chemical diffusion through the layer is accomplished solely through Brownian motion. In the surface-renewal model.

$$
\begin{equation*}
\mathrm{K}=(\mathrm{D} / t)^{05} \tag{3-3}
\end{equation*}
$$

where $t=$ the residence time of the surface film. The absolute difference in K between both models is small. but if the transfer coefficient for a gas other than that which was originally used to determine K is desired or if the change in ratio of two gas tracers is used to determine K . then the difference between the two models can become significant. For the equation:

$$
\begin{equation*}
\mathrm{K}_{1} / \mathrm{K}_{2}=\left(\mathrm{Sc}_{1} / \mathrm{Sc}_{2}\right)^{n} \tag{3-4}
\end{equation*}
$$

where 1 and 2 denote different gases and the Schmidt numbers $\left(\mathrm{Sc}_{1}\right.$ and $\left.\mathrm{Sc}_{2}\right)$ are the kinematic viscosity of water $\left(\mathrm{cm}^{2} \mathrm{sec}^{-1}\right)$ divided by the molecular diffusion coefficients of the gases at a given temperature, n is equal to -1.0 for the thin-film model and -0.5 for the surface-renewal model. Though both models are still used in estimating gas flux from natural systems (thin-film: Schmidt and Conrad 1993, surface-renewal: Watson et al. 1991), it is becoming clear from multiple tracer studies that the surface-renewal model is more accurate at wind speeds above $2 \mathrm{~m} / \mathrm{sec}$ (or the onset of capillary waves). Below
wind speeds of $2 \mathrm{~m} / \mathrm{sec}, \mathrm{n}$ is typically assigned a value of -0.67 (Watson et al. 1991. Jähne et al. 1987b, Holmen and Liss 1984, Ledwell 1984).

The transfer coefficient is primarily a function of wind-generated turbulence and increases non-linearly with increasing wind speed. The non-linear relationship is primarily due to an increase in the interfacial area which increases as a result of wave formation and, at higher wind speeds, bubble injection (Liss 1983, Merlivat and Memery 1983, Jähne et al. 1987, Woolf 1993. Farmer et al. 1993, Livingstone and Imboden 1993). Estimates of K have been determined in the field as well as in wind-water tunnels and are usually correlated with concurrently measured wind speeds. Reviews of some of the more common techniques used to determine K are given by Broecker and Peng (1984) and Liss (1983). In natural systems, most estimates of K have involved measuring the invasion or evasion of one or more natural or purposeful tracers in the water over a period of days to months. While these methods may be measuring a time averaged K quite accurately. they have not answered questions concerning small scale or short term variability. Nor do they accurately reflect the dependence of $K$ on the instantaneous wind speed (Broecker and Peng 1984. Broecker et al. 1986. Smith and Jones 1986. Wesely 1986). In this study. wind tunnel estimates of $K$ versus wind speed ( U ) were chosen over those determined in in situ conditions primarily because wind speeds inside of the tunnel could be carefully controlled. $\mathrm{U} / \mathrm{K}$ correlations were chosen over empirically derived in situ (timeaveraged) transfer coefficients primarily due to the hydrodynamic complexity of Green Bay and the resultant difficulties associated with modeling the flux of a tracer (e.g. radon. Imboden and Emerson 1978).

## $\underline{\mathrm{U} / \mathrm{K} \text { Correlation }}$

The $\mathrm{U} / \mathrm{K}$ correlation has been investigated in a fair number of wind-water tunnel experiments. The results of most of these studies are compiled in Jähne et al. (1987b) and Barber et al. (1988). The wind speed / transfer coefficients of Broecker et al. (1978) (hereinafter referred to as B 78 ) were chosen over the results of other studies due to the relatively large size of the Hamburg tunnel ( 18 meters), the use of $\mathrm{CO}_{2}$ to estimate K . and the extent to which the $U$ / $K$ relationship was established ( $\sim 16 \mathrm{~m} / \mathrm{sec}$ wind speed at a height of 60 cm ). Although the coefficients for the bilinear relationship between wind speed and K were not reported in B78 (see B78, Figure 6), the coefficients describing the bilinear relationship between the friction velocity ( $\mathrm{U}^{*}$ ) and K (normalized to methane at $20^{\circ} \mathrm{C}$ ) as determined by B78 are given in Barber et al. (1988) (hereinafter referred to as B88). $\mathrm{B} 88^{\prime} \mathrm{s} \mathrm{U}^{\circ} / \mathrm{K}$ relationship for methane at $20^{\circ} \mathrm{C}$ (as determined by B 78 ) is plotted in Figure 3-1a. In Figure 3-la, the $y$ intercept $=2.0$ and the slope of the first line $=0.09$. The critical friction velocity occurs at $11.35 \mathrm{~cm} / \mathrm{sec}(11 \mathrm{~cm} / \mathrm{sec}$ in B88) and marks the approximate point at which capillary waves begin to form. The slope of the second line $=$ 1.26. The friction velocity $\left(U^{*}\right)$ of wind is often used in lieu of the wind speed since $U^{*}$ is independent of the height at which $U$ is measured. B88 calculated $U^{*}$ with the equation:

$$
\begin{equation*}
\mathrm{U}^{*}=\mathrm{k} \mathrm{U}_{\mathrm{z}} /\left(\mathrm{k} /\left(\mathrm{C}_{\mathrm{DN}}\right)^{0.5}-\ln 10 / \mathrm{z}\right) \tag{3-5}
\end{equation*}
$$

where $\mathrm{k}=$ the von Karmen's constant. $\mathrm{C}_{\mathrm{DN}}$ is the neutral drag coefficient, and z is the height at which the wind speed ( U ) was measured. The von Karmen's constant was taken

Figure 3-1. A comparison of the relationships between friction velocity $\left(U^{*}\right)$, wind speed (U), and the transfer coefficient ( K ) across the air-water interface as determined by Broecker et al. (1978). a) The $U^{*} / \mathrm{K}$ relationship for methane at $20^{\circ} \mathrm{C}$ as given by Barber et al. (1988). See text for bilinear coefficients. b) The $\mathrm{U} / \mathrm{K}$ relationship for $\mathrm{CO}_{2}$ at $10.5^{\circ} \mathrm{C}$ as determined by Broecker et al. (1978).

as 0.4 and the neutral drag coefficient was assumed to be constant at $1.3 \times 10^{-3}$. The transfer coefficients were normalized to methane at $20^{\circ} \mathrm{C}$ using equation 3-4. It was assumed that $n=-0.67$ for $U_{06}$ values up to $\sim 2.7 \mathrm{~m} / \mathrm{sec}$ and $n=-0.5$ for $U_{06}$ values > $-2.7 \mathrm{~m} / \mathrm{sec}$. The Schmidt number for methane at $20^{\circ} \mathrm{C}$ was taken as 620 . The Schmidt number for carbon dioxide at $10.5^{\circ} \mathrm{C}$ (i.e. the gas and temperature reported by B 78 ) was taken as 1040 . The back-calculated $\mathrm{U}_{06} / \mathrm{K}$ relationship for $\mathrm{CO}_{2}$ at $10.5^{\circ} \mathrm{C}$ is shown in Figure $3-1 \mathrm{lb}$ and agrees well with B 78 s Figure 6.

## U/z Relationship

In the field of micro-meteorology, considerable effort has been spent on discerning the height dependency of wind. The results of these efforts have been used by geochemists to correlate wind speed dependent processes and the wind speed measured at various heights to that of a standard height (e.g. $U_{10}$ ) or. as shown above. a height independent wind speed (i.e. the friction velocity $U^{\prime \prime}$ ). More often than not, geochemists have simplified the $U / z$ relationship by using a neutral drag coefficient (which implies a static $U / z$ profile). In reality, the slope of the profile depends on a variety of meteorological factors: the most significant being the air-water temperature gradient and its effect on the buoyancy and shear of the atmospheric surface layer (Kraus and Businger 1994). The extent to which temperature gradients affect the slope of the wind profile was explored with a computer program written by Arlindo da Silva at the University of Wisconsin Milwaukee (see Appendix 6). Based on inputs of barometric pressure, dew point (or relative humidity), water temperature, air temperature, and the observed wind speed at a given height, the program was able to generate a wind / height profile based on the principles outlined in Large and Pond (1981, 1982).

Two extreme cases for air-water temperature gradients of $\pm 10^{\circ} \mathrm{C}$ are illustrated in Figure 3-2. In Figure 3-2a. profiles for a $5 \mathrm{~m} / \mathrm{sec}$ wind speed at $\mathrm{z}=5 \mathrm{~m}$ show a stable (stratified) wind profile for warm air over cooler water (dotted line) and an unstable wind profile for cold air over warmer water (dashed line). The solid line shows the wind profile generated using equation 3-5 $\left(C_{D N}=1.3 \times 10^{-3}\right)$. Figure 3-2b shows similar profiles for $U_{10}$ $=5 \mathrm{~m} / \mathrm{sec}$ and illustrates the fact that the potential error associated with estimating K increases with the height at which $U$ is measured. Though the differences in wind speed may seem trivial, the differences in corresponding transfer coefficients are huge (see Figure 3-1b). For the three profiles shown in Figure 3-2b, $\mathrm{K}_{\mathrm{CO} 2.105^{\circ} \mathrm{C}}=3.5 \mathrm{~cm} / \mathrm{hr}$ (dotted line), $9.1 \mathrm{~cm} / \mathrm{hr}$ (solid line), and $13.8 \mathrm{~cm} / \mathrm{hr}$ (dashed line).

## Green Bay Wind Data

Hourly wind speeds were recorded during the 1994 and 1995 field seasons at both the Green Bay airport and NDBC buoy \# 45002 (see Chapter 2). A comparison of the two data sets showed that while both data sets tracked the progression of storms in unison the wind speeds recorded at the airport were generally lower than those recorded on open water. This is not surprising since (overland) mesoscale obstructions can reduce wind speeds by up to $50 \%$ (Schwab and Morton 1984. Fujita and Wakimoto 1982). Frequency analysis of both data sets. shown in Figure 3-3a. confirm the lower overland wind speeds.

There are a number of simple models for estimating overwater wind speeds from overland wind speeds. but none of them are particularly accurate (Schwab and Morton 1984). To demonstrate this, estimates of overwater wind speed were generated using August 1994 Green Bay airport wind speeds ( $\mathrm{n}=744$ ) and the method of Resio and Vincent (1977) (as reported in Schwab (1978)). For:

Figure 3-2. The effect of air-water temperature gradients on the wind speed / height profile for a) $U_{5}=5 \mathrm{~m} \mathrm{sec}^{-1}$ and b) $U_{10}=5 \mathrm{~m} \mathrm{sec}^{-1}$ ( $\mathrm{RH}=80 \%$ at 992 hPa ). The profiles were calculated using a computer program written by Arlindo da Silva at the University of Wisconsin-Milwaukee and based on the principles outlined in Large and Pond (1981, 1982).
wind profiles for $5 \mathrm{~m} / \mathrm{sec}$ wind at 5 m height

— - 05 C arr. 105 C water cuassical loganturme profile
a
wind profiles for $5 \mathrm{~m} / \mathrm{sec}$ wind at 10 m height

b

Figure 3-3. Comparison of hourly wind speeds recorded at the NDBC buoy \#45002 ( $45.30 \mathrm{~N} 86.42 \mathrm{~W} . \sim 85 \mathrm{~km}$ NE of Sturgeon Bay) and the Green Bay airport (NOAA Station $14898,44.48 \mathrm{~N} 88.14 \mathrm{~W}, \sim 75 \mathrm{~km} \mathrm{SW}$ of Sturgeon Bay) a) Frequency (\%) of wind speeds for complete 1994 and 1995 wind data sets. b) Difference between wind speeds recorded at buoy \#45002 and "corrected" wind speeds from the Green Bay airport during the month of August 1994. Green Bay airport (overland) wind speeds were translated to overwater wind speeds using the method of Resio and Vincent (1977).


$$
\begin{equation*}
\mathrm{U}_{\mathrm{w}}=\mathrm{U}_{\mathrm{L}}\left(1.2+1.9 / \mathrm{U}_{\mathrm{L}}\right)\left[1-\Delta \mathrm{t}|\Delta \mathrm{t}|(|\Delta \mathrm{t}| / 1900)^{1.3}\right] \tag{3-6}
\end{equation*}
$$

$U_{W}$ and $U_{L}$ represent overwater and overland wind speeds in $\mathrm{m} / \mathrm{sec}$ and $\Delta t$ equals the airwater temperature difference in ${ }^{\circ} \mathrm{C} . \Delta \mathrm{t}$ was taken as $-0.4^{\circ} \mathrm{C}$ based on the average airwater temperature difference recorded at buoy $\# 45002$ from 1989 to 1993. Where airport wind speeds were zero, the estimated overwater wind speed (limit) of $2.02 \mathrm{~m} / \mathrm{sec}$ was used. Estimated values of overwater $U_{10}$ were divided by 1.05 to obtain wind speeds at a height of 5 meters (see below. Table 3-1).

The differences between observed (buoy) - estimated overwater wind speeds are presented in Figure 3-3b. Estimates of overwater wind speed correlated poorly with observed overwater wind speeds $\left(r^{2}=0.34\right)$. but the mean difference between the two data sets was essentially zero over the time scale of a month. Since surface water gas measurements were made on a similar (~monthly) time scale, either wind speed data set would have resulted in similar gas flux estimates across the air-water interface as long as the frequency of wind speeds above and below the critical wind speed required to generate capillary waves (i.e. $\sim 2 \mathrm{~m} / \mathrm{sec}$. see Figure $3-\mathrm{lb}$ ) was the same for each data set.

The high frequency of $0 \mathrm{~m} / \mathrm{sec}$ wind speeds for the airport data (and the absence of wind speeds below 3 knots) are suspicious however, and suggest a faulty anemometer. In view of the complexities involved in predicting wind speed over water from land-based measurements and the poor agreement between modeled and observed wind speeds over water (Schwab and Morton 1984), the wind speeds from buoy \#45002 were used to estimate transfer coefficients across the air-water interface of Green Bay.

## $\mathrm{U}_{50}$ to $\mathrm{U}_{06}$ translation

Wind speeds recorded at buoy \#45002 were translated from $U_{50}$ to $U_{06}$ with a reduction factor calculated using A. da Silva's model and the average monthly wind speed. air temperature and water temperature recorded at buoy \#45002 from 1989 to 1993. The relative humidity and barometric pressure were assumed to be $80 \%$ and 992 hPa respectively. The reduction factors and monthly meteorological data are presented in Table 3-1. Wind speeds measured at a height of 5 meters were multiplied by the " 0.6 m x factor" to obtain $U_{06}$. The calculated drag coefficients $\left(C_{D}\right)$ ranged from $1.31 \times 10^{-3}$ in December to $0.77 \times 10^{-3}$ in June. The stability parameters ( $z / \mathrm{L}$. where $\mathrm{L}=$ Obukhov scale length of turbulence) show stable stratification ( $z \mathrm{~L}>0$. Kraus and Businger 1994) from April through July. The average monthly wind profiles calculated with the coefficients in Table 3-1 are shown in Figure 3-4. Average monthly wind speeds were also used to fill small gaps in the data set due to the fact that Buoy \#45002 was hauled out for servicing during the winters of 1994 and 1995.

## Green Bay Temperature Data

Surface water temperatures of Green Bay were obtained for every $\sim 4^{\text {th }}$ day of open water from AVHRR data according to the methods described in chapter 2. The temperatures were weight averaged in each of the zones outlined in Figure 2-9 (except zone 5 . see below). The weight averaging method entailed interpolating the temperatures over a grid using an exact inverse distance method. The entire grid was then integrated and divided by the base area of the grid. The grid nodes were spaced at 2 km intervals corresponding with the approximate resolution of the AVHRR data. The data-set for each zone only included temperatures from within the zone; temperatures outside of the zone

Table 3-1. Wind speed correction factors. Average (1989-1993) monthly water temperatures, air temperatures and wind speeds recorded at buoy \#45002 were used to calculate specific drag coefficients ( $C_{D}$ ). stability parameters ( $z / L$ ), and wind speed correction factors where the $" 0.6 \mathrm{~m} \times$ factor" $=\mathrm{U}_{06}: \mathrm{U}_{5.0}$ and the " 10 mx factor" $=$ $\mathrm{U}_{100}: \mathrm{U}_{50}$.


Figure 3-4. Average monthly Green Bay wind profiles based on average (1989-1993) monthly wind speeds $\left(U_{5.0}\right)$ at buoy \#45002 and the air column stability / drag coefficients listed in table 3-1.

were blanked. The 1994-1995 surface water temperatures for zones 1-4.6. and 7 are shown in Figure 3-5. Due to its small size (and the resultant paucity of AVHRR data), zone 5 was assumed to have the same temporal temperature profile as zone 2 based on their similar mean depth. A cursory comparison between the weight averaged satellite derived surface temperatures and directly measured Sea-Bird temperatures in 1995 (zone 4) shows fairly good agreement considering the resolution of the AVHRR data ( $\pm 0.5^{\circ} \mathrm{C}$ ) and uncertainties in evaporative surface cooling (Schwab et al. 1992, Van Scoy et al. 1995), bias in the surface water transect route, error due to interpolation during cloud cover, and the possibility of shallow (temporary) stratification above the -2 meter deep intake pipe that supplied water to the Sea-Bird thermistor (Figure 3-6).

## Green Bay Transfer Coefficients

Daily estimates of K were determined as follows. Hourly wind speeds were converted to $\mathrm{U}_{06}$ using the appropriate reduction factors given in Table 3-1. The translated wind speeds were then used to determine hourly estimates of $\mathrm{K}_{\mathrm{CO}, 10.5^{\circ} \mathrm{C}}$ as determined by B78 (Figure 3-1b). Each estimate of $\mathrm{K}_{\mathrm{CO} 2.10 .5^{\circ} \mathrm{C}}$ was then translated to $\mathrm{K}_{\mathrm{CH} 4}$ or $\mathrm{K}_{\mathrm{CO2}}$ at in situ temperatures for all seven zones using equation 3-4. the temperatures shown in Figure 3-5, and the Schmidt number / temperature relationships determined by Jähne et al. (1987a). For carbon dioxide, a $3^{\text {rd }}$-order polynomial fit of Jähne`s data gave:

$$
\begin{equation*}
S c_{\mathrm{CO} 2}=1911.374-113.676(\mathrm{t})+2.967\left(\mathrm{t}^{2}\right)-0.029\left(\mathrm{t}^{3}\right), \tag{3-7}
\end{equation*}
$$

and for methane.

Figure 3-5. Green Bay open water surface temperatures for zones 1-4, 6. and 7 based on AVHRR satellite data. The light gray line follows surface water temperatures in zone 1: the southernmost. shallow area of southern Green Bay. The dark gray line follows surface temperatures in zone 7: the northernmost. deep area of southern Green Bay.

| temp |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\bigcirc$ | $\stackrel{\rightharpoonup}{\circ}$ | $\stackrel{\rightharpoonup}{v}$ | N | N | ¢ |



Figure 3-6. Satellite versus ground based surface water temperature. The AVHRR satellite data plotted here are averages of day and night-time surface temperatures with a temporal resolution of $\sim 4$ days. The ground based measurements were made on water pumped from a depth of $\sim 2$ meters while onboard the R/V NEESKAY during normal gassampling transects. The transect routes are shown in appendix 3.

1995
zone 4


$$
\begin{equation*}
\mathrm{Sc}_{\mathrm{CH} 4}=1898.131-110.085(\mathrm{t})+2.834\left(\mathrm{t}^{2}\right)-0.028\left(\mathrm{t}^{3}\right) \tag{3-8}
\end{equation*}
$$

where $\mathrm{t}=$ the in situ temperature in ${ }^{\circ} \mathrm{C}$. Hourly estimates of K for each gas in each of the seven zones were then summed to give daily estimates of $K$ in each zone. The results are shown in Figure 3-7. The transfer coefficients for $\mathrm{CH}_{4}$ and $\mathrm{CO}_{2}$ are nearly similar due to their similar diffusion coefficients. Differences in $K$ between zones were generally small and only became significant ( $\sim 20 \%$ ) during spring and autumn when differential heating (and cooling) occurred due to differences in water column depth. The average $U$ labeled sections denote periods when only mean monthly wind speeds from 1989-93 were available (Figure 3-7). The zigzag pattern displayed during these periods arises due to steadily falling temperatures and a monthly jump in $\bar{U}$ (see Table 3-1). The frequencies of transfer coefficients for each month of wind data recorded during 1994 and 1995 are plotted in Figure 3-8 (transfer coefficients determined from monthly wind averages are excluded) and show good agreement with the temporal trends in average (1989-1993) temperature and wind (Table 3-1, Figure 3-4).

## Conclusions

The calculated transfer coefficients shown in Figure 3-7 are higher than most values of K based on similar $\mathrm{U}_{50}$ values (see Watson et al. 1991. Barber et al. 1988. Liss 1983). This is due in part to the choice of $B 78$ 's $\mathrm{U} / \mathrm{K}$ relationship as well as the corrections made for the stability of the air column. The relative contribution of the stability corrections to the value of K . the effects of averaging, and equivalent estimates of K based on several other $\mathrm{U} / \mathrm{K}$ relationships are presented in Figure 3-9. In zone 4 (1995),

Figure 3-7. Daily Green Bay transfer coefficients for methane and carbon dioxide based on hourly wind speeds and AVHRR derived surface temperatures. Sections labeled "avg $U$ " denote periods when only monthly wind speed averages (from 1989-1993) were available. Both panels show all estimates of K for both $\mathrm{CH}_{4}$ and $\mathrm{CO}_{2}$ in all seven zones (i.e. 14 lines).


Figure 3-8. Monthly frequency (\%) of Green Bay transfer coefficients based on hourly wind speeds recorded at buoy \#45002 during 1994 and 1995. November 1995 frequencies based on first 11 days only.


Figure 3-9. U/ K $\mathrm{K}_{\mathrm{CH} 4}$ comparisons for zone 4 (4/1/95-10/31/95). The "measured $\mathrm{U}(5 \mathrm{~m}){ }^{\text {. }}$ $=$ the averaged hourly wind speeds recorded at a height of 5 meters at buoy $\# 45002$; the "complex $U(0.6 \mathrm{~m}) "=U_{5} \times " 0.6 \mathrm{~m}$ factor" given in table $3-1 ; U^{*}=$ the friction velocity calculated using $U_{5}$ and equation 3-5; "simple $U(0.6 \mathrm{~m}, 10 \mathrm{~m}) "=\mathrm{U}_{06.10}$ back-calculated from the friction velocity and equation 3-5; "temp" = the averaged AVHRR surface temperature. The "original" $\mathrm{K}_{\mathrm{CH} 4}=$ the sum of hourly K estimates divided by the number of days in each month; the "monthly avg" $\mathrm{K}_{\mathrm{CH}}=\mathrm{K}$ estimate based on the average monthly wind speed (complex $\mathrm{U}_{06}$ ) and temperature; the "simple" $\mathrm{K}_{\mathrm{CH}}=\mathrm{K}$ estimate based on the friction velocity and temperature. See text for explanation and derivation of other transfer coefficients.

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the average $\mathrm{K}_{\mathrm{CH}_{4}}$ for wind speeds recorded between April $1^{\mathbb{x}}$ and October $31^{s}$. was 443 cm day ${ }^{-1}$. Estimates of $K$ based on monthly averages of hourly wind speeds were only slightly less ( $\sim 3 \%$ ) than the monthly averages of hourly K estimates since wind speeds rarely dropped below $\sim 3 \mathrm{~m} / \mathrm{sec}$ (see Figure $3-1$ ). Corrections for the stability of the air column however played a larger role. The transfer coefficients calculated using the $U_{5.0}$ / $U^{*}$ relationship given in equation 3-5 were $-26 \%$ lower. Estimates of K calculated using the Liss and Merlivat (1986) relationship as reported by Van Scoy et al. (1995) where for wind speeds greater than $3 \mathrm{~m} / \mathrm{sec}$ and less than or equal to $13 \mathrm{~m} / \mathrm{sec}$ :

$$
\begin{equation*}
\mathrm{K}\left(\mathrm{~cm} \mathrm{day}{ }^{-1}\right)=87.7\left[2.85 \mathrm{U}_{10}-49.3\right](600 / \mathrm{Sc})^{105} \times 0.274 \tag{3-9}
\end{equation*}
$$

were $\sim 67 \%$ lower than the values calculated here. Some of the lowest transfer coefficients ( $20-40 \mathrm{~cm} /$ day) have been measured in small (presumably sheltered) lakes using isotopic tracers (e.g. ${ }^{222} \mathrm{Rn}$ and ${ }^{3} \mathrm{He}$, Emerson 1975. Torgersen et al. 1982) Cole et al. (1994) used these values to extrapolate a constant $\mathrm{K}_{\mathrm{CO} 2}\left(\cong \mathrm{~K}_{\mathrm{CH}_{4}}\right.$ ) of 50 cm day $^{-1}$ for all lakes (including Lake Michigan) when estimating $\mathrm{CO}_{2}$ flux from lakes to the atmosphere. At the other end of the spectrum, small scale, short term micrometeorologic flux measurements determined using the eddy correlation technique give apparent $K$ values that are an order of magnitude higher than the entire range of "geochemically-derived" transfer coefficients determined in either field or laboratory conditions. Smith et al. (1991) give an approximate $\mathrm{U}_{10} / \mathrm{K}$ relationship of:

$$
\begin{equation*}
\mathrm{K}\left(\mathrm{~m} \mathrm{sec}^{-1}\right)=6.5 \times 10^{-5} \mathrm{U}_{10} \tag{3-10}
\end{equation*}
$$

which translates to an average Green Bay transfer coefficient of $\sim 38$ meters day ${ }^{-1}$. The eddy correlation technique has generated considerable debate (see Wesley 1986. Smith and Jones 1986. Broecker et al. 1986) and points out the need to resolve the dependence of K on the time scale of measurement.

The K values determined here will be used in the following chapters to estimate the net evasion (or invasion) of $\mathrm{CO}_{2}$ and $\mathrm{CH}_{4}$ from or to Green Bay. Constraints placed on the air-water flux estimates by previously determined components of the Green Bay carbon budget (Klump and Fitzgerald. 1998) should in turn illuminate the relationship between wind speed and the apparent kinetics of gas exchange across the air-water interface of Green Bay.

## Chapter 4

## The Dynamics of Surface Water Methane in Green Bay

## Introduction

Biogenic methane is produced by a group of bacteria that require strict anaerobic conditions. In aquatic systems that maintain an oxygenated water column. these conditions are only found within sediments and, on a much smaller scale, the intestinal tracts of planktonic animals (Oremland 1979).

As methane diffuses away from its source it eventually crosses an oxic-anoxic interface. Where oxygen and methane coexist. a group of aerobic (methanotrophic) bacteria use methane as a carbon source for growth. The fraction of methane oxidized to that produced is typically less than one as evidenced by the fact that most of the world`s surface waters are supersaturated with methane with respect to the atmosphere (Barber et al. 1988). Methane that is not oxidized eventually passes through the air-water interface to the atmosphere.

The highest rate of methane oxidation generally occurs at the oxic-anoxic interface in a narrow zone where the flux of methane and oxygen is at a maximum. Away from this zone. methane oxidation typically drops to a level below detection (Rudd and Hamilton 1978, Harrits and Hanson 1980, Kuivila et al. 1988).

A review of the literature shows that for lakes that maintain an oxygenated water column throughout the year, methanotrophic activity is limited to the sediment (Lidstrom and Somers 1984. Heyer and Babenzien 1985, Kuivila et al. 1988. Schmidt and Conrad 1993, Scranton et al. 1993, Thebrath et al. 1993). If methane is only affected by biological activity within the sediment. then the gas is essentially inert within the water column. The
flux of methane across the air-water interface must therefore equal the flux of methane across the sediment-water interface over a sufficiently long time scale.

In Green Bay, the water column is oxygenated throughout the year and the oxicanoxic interface is generally found at a depth of $\sim 5 \mathrm{~mm}$ into the sediment (Buchholz et al. 1995; Klump et al. 1997; Val Klump, personal communication). There have been reports of anoxic "blobs" of water in the southern bay (John Kennedy, personal communication) but none were observed during this study. It was assumed, therefore, that methane oxidation within the water column of southern Green Bay is negligible relative to other source and sink terms.

If methane oxidation in the water column is negligible, then:

$$
\begin{equation*}
\mathrm{J}_{\mathrm{aw}}=\mathrm{J}_{\mathrm{sw}}+\mathrm{I}-\mathrm{E} \tag{4-1}
\end{equation*}
$$

where $\mathrm{J}_{\mathrm{aw}}=$ the flux of methane across the air-water interface. $\mathrm{J}_{\mathrm{sw}}=$ the flux of methane across the sediment-water interface. $\mathrm{I}=$ riverine inputs of methane and $\mathrm{E}=$ methane export to northern Green Bay and Lake Michigan. The flux of methane across the sediment-water interface of southern Green Bay has been estimated at $14 \times 10^{7}$ moles year ${ }^{-1}$ by Klump and Fitzgerald (1998) and reasonable estimates of I and E can be made with a knowledge of river and water column methane concentrations, river water discharge and bay-lake exchange rates. The result ( $\mathrm{J}_{\mathrm{aw}}$ ) is an independent estimate of the mean flux of methane across the air-water interface at steady state (equation 4-1). Hence it should be possible to calculate a mean transfer coefficient (K) which supports this flux based upon the observed air-water methane concentration difference $(\Delta \mathrm{C})$ (equation 3-1).

The mean value of $K$ does not rely on measurements of its dependence on wind speed. temperature and boundary layer physics since it derives from mass balance principles. To a first approximation then. calculation of the mean transfer coefficient can serve as a "cross check" on the values of K derived in Chapter 3.

In addition to providing a constraint on the kinetics of air-water gas transfer. methane is of considerable interest in its own right. Though the atmospheric concentration of methane is relatively low ( $\sim 1.9 \mathrm{ppm}$ ), methane's potential for trapping infrared radiation is approximately 25 times greater than that of carbon dioxide (Lashof and Ahuja 1990). When it was discovered in the late 1970s that current tropospheric concentrations of the gas are rising at approximately 1\% per year (Blake and Rowland 1988), a concomitant search began for its source. A recently published mass balance (Schlesinger 1997) suggests that freshwater lakes and rivers contribute only $\sim 0.9 \%$ (or $5 \times 10^{12} \mathrm{~g}$ $\mathrm{CH}_{4} / \mathrm{yr}$ ) of the total efflux of methane to the atmosphere. but the origin of this estimate traces back to Ehhalt (1974). Ehhalt based his estimate on two studies of summertime methane ebullition from Great Fresh Creek (Conger 1943) and Lake Erie (Howard et al. 1971), and a study of methane oxidation in Lake Beloye (Russia) by Rossolimo (1935). Results presented in this study would significantly add to the data set of methane flux measurements from lakes and help to generate a more accurate estimate of the global contribution of methane from freshwater systems.

An accurate estimate of the current flux of methane to the atmosphere, however, can in no way predict the response of methanogens to a changing environment. A variety of physical and biological factors affect the concentration of surface water methane (Figure 4-1). Though many of the factors are interdependent, some have direct bearing on

Figure 4-1. The forces influencing surface water methane in Green Bay.

the rate of methane production while others do not. Examples of the former subset include the quantity and quality of organic substrate from which methanogens grow, the population of methanogenic bacteria (not shown) and the effect of sediment temperature on bacterial metabolism. While fluctuations in methane flux due to changes in bacterial population and/or nutrient limitation would be difficult to prove at a single study site. fluctuations in methane flux due to changes in sediment temperature would be expected. Incubation experiments in the laboratory have shown that the rate of methane production is highly dependent on temperature (Koyama 1963). In Green Bay, sediment temperatures fluctuate up to $20^{\circ} \mathrm{C}$ over an annual cycle. As the sediments warm during summer months. increases in methane production should translate to higher fluxes of methane to the water column and atmosphere. Establishing a correlation between sediment temperature and methane flux to the atmosphere would improve our ability to model the effects of global warming.

## Surface water methane

Nearly 1700 surface water samples were measured for methane during the open water transects of 1993, 1994 and 1995. Surface water methane concentrations and sampling sites are shown in Figure 4-2. Each of the measurements, their coordinates, and the physical parameters relevant to calculating each concentration are also given in Appendix 3.

Surface water methane concentrations ranged from $0.003 \mu \mathrm{M}$ ( $\sim$ atmospheric equilibrium) to greater than $4.8 \mu \mathrm{M}$ and averaged $\sim 0.06 \mu \mathrm{M}$ over southern Green Bay. The mean surface water methane concentration in each of the seven zones of the study site

Figure 4-2. Green Bay surface water methane concentrations measured during transect cruises of 1993. 1994 and 1995. The axis range is adjusted to the highest observed concentration for each day`s cruise. The transect distance represents the cumulative distance traveled in kilometers. The location of each sample point is plotted with a circle. The area of each circle is proportional to the concentration of methane.

02-Nov-93


03-Nov-93


02-Jun-94


03-Jun-94


13-Jul-94

14-Jul-94


15-Jul-94


02-Aug-94


03-Aug-94


## 23-Aug-94



13, 14, $15 \operatorname{Sep} 94$



## 26-Oct-94



## 18-Apr-95



20-Apr-95


22-May-95


23-May-95


## 24-May-95



## 18-Jul-95



19Jul-95


## 25-Jul-95



## 28-Jul-95



## 29-Aug-95



06-Oct-95


09-Oct-95


10-Oct-95


## 09-Nov-95


tended to decrease as the average water column depth of each zone increased (Figure 43). The reason for this ultimately relates to temperature and is discussed at length below.

The highest concentrations of methane were always found in Sturgeon Bay and the Fox River. At the beginning of this study, I assumed that methane originated in the sediment from biological sources (planktonic sources were assumed negligible (Schmidt and Conrad 1993)). When it was discovered that submerged natural gas pipelines ran under both areas, the possibility existed that a natural gas leak could account for the high concentrations of methane. To test this theory, surface water radon and methane were measured along a transect across Green Bay and into Sturgeon Bay, terminating over the pipeline (Figure 4-4). Since natural gas should not contain radon. an increase in only methane would have suggested that the pipeline might be leaking. Clearly, this was not observed. The concentration of both gases rose in tandem as the water column depth decreased in Sturgeon Bay. This strongly suggested that the methane originated from the sediment and that the high concentrations of methane were a result of relatively warm sediment temperatures and turbulent mixing in a shallow unstratified water column.

To simplify flux calculations and interpretations of large scale changes over space and time, methane concentrations measured over an entire cruise ( $\sim 3$ days) were spatially weight averaged in each of the seven zones of the study site. This was accomplished by interpolating the data over a grid of each zone using an exact inverse distance method (equation 2-19). Each grid was then integrated and divided by its base area. Grid nodes were spaced at 100 meter intervals in zone 5, 250 meter intervals in zone 1 , and 500 meter intervals in zones $2,3,4,6$, and 7 . The data set for each particular zone only included measurements from within the zone: measurements made outside of the zone were

Figure 4-3. The mean concentration of methane ( $\pm 1 \mathrm{~S}$. D.) for all cruises in zones 1-7 versus water column depth.

# surface $\left[\mathrm{CH}_{4}\right]$ versus water column depth 



Figure 4-4. Surface water methane and radon measured along a transect across Green Bay and into Sturgeon Bay. High concentrations of methane occurred over a submerged natural gas pipeline running across Sturgeon Bay. The increase in both radon and methane in Sturgeon Bay suggests that the methane originated from the sediments. The values reported here are raw. Neither methane nor radon concentrations were corrected for a lag in response to equilibration. Quenching effects on the radon activity caused by gases other than helium in the counting cell were ignored.

blanked. If no (or insufficient) measurements were made in a zone. the zone was excluded from consideration.

The temporal variations in spatially weighted average surface water methane concentrations are presented in Figure 4-5. The extent to which these concentrations were affected by the physical scalars shown in Figure 4-1 is explored below.

## Temperature

Laboratory studies have shown that the rate of methanogenesis is strongly dependent on temperature. Sediment cores taken from the field and incubated in the laboratory have shown a 2.8 to 4.3 fold increase in methane production for every $10^{\circ} \mathrm{C}$ increase in temperature between 5 and $30^{\circ} \mathrm{C}$ (Koyama 1963, Klump and Martens 1989. Kiene 1991. Thebrath et al. 1993) The variation in $Q_{10}$ (i.e. change in production over 10 ${ }^{\circ} \mathrm{C}$ ) probably relates to the quality or quantity of organic substrate available to the methanogens. In the examples mentioned above. the $\mathrm{Q}_{10}$ of 2.8 was observed in sediments obtained from the littoral regions of Lake Constance (Thebrath et al. 1993) while the high value (4.3) was measured in rice paddy soils (Koyama 1963). Incubation experiments conducted on sediment obtained from an organic rich region of Green Bay (GB32) showed a $Q_{10}$ of $\sim 3.5$ ( J. V. Klump. unpublished data). If sediment temperatures increase and the ratio of methane production to methane oxidation remains greater than one. then an increase in water column methane and/or methane flux should be observed. Surprisingly, this has rarely been shown. To my knowledge, only one study has found a positive correlation between the flux of methane across the air-water interface and temperature (Baker-Blocker et al. 1977).

Figure 4-5. The temporal variation of spatially weight-averaged surface water methane concentrations in zones 1-7 of southern Green Bay. The zones are reproduced here for convenience and appear as shaded areas within the Green Bay shoreline. Concentrations measured during the 1994 transects appear as light gray circles; 1995 values are plotted as dark gray circles. Ice cover is plotted as a line using the same color scheme. Note the change of scale on the Y axis in each zone. All relevant data is tabulated below each figure. See text for description of interpolation methods.

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| 96-10N-60 | 96.15004 | 86-6ny-62 | 96. $\ln 5 \cdot 61$ | 86-Avw-2\% | 96-1dv-0z | 18.730.92 | pedos-ct | \%-Env-ct | re-Onv-zo | vo-mp-ct | W-unf-co | C6.AON.EO | 3180 |

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For the data presented in Figure 4-5. only one of the seven zones defined in southern Green Bay show a pronounced seasonal cycle. In zone 5 (Sturgeon Bay), surface water methane concentrations clearly rose from spring to summer and decreased again in autumn. The concentrations are plotted against the spatially weighted average surface temperatures in Figure 4-6a. The temperatures were weight averaged using the same (inverse distance) interpolation method described for methane. The slope of the relationship shows that for every $10^{\circ} \mathrm{C}$ increase in temperature, surface water methane concentrations rose by a factor of $\sim 2.1$. This could be used to back-calculate the minimum methane production rate if two assumptions are made. First. I assumed that sediment temperatures were within $\sim \pm 1^{\circ} \mathrm{C}$ of the surface water temperatures and isothermal to a depth of at least $\sim 30 \mathrm{~cm}$ (Klump and Martens 1989. Birge et al. 1928). This assumption was based on the fact that Sturgeon Bay (zone 5) is shallow with a mean depth of 5.4 meters. Based on the temperature profiles shown in Appendix 4. the water column was usually isothermal (the exception occurred during the June 1994 cruise when stratification was just setting up and the thermocline occurred at a depth of $\sim 3$ meters). To a first approximation. I also assumed that the wind velocity over Sturgeon Bay was relatively constant. Sturgeon Bay is unique among the seven zones in that it lays perpendicular to the predominant wind direction in a narrow strip between hills that rise nearly 70 meters on both sides.

Using a simple one dimensional model derived from Newton's law of cooling,

$$
\begin{equation*}
\left[\mathrm{CH}_{4}\right]_{\text {water column }} \cong\left(\mathrm{J}_{\text {sed }} / \mathrm{K}\right)+\mathrm{Ce}^{-1 \mathrm{~K} d x}, \tag{4-2}
\end{equation*}
$$

Figure 4-6. The relationship between surface water temperature and methane in Sturgeon Bay (zone 5). All values shown in figure 4-5 (zone 5) are presented here with the exception of measurements made during June 1994. a) Methane concentration versus temperature. With constant wind speeds, and the assumptions implied in equation 4-2, a $10^{\circ} \mathrm{C}$ increase in temperature would result in a 2.7 fold increase in methane flux to the atmosphere. b) Methane flux versus temperature. Based on the observed (1989-1993) average monthly wind speeds at buoy \#45002, methane flux to the atmosphere increased by a factor of 1.8 for a temperature increase of $10^{\circ} \mathrm{C}$.
$J_{\text {sed }}=$ the flux of methane from the sediments, $K=$ the transfer coefficient across the airwater interface. C is a constant of integration. d is the water column depth. and $t$ is time. It follows that at steady state, the last term in equation 4-1 goes to zero and the concentration of surface water methane is approximately equal to $J_{\text {sed }} / K$. The term $J_{\text {sed }} / \mathrm{K}$ is actually equal to the concentration difference between water column methane and water in equilibrium with atmospheric $\mathrm{CH}_{4}$ (i.e. $\Delta \mathrm{C}$ in equation 3-1) but the latter term in this instance is insignificant. If the water temperature rises $10^{\circ}$. not only does the concentration of methane increase by a factor of 2.1 , but the transfer coefficient also increases by a factor of 1.3 since K is in part determined by the molecular diffusion coefficient of methane which increases by a factor of $\sim 1.3$ over $10^{\circ} \mathrm{C}$ (Jähne et al. 1987a). For the system to remain at steady state then, methane flux from the sediment must increase by a factor of $\sim 2.7$. If the inventory of methane in the sediments is to remain constant, then methane production must also increase by a factor of 2.7. This is very close to the $\mathrm{Q}_{10}$ value of 2.8 obtained from the iittoral sediments of Lake Constance. If the $Q_{10}$ for zone 5 is indeed higher. then either the inventory of sediment methane must increase, the ratio of methane production to oxidation must decrease. or direct venting to the atmosphere must occur through ebullition. Since ebullition has never been observed at the surface of Green Bay or during benthic chamber studies, the first scenario seems most plausible.

In reality, average wind speeds over Sturgeon Bay probably varied from month to month. Using the average monthly wind speeds recorded at buoy \#45002 during 1989 to 1993 (see Table 3-1), methane flux estimates from Sturgeon Bay were calculated using
equation 3-1. Flux estimates plotted against the spatially weighted average surface temperatures in Figure 4-6b show methane flux to the atmosphere increased by a factor of only 1.8 for a $10^{\circ} \mathrm{C}$ rise in sediment temperature.

## Riverine Input

Although zone 1 is also shallow with a mean depth of $\sim 2.3$ meters, no correlation between methane and water temperature was observed. In fact. the concentration of methane actually appeared to decrease as temperatures rose (Figure 4-7a). No explanation for this can be offered at this time except that the same patterns were observed in the lower Fox River.

The possibility that fluctuations in methane concentration might simply reflect a dilution rate was explored by obtaining USGS metered flow rates from the lower Fox River into Green Bay (Figure 4-7b). In spite of a substantial range in flushing rates (defined as the number of days required to fill zone 1 based on the flow rate of water from the Fox River measured during the day of the cruise), the concentration of methane in zone 1 was not effected by the flow rate of Fox River (Figure 4-7c).

As mentioned above, the concentration of methane in zone 1 did appear to be correlated with that of the Fox River, but the relationship was weak (Figure 4-7d). However. if the mass (i.e. concentration $x$ flow rate) of methane flowing out of the Fox River was plotted against the concentration of methane in zone 1 , the relationship was striking (Figure 4-8, top). An exponential fit of the data shows the concentration of methane in zone 1 rising to an apparent maximum of $\sim 0.637 \mu \mathrm{M}$. Beyond this point, increases in methane flux from the Fox River are matched by a concomitant flux of methane out of zone 1 to either the atmosphere or zone 2 . At the other end of the

Figure 4-7. The influence of temperature and flow rate on the methane concentrations in Fox River and zone 1. a) Zone 1 methane versus zone 1 temperature. b) The flow rate of water out of Fox River and into zone 1 as determined by the U. S. Geological Survey. Archived data for 1995 were only available to September $30^{\text {th }}$. c) Zone 1 methane versus the flushing rate of zone 1 . Flushing rates were calculated as the time required to fill zone $1\left(\sim 0.146 \mathrm{~km}^{3}\right)$ with water flowing from the Fox River based on the flow rate measured during the day of the cruise. d) The spatially weight averaged concentration of methane measured in zone 1 versus the average concentration of methane measured in the Fox River (approximately 3 km upstream).


Figure 4-8. The discharge of methane from the Fox River. Top) The efflux of methane from the Fox River versus the weight averaged concentration of methane in zone 1 (left axis) and the total mass of methane in zone 1 (right axis). The flux of riverine methane was calculated as the product of the measured concentration and water flow rate. Bottom) A diagram of the other processes affecting the concentration of methane in zone 1.

spectrum, the exponential curve intersects the Y axis at a concentration of $0.085 \mu \mathrm{M}$. This is very close to the average methane concentration of $0.100 \mu \mathrm{M}$ observed in zone 2.

The full significance of the exponential response is not yet understood. As shown in the bottom of Figure 4-8, there are several unknown sources and sinks influencing the mass balance of methane in zone 1 and each of them would influence the concentration of methane in an exponential fashion as well. What is apparent is that the residence time for methane in zone 1 is extremely short. The principle sink must be the atmosphere. Using equation 4-2. it can be shown that based on air-water transport alone, the half-life for methane in the water column is only $\sim 19$ hours for a moderate piston velocity of 2 meters per day and decreases to $\sim 4$ hours for a piston velocity of 9 meters per day (which was the theoretically calculated velocity observed on the 25 October 1994 cruise). If one takes into account the advective and diffusive exchange of methane with zone 2 of Green Bay. the residence time is shortened even further (Mortimer 1978, Modlin and Beeton 1970). The values used to generate Figures 4-7 and 8 are presented in Table 4-1.

## Water column depth and the thermocline

The depth of the water column influences the concentration of surface water methane in both direct and indirect ways. In a direct sense, the water column itself acts like a capacitor. In shallow water. variations in methane supply or removal quickly alter the total amount of methane on an areal basis. As a result. repeated measurements of methane over sufficiently long time scales should show considerable variability. As the water column increases in depth, similar forces acting to add or remove methane from the water column affect the areal mass of methane to a lesser degree. Accordingly, surface water measurements of methane over deep water should appear relatively stable over time.

Table 4-1. Fox River temperature, discharge and methane concentrations as measured during the transect cruises of 1994 and 1995.

## 




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This is shown in Figure 4-3 where the error bars bracketing the mean concentration observed in each of the seven zones decrease with depth.

The exponential decrease in surface water methane with depth in Figure 4-3 is only indirectly related to the water column depth. The situation is complicated by the effects of temperature on the water column and the rate of methanogenesis itself. In Green Bay. surface waters warm and stratify in June. As the stratification intensifies over summer, the density gradient across the thermocline intensifies. This reduces the amount of eddy diffusion between the layers of water and consequently further limits the transfer of heat to deeper waters. The temperature profiles shown in Appendix 4 bear this out. In the summer. sediment temperatures at GB6 were probably close to $25^{\circ} \mathrm{C}$ while further north in 30 meters of water, the sediment temperatures were $\sim 8^{\circ} \mathrm{C}$. If the relationship between sediment temperature and methane production observed in zone 5 hold here, then a $\sim 3$ to 5 fold difference in methane production potential occurs between the two sites based upon temperature alone. The difference in surface water methane is further amplified since methane diffusing up from deep sediments encounters the same density barrier that keeps heat from diffusing downwards. This can result in an increase in methane in the hypolimnion and a temporary disparity between sediment-water. thermocline and air-water methane fluxes. Of course, a variety of other factors are influencing surface water methane concentrations at the same time. Teasing apart the effect of the thermocline on "steady state" conditions and temperature on methane production may not be possible. It is intriguing, however, that the lowest concentrations of surface water methane were observed in June when the thermocline was just getting established at a depth of 3 meters.

## Ice cover

Ice covers Green Bay for 3 to 4 months of each year (Figure 4-9). During that time, gas exchange between the bay and troposphere decreases to an insignificant level. Advective transport between each of the zones and Lake Michigan also declines to the point where the flow of water out of Green Bay matches the rate of riverine input. For Green Bay south of Chambers Island, this translates to an increase the residence time of water from $\sim 8$ months to approximately 3 years (Mortimer 1978. Miller and Saylor 1993). The dominant oscillatory currents during this period are caused by the lunar semidiurnal tide (Gottlieb et al. 1990). Since the major sink for water column methane (i.e. ventilation to the atmosphere) effectively shrinks to zero, methane released from the sediments over this period will tend to accumulate and the concentration of methane should rise. Unfortunately, the rate of methane increase was not measured. However. single time point measurements suggest that the flux of methane from the sediment during winter is low.

In Figure 4-10, the spatially weighted average concentrations of zone 3 methane measured during the last cruise of 1994 (October 25) and the first cruise of 1995 (April 20) are compared with the concentration of methane measured directly under the ice on February $25^{\text {th }} .1997$ at station GB21 (also in zone 3). The arrows accompanying each concentration point indicate the probable trend in methane concentration (they do not represent actual concentrations). Beginning in autumn, as surface temperatures gradually decrease, the water column destabilizes and mixes. Methane that had been accumulating in the hypolimnion over the summer months now mixes throughout the water column, raising the surface water concentration. Since the increase in methane is not supported by an

Figure 4-9. Green Bay ice cover during 1994 and 1995. The date of ice in and ice out for each of the seven surface area zones were determined using ice charts obtained from the NOAA/NAVY Ice Center (see methods section in Chapter 2).


| ZONE | ICE DATA FOR GREEN BAY |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | I | II | III | $\boldsymbol{N}$ | $V$ | $V$ | VII |
| ICEIN 93/94** | 01 JAN | 01 JAN | 01 Jan | 01 JAN | 01 Jan | 01 JAN | 01 Jan |
| ICEOUT 94 | 11 APR | 11 APR | 11APR | 12 APR | 12 APR | 15 APR | 15 APR |
| ICE IN 9495 | 19 DEC | 4 JAN | 4 JAN | 6 Jan | 6 JAN | 18 JAN | 20 JAN |
| ICE OUT 95 | 29 MAR | 6 APR | 6 APR | 6 APR | 6 APR | ${ }^{03}$ APR | 1 M |
| CEIN 95/96 | 6 DEC | 8 DEC | 8 dec | 10 DEC | 10 DEC | 12 DEC | 18 DEC |

*all regions $+90 \%$ covered by 03 Jan

Figure 4-10. The effect of ice cover on methane concentrations in Green Bay. a) The dark gray circles represent the weight averaged concentrations of methane measured in zone 3 on October $25^{\text {th }} .1994$ and April $20^{\text {th }}, 1995$. The gray bar indicates ice cover. The light gray circle represents the concentration of methane measured directly under the ice at station GB21 (in zone 3) on February $25^{\text {th }}$. 1997. All events are plotted against a calendar year beginning on October $25^{\text {th }}$. See text for further explanation. b) The methane concentration versus depth at station GB21 on February $25^{\text {th }} .1997$.

## Zone 3


increase in methanogenesis. concentrations fall off to a new "steady state" where the flux of methane from the sediment approximately equals the flux of methane to the atmosphere. As mentioned above. once ice forms. the concentrations of methane will increase until spring ice melt. Assuming that conditions under the ice are approximately equal on an inter-annual basis. then the concentration of $0.060 \mu \mathrm{M}$ methane measured on February $25^{\text {th }}$ after $\sim 40$ days of ice cover strongly suggested that the net rate of methane production under ice was low.

After the ice breaks up. the same process that occurred in late fall occurs again as methane not supported by the rate of production gets vented to the atmosphere. Estimating the flux of methane to the atmosphere during this period is difficult since measurements of methane under the ice just before spring melt are difficult to obtain. Taking advantage of the slow response time of deep water, it is possible to back calculate a rough estimate of the methane concentration just before ice-out. In 1995. zone 7 was considered ice-free on March $31^{\star x}$. Nineteen days later. the average concentration of methane was measured at $0.031 \mu \mathrm{M}$. Based on an average water column depth of 20.8 meters and an assumed (moderate) piston velocity of 2 meters per day, the half life of methane in the water column was $20.8 / 2 * 0.693$ or $\sim 7.2$ days. If the flux of methane from the sediment was set to zero during this period. then the maximum water column concentration possible at ice-out would have been approximately $0.031 * 2^{26+4}$ or $\sim 0.190$ $\mu \mathrm{M}$. If the flux of methane from the sediment is considered, the maximum concentration drops considerably. Taking the difference between the maximum concentration at ice out and the observed concentration on March $31^{s}$ and multiplying by the volume of water in southern Green Bay gave an upper flux estimate of $\sim 0.16 \mu \mathrm{M} * 22.5 \mathrm{~km}^{3}$ or $\sim 0.4 \times 10^{7}$
moles $\mathrm{CH}_{4}$ over the 19 day period. This would only amount to $\sim 3 \%$ of the expected annual flux of methane across the air-water interface based on the sediment-water flux estimates of Klump and Fitzgerald (1998). Therefore, in terms of an annual estimate of methane flux across the air-water interface, the possible error associated with missing a major flux event just after ice-out is small.

## Atmospheric Exchange

Daily estimates of methane flux across the air-water interface in each of the seven zones of southern Green Bay were calculated using equation 3-1. where $K=$ the transfer coefficients derived in Chapter 3 (Figure 3-7), and $\Delta C=C_{w}-C_{3}$, where $C_{w}=$ the dissolved methane concentrations of the mixed layer (epilimnion) and $\mathrm{C}_{\mathrm{a}}=$ the concentration of methane in the surface water micro-layer which was assumed to be in equilibrium with atmospheric methane. The concentration of methane in the air over Green Bay was measured throughout the study and interpolated over a year to give a mean mole fraction of 1.96 ppm (Figure 4-11). The partial pressure of methane was taken as the product of the mole fraction and the average atmospheric pressure ( 992 hPa ) to give $1.92 \mu \mathrm{~atm}$. The molarity of methane in equilibrium with atmospheric methane $\left(\mathrm{C}_{a}\right)$ was calculated as the product of the partial pressure of methane and its solubility coefficient (see equations 2-1 and 2-2) which was calculated using the surface temperatures derived in Chapter 3 (Figure 3-5). Daily estimates of $C_{w}$ in each of the 7 zones of southern Green Bay were based on linear interpolations between the spatially averaged concentrations measured during each of the transect cruises shown in Figure 4-5. The concentrations of methane just prior to and after ice cover were taken as the mean of the last and first concentrations measured during 1994 and 1995 respectively.

Figure 4-11. Atmospheric methane mole fractions measured over Green Bay during 1993 , 1994. and 1995. The mean concentration for the samples shown ( $\mathrm{n}=59$ ) is 2.05 ppm . Interpolation over the entire year gave an average concentration of 1.96 ppm .

## atmospheric methane



The net flux of methane from Green Bay to the atmosphere is shown together with daily flux estimates in Figure 4-12a (1994) and 4-12b (1995). Average daily flux estimates from Green Bay to the atmosphere are given for each year. month and zone in Table 4-2. The annual flux of methane from each zone is given in Figure 4-13. Flux estimates from the first few days of January 1995 (before the onset of ice cover). were included in the 1994 flux estimate. Based on the air column stability-corrected $\mathrm{U} / \mathrm{K}$ relationships of Broecker et al. (1978). $\sim 13 \times 10^{7}$ moles of methane were vented to the atmosphere from southern Green Bay in 1994. In 1995. the value increased to $\sim 16 \times 10^{7}$ moles.

## Inter-annual variability

The flux of methane to the atmosphere varied considerably on both an intra- and inter-annual basis. While much of the variability due to seasonality was understandable. the differences observed between 1994 and 1995 were intriguing. In zones 2 and 3 for instance, methane flux to the atmosphere increased ~50\% from 1994 to 1995 .

An intriguing explanation for this may have to due with the dramatic difference in wind directions that occurred in 1994 and 1995. Hourly wind velocities recorded at buoy \#45002 were broken down into their $u$ (east) and $v$ (north) component vectors and summed. The results are shown in Figure 4-14a. The vectors both begin at the origin on April $1^{x}$ and run in the direction that the wind came from. The first of each month is indicated with a circle, the numeral above each circle indicates the month. In 1994. the wind blew fairly consistently from the southwest, straight up the major axis of the bay. In 1995 however. the wind tended to come from the southeast and blow across the minor axis of the bay. Only during September and October of 1995 did the average direction veer southwest.

Figure 4-12. Methane flux from Green Bay to the atmosphere based on air column stability-corrected wind speeds from buoy \#45002, the U/K relationship of Broecker et al. (1978) and air-water methane concentration gradients derived in this chapter. a) 1994 flux estimates for Green Bay zones 1-7. b) 1995 flux estimates for Green Bay zones 1-7. Gray lines show daily flux estimates. Black lines show the accumulative flux over time.


1905 methane fix
Groen Bay zone 1


1905 methane flux
Gruen Bry zone 2
5


1995 mathane frux
Green Bay zonse 3


## 995 methatie fux

 Grven Bay zone 6
## 935 methane flux

 roen Bay zone 5


995 methane flux
Grem Byy zone?

b

Table 4-2. Average daily methane flux estimates from Green Bay to the atmosphere. Values are given for each year, month and zone. Asterisks denote months when ice covered a particular zone for the entire month. Values given for January, March. April and December reflect the average flux for ice free periods. See Figure 4-9 for specific ice cover dates.

Green Bay<br>methane efflux to atmosphere<br>$\mathrm{mmol} \mathrm{m}^{-2}$ day $^{-1}$

| ZONE | 21 | 22 | 23 | 24 | 25 | 26 | 27 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1994 |  |  |  |  |  |  |  |
| 1 | - | - | - | - |  |  |  |
| 2 | * | - | - | - |  |  |  |
| 3 | - | - | - | - | - | - |  |
| 4 | 2.02 | 0.18 | 0.14 | 0.21 | 0.33 | 0.15 | 0.06 |
| 5 | 1.51 | 0.06 | 0.05 | 0.07 | 0.17 | 0.04 | 0.02 |
| 6 | 1.53 | 0.14 | 0.05 | 0.06 | 0.31 | 0.05 | 0.04 |
| 7 | 1.99 | 0.42 | 0.15 | 0.16 | 1.06 | 0.18 | 0.13 |
| 8 | 1.27 | 0.58 | 0.24 | 0.30 | 1.92 | 0.23 | 0.17 |
| 9 | 1.43 | 0.60 | 0.25 | 0.19 | 1.08 | 0.14 | 0.11 |
| 10 | 3.49 | 0.46 | 0.37 | 0.50 | 0.95 | 0.32 | 0.13 |
| 11 | 3.18 | 0.29 | 0.30 | 0.47 | 0.62 | 0.31 | 0.11 |
| 12 | 3.09 | 0.31 | 0.27 | 0.42 | 0.56 | 0.28 | 0.11 |
| 1995 |  |  |  |  |  |  |  |
| 1 | - | 0.39 | 0.30 | 0.44 | 0.63 | 0.30 | 0.13 |
| 2 | - |  |  |  |  |  | 0.0 |
| 3 | 1.79 | * | - | - | - | 0 | 0.04 |
| 4 | 1.94 | 0.24 | 0.15 | 0.20 | 0.34 | 0.16 | 0.08 |
| 5 | 1.29 | 0.12 | 0.08 | 0.09 | 0.40 | 0.07 | 0.05 |
| 6 | 0.95 | 0.09 | 0.06 | 0.07 | 0.55 | 0.07 | 0.05 |
| 7 | 0.94 | 0.18 | 0.09 | 0.11 | 1.23 | 0.11 | 0.07 |
| 8 | 2.65 | 0.98 | 0.49 | 0.32 | 2.50 | 0.18 | 0.10 |
| 9 | 4.13 | 1.33 | 0.71 | 0.52 | 274 | 0.29 | 0.15 |
| 10 | 4.39 | 0.98 | 0.61 | 0.72 | 1.60 | 0.38 | 0.18 |
| 11 | 3.73 | 0.60 | 0.41 | 0.80 | 0.83 | 0.34 | 0.15 |
| 12 | 2.94 | 0.34 | 0.25 | 0.42 | 0.53 | 0.26 | 0.11 |

*ice

Figure 4-13. Methane flux sums from southern Green Bay (zones 1-7) to the atmosphere in 1994 and 1995. Top left) Annual methane flux per square meter of zones 1-7. Top right) Annual methane flux per zone. Bottom) Tabulated methane flux sums from southern Green Bay to the atmosphere.

## Green Bay methane flux

 mmol $\mathrm{m}^{-2}$ year $^{-1}$
Green Bay methane flux moles zone ${ }^{-1}$ year $^{-1}$


| $20 n e$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ares (m2) | $6.4 E+07$ | $2.3 E+08$ | $3 E+08$ | $3.8 E+08$ | $1.4 E+07$ | $2.7 E+08$ | $3.8 E+08$ |

1994

| sum mmol/m2 | 539 | 93 | 55 | 73 | 215 | 55 | 29 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| molesi2one | $3.4 E+07$ | $2.1 E+07$ | $1.6 E+07$ | $2.8 E+07$ | 3074572 | $1.5 E+07$ | $1.1 E+07$ |

TOTAL
moles $\mathrm{CH} \quad 1.3 E+08$
1995

| sum mmolm2 | 633 | 139 | 80 | 89 | 315 | 51 | 27 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| moles/zone | $4.0 E+07$ | $3.2 E+07$ | $2.4 E+07$ | $3.4 E+07$ | $4.5 E+06$ | $1.4 E+07$ | $1.0 E+07$ |
| TOTAL |  |  |  |  |  |  |  |
| moles CH4 | $1.6 E+08$ |  |  |  |  |  |  |

Figure 4-14. Inter-annual variability in wind direction and water column temperatures. a) Wind vectors for 1994 (gray circles) and 1995 (open circles) based on hourly wind velocities measured at buoy \# 45002. The vectors begin at the origin on April $1^{s}$ and run toward the direction the wind is coming from till October $31^{»}$. b) Temperature profiles showing intrusion of cold Lake Michigan water into the hypolimnion of Green Bay at station GB43 (zone 6) and station GB17 (zone 3).

a

b

Because of the morphology and hydrodynamic properties of the bay. the circulation patterns must have been different in 1994 and 1995. In Green Bay, wind induced water currents tend to travel $0-40^{\circ}$ to the right of the prevailing wind direction due to the Coriolis force (Mortimer 1978). The degree of deflection between surface winds and the net direction of water influenced by surface wind (i.e. the Ekman layer) depends primarily on water depth and wind speed. For a wind speed of $5 \mathrm{~m} / \mathrm{s}$, the theoretical depth of the Ekman layer is approximately 30 meters (Pond and Pickard 1978). If the water column is shallow enough, the currents generated by surface winds encounter the bottom sediments. When this happens, friction with the bottom overcomes the Coriolis force and the water mass appears to deflect to the left (when viewed relative to the surface current). The net direction of the movement of the water mass then falls closer to the direction of wind. When the water column depth decreases to approximately $10 \%$ of the Ekman layer depth. the net direction of water flow is essentially equal to that of surface winds (Pond and Pickard 1978). As wind speeds increase, the depth of the Ekman layer increases and hence, the probability that friction with the bottom will cause a decrease in the net deflection between wind and water currents. As water begins to move in response to the friction caused by wind. conservation of mass dictates that an equal mass of water replaces that which was moved. For a southerly wind over Green Bay, water will tend to move northeastward along the major axis of the bay. If the surface behaves as one sheet, then bottom water must replace the mass of water displaced to the north. This sets up a "conveyor belt" of water motion that has been observed in many estuarine environments including Green Bay (Miller and Saylor 1993). The description is oversimplified, but it suffices for the following argument.

Specifically, the northeastward flow of surface water in 1994 probably exceeded that of 1995 , resulting in a greater upwelling of hypolimnetic water in the southern bay and intrusion of bottom water from the north. The temperature profiles in Figure 4-14b confirm this. In August of 1994, bottom water temperatures at station GB43 were actually colder than those measured in June. This could only have occurred through an intrusion of cold Lake Michigan water. The temperature profiles at station GB17 show this to an even greater extent. A concomitant decrease in surface sediment temperature would have dramatically reduced the rate of methane production based on the temperature/methane flux relationship observed in zone 5 (Figure 4-6).

The effect of temperature on the observed differences in methane flux can be modeled. in part. for the month of August in zone 3 (Figure 4-15a). The average wind direction in August 1995 was perpendicular to that of 1994 (Figure 4-15b). Average wind speeds differed by only $0.5 \mathrm{~m} / \mathrm{sec}(1994.5 .9 \mathrm{~m} / \mathrm{sec}$ : $1995.5 .4 \mathrm{~m} / \mathrm{sec}$ ) and yet the average flux of methane doubled from $0.24 \mathrm{mmol} \mathrm{m}^{-2}$ day $^{-1}$ in 1994 to $0.49 \mathrm{mmol} \mathrm{m}^{-2}$ day $^{-1}$ in 1995 (Table 4-2). Temperature profiles of the water column at GB 17 showed that while surface temperatures differed by only $\sim 2^{\circ} \mathrm{C}$, bottom water and (presumably) surface sediment temperatures were $\sim 12{ }^{\circ} \mathrm{C}$ warmer in 1995 (Figure $4-15 \mathrm{c}$ ). Based on the slope of the methane flux/temperature correlation shown in Figure 4-6b, the flux of methane to the atmosphere should have increased by a factor of $e^{(0.06 \cdot 12)}$ or 2.05 in 1995. This closely agrees with the observed factor of 2.04 (Figure $4-15 \mathrm{~d}$ ). Thus, it stands to reason that a significant fraction of the observed inter-annual difference in methane flux to the atmosphere can be explained by differences in sediment temperature that occurred during the two field seasons.

Figure 4-15. August wind directions and the inter-annual variability of surface water methane in zone 3. a) Location of station GB 17 in zone 3. b) Wind vectors for August 1994 (gray circles) and 1995 (open circles) based on hourly wind velocities measured at buoy \# 45002 . The vectors begin at the origin on August $1^{\text {st }}$ and run toward the direction the wind is coming from till August $31^{\star}$. c) Temperature profiles showing intrusion of cold Lake Michigan water into the hypolimnion of zone 3 in August of 1994 and the absence of an intrusion in August of 1995. d) Calculation of expected increase in methane flux based on a $12^{\circ} \mathrm{C}$ temperature increase and the temperature / methane flux correlation observed in zone 5 .
zone 3

a

GB17 :emp (C)

c

## wind vector



| august average |  | 1994 | 1995 |
| :--- | :---: | :---: | :---: |
| CH4 flux | mroum2 dey | 0.24 | 0.49 |
| wind speed | masec | 5.9 | 5.4 |
| surface temp | $c$ | 21 | 23 |


| CH4 fiux increase | formula | flux ratio |
| :---: | :---: | :---: |
| observed | $0.49 / 0.24$ | 2.04 |
| predicted | $\exp (0.06 * 12)$ | 2.05 |

## Southern Green Bay Methane Budget

Klump and Fitzgerald (1998) have estimated that approximately $14 \times 10^{7}$ moles of $\mathrm{CH}_{4}$ flux from the sediments to the water column in southern Green Bay each year (Figure 4-16). The Fox River contributes an additional $0.8 \times 10^{7}$ moles of $\mathrm{CH}_{4}$ based on an average surface water ( $\sim 2 \mathrm{~m}$ ) concentration of $\sim 2 \mu \mathrm{MCH}_{4}$ and the total Fox River flow measured during $1994\left(4 \times 10^{9} \mathrm{~m}^{3}\right)$. Methane contributions from other rivers entering southern Green Bay were ignored based on the rapid attenuation in methane concentrations observed on July $14^{\text {th }} .1994$ when the sampling transect ran into and out of the mouth of the Menominee River (see Figure 4-2). The net advective flux of methane to northern Green Bay (past Chambers Island) was estimated to be less than $\pm 0.1 \times 10^{7}$ moles per year. A maximum positive flux was calculated by assuming the entire water mass of southern Green Bay exchanged with water from the northern end of the bay in 0.8 years. If the methane concentration in northern Green Bay was taken as 0. then the average surface water methane concentration of 30 nM in zone 7 multiplied by the volume of southern Green Bay ( $22.5 \mathrm{~km}^{3}$ ) times the annual exchange rate (1.25) gave a positive flux of $0.084 \times 10^{7}$ moles $\mathrm{CH}_{4}$ per year. In reality, there was probably a small influx of methane from the northern portion of the bay. The maximum vertical gradient in methane concentration at station GB67 was assumed to occur at the end of summer. On September 14 ${ }^{\text {th }}$. 1994. the hypolimnetic methane concentration was only $\sim 10 \mathrm{nM}$ greater than that of surface waters. Taking the product of the concentration difference and flushing volume gave an influx of $0.028 \times 10^{7}$ moles $\mathrm{CH}_{4}$ to southern Green Bay. In either case, the fluxes were insignificant in terms of the overall methane budget.

Figure 4-16. Methane budget for southern Green Bay (zones 1-7).




Using the mass balance approach (equation 4-1). the expected annual flux of methane across the air-water interface was equal to $J_{s w}+I-E$ or

$$
(14+0.8 \pm 0.1) \times 10^{7} \cong 14.8 \times 10^{7} \text { moles } \mathrm{CH}_{4}
$$

Estimates of methane flux to the atmosphere based on Fick's first law (equation 31) ranged from an average of $\sim 14.5 \times 10^{7}$ moles per year to $\sim 1.5 \times 10^{7}$ moles per year depending on the choice of transfer coefficients (see Figure 3-9). The highest fluxes of methane ( $\sim 14.5 \times 10^{7}$ moles $\mathrm{CH}_{4}$ year ${ }^{-1}$ ) were generated using the air column stabilitycorrected transfer coefficients of Broecker et al. (1978) (Figure 4-17). If a neutral drag coefficient of $1.3 \times 10^{-3}$ was used throughout the year to estimate the wind speed at 0.6 m from data recorded at 5 m (i.e. the $\mathrm{U}_{0.6}: \mathrm{U}_{50}$ factor). estimates of the annual flux of methane from Green Bay were reduced by $\sim 25 \%$ to $\sim 11 \times 10^{7}$ moles. Using the Liss and Merlivat (1986) relationship to calculate the transfer coefficient (K) resulted in a flux estimate reduction of $\sim 67 \%$ to $\sim 5 \times 10^{7}$ moles $\mathrm{CH}_{4}$. For a constant K value of 50 cm day ${ }^{-}$ ${ }^{1}$ (Cole et al. 1994), methane flux estimates decreased $\sim 90 \%$ to $\sim 1.5 \times 10^{7}$ moles $\mathrm{CH}_{4}$.

Correspondingly, the amount of (water column) methane oxidation required to balance the methane budget ranged from $\sim 0$ to $90 \%$ of the methane flux from the sediments. In light of the fact that significant methane oxidation has not been observed in oxygenated water columns (Lidstrom and Somers 1984. Heyer and Babenzien 1985. Kuivila 1988, Schmidt and Conrad 1993. Scranton et al. 1993, Thebrath et al. 1993), flux estimates based on shear corrected wind speeds and the $\mathrm{U} / \mathrm{K}$ relationship of Broecker et al. (1978) seemed most appropriate.

Figure 4-17. Total flux of methane from southern Green Bay (zones 1-7) and its dependence on the wind speed / transfer coefficient relationship. "Broecker" refers to the $\mathrm{U} / \mathrm{K}$ relationship determined by Broecker et al. (1978) where the wind speed ( U ) is corrected for the air-water temperature gradient and its affect on shear in the air column. "Neutral CD" refers to Broecker"s U/K relationship assuming a constant drag coefficient of $1.3 \times 10^{-3}$. "Liss and Merlivat" refers to the $\mathrm{U} / \mathrm{K}$ relationship given by Liss and Merlivat (1986). "Cole" refers to a constant K value of 50 cm day $^{-1}$ (Cole et al. 1994).

# Green Bay methane flux 

 versus K estimate

## $K$ estimate

Using similar values of $\mathrm{U}_{06}$. the Broecker et al. (1978) transfer coefficients resulted in methane flux estimates which were 2.2 times higher than those of Liss and Merlivat (1986). A recent study by Keeling et al. (1998) corroborates this finding. Based on seasonal variations in the ratio of atmospheric oxygen to nitrogen in the northern hemisphere, the Liss and Merlivat (1986) relationship underestimated the rate of air-water gas exchange required to support the observed atmospheric cycles by a factor of 2.47 . The implications of these finding are significant because the $U / K$ relationship of Liss and Merlivat (1986) has been used extensively over the past decade to estimate air-water gas transfer (Wanninkhof 1992).

The accumulative error associated with my methane flux estimates is probably less than $\pm 20 \%$. Annual flux estimates for 1994 and 1995 agreed to within $20 \%$ in spite of the fact that surface water methane concentrations were measured over different dates and transect routes. In addition, much of inter-annual discrepancy was shown to be due to differences in wind direction which resulted in warmer sediment temperatures and a higher methane production rate in 1995.

The average air-water flux of methane ( $14.5 \times 10^{7}$ moles year ${ }^{-1}$ ) calculated from Fick's first law (equation 3-1) agreed to within $2 \%$ of the mass balance calculation (equation 4-1). However, the strength of this correlation rests on the assumption that methane oxidation in the water column of Green Bay is negligible. This needs to be confirmed directly.

Conclusions
The methane data presented here represent one of the larger surveys of methane ever undertaken and the first to incorporate the use of a disk equilibrator. The equilibrator
showed a considerable lag in equilibrating with in situ methane concentrations with an efolding time of $\sim 14$ minutes. but this could be corrected for if the flow rate of water passing through the equilibrator and volume of air in the equilibrator headspace was known.

Surface water methane concentrations varied considerably over both temporal and spatial scales. The lowest concentrations of methane generally occurred in deep water near Chambers Island and did not differ significantly from water in equilibrium with atmospheric methane ( $\sim 3 \mathrm{nM}$ ). The highest concentration of methane was measured in the Fox River $(4.86 \mu \mathrm{M})$. In order to isolate specific factors that might have had an influence on surface water methane concentrations, the $1635 \mathrm{~km}^{2}$ study site was divided into seven zones ranging in size from 14 to $380 \mathrm{~km}^{2}$. When the methane values measured during each cruise were spatially weight averaged over the seven zones, several striking patterns emerged. In the area south of Long Tail Point (defined as zone 1), methane concentrations were closely linked to the outflow of methane from the Fox River. In Sturgeon Bay (zone 5). methane correlated strongly with temperature. Concentrations doubled for every $10^{\circ} \mathrm{C}$ increase in temperature. Using average monthly wind speeds. methane flux to the atmosphere increased by a factor of 1.8 for every $10^{\circ} \mathrm{C}$ increase in temperature.

Estimates of methane flux from southern Green Bay to the atmosphere based on air-water concentration gradients, shear corrected wind speeds and the $\mathrm{U} / \mathrm{K}$ relationship of Broecker et al. (1978) resulted in annual fluxes of $13 \times 10^{7}$ moles $\mathrm{CH}_{4} \mathrm{yr}^{-1}$ in 1994 and $16 \times 10^{7}$ moles $\mathrm{CH}_{4} \mathrm{yr}^{-1}$ in 1995. Inter-annual differences in methane flux were shown to
be largely due to dramatic differences in wind direction-which altered the hydrodynamics of the bay and ultimately, sediment temperatures.

The two-year average annual flux of methane to the atmosphere agreed to within 2\% of the estimate of methane influx from sediments and rivers to southern Green Bay ( $14.8 \times 10^{7}$ moles $\mathrm{CH}_{4} \mathrm{yr}^{-1}$ : Klump and Fitzgerald (1998) and this study). The implied support for the $\mathrm{U} / \mathrm{K}$ relationship of Broecker et al. (1978) suggests that the kinetics of air-water gas exchange are 2.2 times higher than that predicted by the frequently used U / K relationship of Liss and Merlivat (1986).

## Chapter 5

## The Dynamics of Surface Water Carbon Dioxide in Green Bay

## Introduction

Carbon is arguably the keystone element in an ecosystem and an understanding of the carbon cycle is essential to understanding how an ecosystem functions. However, the chemistry of both organic and inorganic carbon is complex and the flux of carbon within and between biological and non-biological compartments can be rapid.

The situation is somewhat simplified as $\mathrm{CO}_{2}$ is often the primary medium of exchange. In aquatic environments, photosynthetic autotrophs take up $\mathrm{CO}_{2}$ during the day (and respire it at night) while heterotrophic organisms consume organic carbon and respire $\mathrm{CO}_{2}$. Dead organisms fall to the sediment where the organic carbon is either buried permanently or respired to (predominantly) $\mathrm{CO}_{2}$.

If the rate of photosynthesis $(P)$ differs from respiration $(R)$, then the concentration of $\mathrm{CO}_{2}$ either increases (for $\mathrm{P} / \mathrm{R}<1$ ) or decreases (for $\mathrm{P} / \mathrm{R}>1$ ). However. physical processes simultaneously drive the $\mathrm{CO}_{2}$ concentration back to thermodynamic equilibrium-either through air-water gas exchange or carbonate precipitation or dissolution. Therefore, the concentration of $\mathrm{CO}_{2}$ at any given time gives an integrated history of the kinetics of individual processes affecting the $\mathrm{CO}_{2}$ concentration. If the dynamics of $\mathrm{CO}_{2}$ are measured across various temporal and spatial scales. then one can begin to understand which processes play an important role in the carbon cycle.

This study was conducted in part to determine whether or not southern Green Bay acts as a net sink or source for atmospheric $\mathrm{CO}_{2}$. A net import of $\mathrm{CO}_{2}$ to Green Bay would imply a $\mathrm{P} / \mathrm{R}$ ratio of greater than one and a system dominated by autotrophic
organisms. If Green Bay was a closed system-without external imputs-autotrophy should dominate just as it does on Earth as a whole (in the sense that some organic carbon is buried). However. the influx and subsequent respiration of allochthonous organic carbon could shift the apparent $\mathrm{P} / \mathrm{R}$ ratio to values less than one.

A recent survey by Cole et al. (1994) found that an overwhelming majority (87\%) of 1835 lakes were supersaturated with $\mathrm{CO}_{2}$ with respect to the atmosphere. This suggests that inputs of terrestrially derived organic carbon play a substantial and dominant role in the apparent balance between heterotrophy and autotrophy in lakes in general (del Giorgio and Peters 1993, del Giorgio et al. 1997). Whether or not this is true in Green Bay can be determined by measuring the concentration gradient of $\mathrm{CO}_{2}$ across the air-water interface over time. Using Fick's first law (equation 3-1), the flux of $\mathrm{CO}_{2}$ from Green Bay to the atmosphere ( $\mathrm{J}_{\mathrm{aw}}$ ) can then be determined as the product of the air-water $\mathrm{CO}_{2}$ gradient and the transfer coefficients that were derived in Chapter 3.

Reasonable estimates of the $\mathrm{P} / \mathrm{R}$ ratio can also be calculated using published estimates of areal primary productivity (i.e. P) in Green Bay (Sager and Richman 1990. 1991). Temporarily ignoring the effects of carbonate precipitation and advective (nonatmospheric) $\mathrm{CO}_{2}$ exchange, the ratio of photosynthesis to respiration can be taken as

$$
\begin{equation*}
\mathrm{P} / \mathrm{R} \cong \mathrm{P} /\left(\mathrm{P}+\mathrm{J}_{\mathrm{aw}}\right), \tag{5-1}
\end{equation*}
$$

where all terms are expressed in units of moles C area ${ }^{-1}$ time ${ }^{-1}$ and a positive flux of $\mathrm{CO}_{2}$ across the air-water interface ( $\mathrm{J}_{\mathrm{aw}}$ ) translates to a net loss of $\mathrm{CO}_{2}$ from the bay to the atmosphere.

Measured rates of primary production span an order of magnitude on a volumetric basis from the hypereutrophic Fox River to the meso-oligotrophic conditions found north of Chambers Island (Sager and Richman 1991). By calculating the $\mathrm{P} / \mathrm{R}$ ratio in each of the seven zones along this trophic gradient (see Figure 2-11). Green Bay should serve as an excellent model for the effect of terrestrial loading on aquatic systems and the relationship between autotrophy and heterotrophy in coastal systems.

## The carbon dioxide system in Green Bay

While a comprehensive description of the carbon dioxide system is beyond the scope of this study (see Butler 1982 and Skirrow 1975). a brief description of some of the terms that will be used are in order. To begin. carbon dioxide differs from most gases in that when it dissolves in water, it hydrates and ionizes to carbonic acid. bicarbonate and carbonate according to the following reactions:

$$
\begin{align*}
& \mathrm{CO}_{2}(\mathrm{~g})=\mathrm{CO}_{2}(\mathrm{aq})  \tag{5-2}\\
& \mathrm{CO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}=\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})  \tag{5-3}\\
& \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})=\mathrm{H}^{-}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})  \tag{5-4}\\
& \mathrm{HCO}_{3}^{-}(\mathrm{aq})=\mathrm{H}^{-}(\mathrm{aq})+\mathrm{CO}_{3}^{--}(\mathrm{aq}) . \tag{5-5}
\end{align*}
$$

Since the concentration of carbonic acid at equilibrium is only $\sim 10^{-3}$ times that of $\left[\mathrm{CO}_{2}\right]$. the two uncharged species are generally combined. In this study. the two species will simply be referred to as $\left[\mathrm{CO}_{2}\right]$.

Using "hybrid" notation (Butler 1982), the concentrations of the various species can be described as:

$$
\begin{equation*}
\mathrm{K}_{\mathrm{n}}=\left[\mathrm{CO}_{2}\right] / f\left(\mathrm{CO}_{2}\right) \tag{5-6}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{K}_{1}=10^{-\mathrm{pH}}\left[\mathrm{HCO}_{3}^{-}\right] /\left[\mathrm{CO}_{2}\right] \tag{5-7}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{K}_{2}=10^{-\mathrm{pH}}\left[\mathrm{CO}_{3}^{2-}\right] /\left[\mathrm{HCO}_{3}\right] \tag{5-8}
\end{equation*}
$$

where the fugacity of $\mathrm{CO}_{2}$ is in atmospheres. the concentrations are expressed on the molality scale, the activity of the hydrogen ion is expressed on the NBS scale (where $\left\{\mathrm{H}^{-}\right\}$ $=\left[\mathrm{H}^{+}\right]$at $\gamma^{+}=1$ ) and the activity coefficients for each of the carbon dioxide species (i.e $\gamma$ o. $\gamma$ - and $\gamma--)$ are included in the equilibrium constant. Total $\mathrm{CO}_{2}\left(\Sigma \mathrm{CO}_{2}\right.$ or $\left.\mathrm{C}_{\mathrm{T}}\right)$ is defined as the sum concentration of $\left[\mathrm{CO}_{2}\right]+\left[\mathrm{HCO}_{3}{ }^{-}\right]+\left[\mathrm{CO}_{3}{ }^{-2}\right]$. Carbonate alkalinity $\left(\mathrm{A}_{\mathrm{C}}\right)$ is defined as $\left[\mathrm{HCO}_{3}{ }^{-}\right]+2\left[\mathrm{CO}_{3}{ }^{2-}\right]+\left[\mathrm{OH}^{-}\right]-\left[\mathrm{H}^{+}\right]$and, in fresh waters like Green Bay, accounts for approximately $99.7 \%$ of the total alkalinity ( $\mathrm{A}_{T}$ ). Skirrow (1975) gives another definition of carbonate alkalinity $\left(\mathrm{C}_{\mathrm{A}}\right)$ as $\left[\mathrm{HCO}_{3}{ }^{-}\right]+2\left[\mathrm{CO}_{3}{ }^{-{ }^{-}}\right]$. At pH values found in Green Bay, $\mathrm{C}_{\mathrm{A}} \cong 99.8 \%$ of $\mathrm{A}_{\mathrm{C}}$. If any two of the four $\mathrm{CO}_{2}$ parameters (i.e. $\mathrm{pH}, f \mathrm{CO}_{2}$.
$\Sigma \mathrm{CO}_{2}$, and $\mathrm{A}_{\mathrm{C}}$ ) are known along with the appropriate equilibrium constants $\left(\mathrm{K}_{0}, \mathrm{~K}_{1}\right.$, and $\mathrm{K}_{2}$ ), then the other two parameters can be calculated using the equations given above.

The value of $\mathrm{K}_{0}$ is given in Chapter 2 (equation 2-14) and is considered accurate since yo is fairly immune to the ionic strength of the medium (Butler 1982). This is not the case for $K_{1}$ and $K_{2}$ and a rigorous determination of these equilibrium constants has yet to be made in Green Bay. Weiler (1975) found that the Lyman`s (1956) equilibrium constants at zero ionic strength gave the best fit between calculated and measured $p \mathrm{CO}_{2}$ in Lake Erie and Lake Ontario. The correlation deteriorated when an attempt was made to correct for ionic strength. The reasons for this were not elaborated on. However, based on a very limited data set, the same conclusions were reached in Green Bay during this study. $\Sigma \mathrm{CO}_{2}$. pH and $f \mathrm{CO}_{2}$ were measured while underway on a transect from the Fox River to Sturgeon Bay on August $29^{\text {th }}$, 1995. Lyman's constants at zero ionic strength as given in Skirrow (1975) were fit to $2^{\text {nd }}$-order polynomial equations to give

$$
\begin{equation*}
\mathrm{pK}_{1}=6.58083-0.01288 \mathrm{t}+0.00015 \mathrm{t}^{2} \tag{5-9}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{pK}_{2}=10.6192-0.01402 \mathrm{t}+0.00010 \mathrm{t}^{2} \tag{5-10}
\end{equation*}
$$

where $\mathrm{t}=$ temperature in ${ }^{\circ} \mathrm{C}$, then used to calculate $\Sigma \mathrm{CO}_{2}$ using pH and $f \mathrm{CO}_{2}$ (Figure 5-1. solid black line). The fit with measured $\Sigma \mathrm{CO}_{2}$ (Figure 5-1, gray circles) was reasonable

Figure 5-1. The calculated versus measured $\mathrm{\Sigma CO}_{2}$ concentration along a transect from Fox River ( 0 km ) to Sturgeon Bay ( 110 km ). The calculated $\Sigma \mathrm{CO}_{2}$ values were determined from $\mathrm{pH}, f \mathrm{CO}_{2}$ and the equilibrium constants of Lyman (1956) at zero ionic strength (solid black line) and the calculated ionic strength ( 0.0047 M , dotted black line). The gray lines represent calculated $\Sigma \mathrm{CO}_{2}$ concentrations at $\pm 0.02 \mathrm{pH}$ units from the measured pH .

## Green Bay DIC 29 August 1995


__ calculated DIC $(I=0)$
$+1-0.02 \mathrm{pH}$ units $(I=0)$
$\cdots . . . . . .$. calaculated DIC $(I=0.0047)$
O measured DIC
considering the spatial heterogeneity of the system and the accuracy of the $\mathrm{pH}(\sim \pm 0.02$ pH units, gray lines) and $\Sigma \mathrm{CO}_{2}(\sim \pm 5 \%, 0.1 \mathrm{ml}$ sample size) measurements. If the equilibrium constants were corrected for the average calculated ionic strength of 0.0047 M (Table 5-1), the calculated $\Sigma \mathrm{CO}_{2}$ (Figure 5-1, dotted line) appeared to be $\sim 10 \%$ high.

The average $\gamma$-calculated for an ionic strength of 0.0047 M was $\sim 0.93$ (Davies equation). An estimate of the activity coefficient for the hydrogen ion $\left(\gamma^{+}\right)$was calculated from Gran titration alkalinity plots (Figure 5-2) that were generated from samples obtained at the Fox River, GB 17. and GB 32. Where

$$
\begin{equation*}
\gamma^{+}=(\mathrm{d} f 1 / \mathrm{dV}) \times(\mathrm{Va} / \mathrm{Ca}), \quad \text { (Butler 1982) } \tag{5-11}
\end{equation*}
$$

and

$$
\begin{equation*}
f 1=[(\mathrm{V}+\mathrm{Va}) / \mathrm{Va}] \times 10^{-\mathrm{pH}} \tag{5-12}
\end{equation*}
$$

$\mathrm{V}=$ volume of the sample, $\mathrm{Va}=$ the volume of the titrant $(\mathrm{HCl}), \mathrm{Ca}=$ the concentration of the titrant, and $\gamma^{+} \cong 0.96$ (Fox River), 0.98 (GB 17), and 0.99 (GB 32). Assuming $\gamma$ - $\cong$ $\gamma+$, it would appear that the activity coefficients calculated using the Davies equation are somewhat lower than they should be. The discrepancies are consistent with what would

Table 5-1. Approximate charge balance, ionic strength. and activity coefficients for southern Green Bay based on average chemical concentrations given in Torrey (1976).

## CHARGE BALANCE

| cation |  |  |  | anion |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | mgrL | mmoll | postive charge |  | $m g 2$ | mmoll | negative charge |
| C. | 35.000 | 0.875 | 1.750 | HCOS |  | 2.150 | 2.150 |
| Mg | 12.000 | 0.494 | 0.988 | C | 12.000 | 0.339 | 0.339 |
| No | 5.000 | 0.217 | 0.217 | 504 | 20.000 | 0.208 | 0.417 |
| $\boldsymbol{K}$ | 1.000 | 0.026 | 0.026 | $\mathrm{CO3}$ |  | 0.040 | 0.080 |
| BORON | 0.100 | 0.009 | 0.028 | NO3 | 0.200 | 0.014 | 0.014 |
|  |  |  |  | PO4 | 0.050 | 0.002 | 0.005 |
|  | $\Sigma$ | 1.621 | 3.008 |  | $\Sigma$ | 2.753 | 3.004 |
| IONIC STRENGTH <br> $1=0.5$ sum(Ciz^2i) |  |  |  |  |  |  |  |
|  | conc | charge | $\mathrm{C}^{*} \mathrm{z}^{\wedge} 2$ |  | conc | charge | $C^{-2 \times 2}$ |
| C. | 0.875 | 2 | 3.500 | HCO3 | 2.150 | 1 | 2.150 |
| 4 Mg | 0.494 | 2 | 1.975 | C | 0.339 |  | 0.339 |
| Na | 0.217 | 1 | 0.217 | SO4 | 0.208 | 2 | 0.833 |
| $K$ | 0.026 | 1 | 0.026 | CO3 | 0.040 | 2 | 0.160 |
| BORON | 0.009 | 3 | 0.083 | NO3 | 0.014 | 1 | 0.014 |
|  |  |  |  | PO4 | 0.002 | 3 | 0.015 |
|  | $\Sigma$ | cation | 5.802 |  |  |  |  |
|  | $\Sigma$ | anion | 3.511 |  |  |  |  |
|  | $\Sigma$ |  | $\begin{gathered} 9.312 \\ \text { moles/iter } \end{gathered}$ |  |  |  |  |
|  | ic stren |  | 0.0047 |  |  |  |  |

activity coefficients
DAVES EQUATION
$\log g=-05 z^{2} 2 \mathrm{fl}$
where $f(i)=\left(\left(^{\wedge} 51+\mu 5\right)-3 n(2981+273)^{\wedge} 2 / 3\right.$

| tomp | charge | gamma |
| :---: | :---: | :---: |
| 15 | 1 | 0.929 |
| 15 | 2 | 0.745 |
| 15 | 3 | 0.516 |

Figure 5-2. Gran titration plots for water samples collected at Fox River. GB17. and GB32. See text for derivation of $\mathrm{H}^{+}$activity coefficient $(\gamma+)$. Black circles indicate points used to calculate $\mathrm{d} f 1 / \mathrm{dV}$. Vo = volume of water sample, $\mathrm{Ca}=$ normality of HCl used to titrate sample. $\mathrm{TA}=$ total alkalinity and $\gamma+=$ calculated activity coefficient for the hydrogen ion $\left(\mathrm{H}^{-}\right)$.

occur if ion-pairing was taking place. Whatever the cause. a more thorough examination is needed. For the time being, Lyman's estimates of $K_{1}$ and $K_{2}$ (equations 5-9 and 5-10) will be used.

The values of $K_{0}, K_{1}$ and $K_{2}$ primarily depend on temperature. Consequentially, the apparent fugacity of $\mathrm{CO}_{2}$ in water also depends on temperature. As water temperatures fluctuate, the solubility of $\mathrm{CO}_{2}$ will change as will the equilibrium distribution of the carbonate species. Separating the effects of biology and temperature on $\mathrm{CO}_{2}$ concentrations, therefore, can be difficult. For this reason, a considerable amount of research has gone into determining the affect of temperature change on $f \mathrm{CO}_{2}$ in seawater (see Millero 1995). Similar work has not been done in freshwater but a reasonable estimate can be made here using the August $29^{\text {th }} .1995 \mathrm{pH}$ and $f \mathrm{CO}_{2}$ data (used to generate Figure 5-1) and the equilibrium constants given by equations 2-14.5-9. and 5-10. To begin. $\left[\mathrm{CO}_{2}\right],\left[\mathrm{HCO}_{3}{ }^{-}\right],\left[\mathrm{CO}_{3}{ }^{2-}\right], \mathrm{C}_{\mathrm{T}}$, and $\mathrm{C}_{\mathrm{A}}$ were calculated from measured values of $\mathrm{pH}, f \mathrm{CO}_{2}$, temperature, and the appropriate equilibrium constants using equations 5-6.57. and 5-8. $C_{A}$ was plotted against $C_{T}$ (Figure 5-3a) to give a $C_{A} / C_{T}$ slope of 1.056. Based on the average southern Green Bay value of $\mathrm{C}_{\mathrm{T}}(\sim 2.3 \mathrm{mmol} / \mathrm{kg}$, Appendix 5$)$, a $\mathrm{C}_{\mathrm{A}} / \mathrm{C}_{\mathrm{T}}$ ratio of 1.028 was used to calculate the change in $\left[\mathrm{CO}_{2}\right]$ and $f \mathrm{CO}_{2}$ with temperature. Assuming constant $\mathrm{C}_{\mathrm{T}}(2300 \mu \mathrm{~mol} / \mathrm{kg})$ and $\mathrm{C}_{\mathrm{A}}(2363.5 \mu \mathrm{~mol} / \mathrm{kg})$ (i.e. a closed system). $\left[\mathrm{CO}_{2}\right]$ was back-calculated for temperatures between $0-25^{\circ} \mathrm{C}$ using the equation (from Skirrow 1975):

Figure 5-3. Effects of temperature on the concentration of $\mathrm{CO}_{2}$ in southern Green Bay. a) The relationship between carbonate alkalinity $\left(\mathrm{C}_{\mathrm{A}}\right)$ and total inorganic carbon $\left(\mathrm{C}_{\mathrm{T}}\right)$ in Green Bay. Gray circles show values calculated from pH and $f \mathrm{CO}_{2}$. Black circles show measured values of total alkalinity ( $\mathrm{A}_{T}$ ) and total inorganic carbon $\left(\mathrm{C}_{\mathrm{T}}\right)$. Differences between $\mathrm{C}_{\mathrm{A}}$ and $\mathrm{A}_{\mathrm{T}}(<0.3 \%)$ were ignored. b) Response of $\left[\mathrm{CO}_{2}\right]$ to temperature at a $\mathrm{C}_{A} / \mathrm{C}_{T}$ ratio of 1.028. c) Response of $f \mathrm{CO}_{2}$ to temperature at a $\mathrm{C}_{\mathrm{A}} / \mathrm{C}_{\mathrm{T}}$ ratio of 1.028. d) Change in response of $f \mathrm{CO}_{2}$ to temperature at a $\mathrm{C}_{\mathrm{A}} / \mathrm{C}_{\mathrm{T}}$ ratio of 1.028 as a function of temperature.


$$
\begin{equation*}
\left[\mathrm{CO}_{2}\right]=\mathrm{C}_{\mathrm{T}}-\mathrm{C}_{\mathrm{A}}+\left(\left(\mathrm{C}_{\mathrm{A}} * \mathrm{~K}_{\mathrm{r}}-\mathrm{C}_{\mathrm{T}} * \mathrm{~K}_{\mathrm{r}}-4 \mathrm{C}_{\mathrm{A}}+\mathrm{Z}\right) / 2\left(\mathrm{~K}_{\mathrm{r}}-4\right)\right. \tag{5-13}
\end{equation*}
$$

where

$$
\begin{equation*}
Z=\left[\left(4 C_{A}+C_{T} * K_{r}-C_{A} * K_{r}\right)^{2}+4\left(K_{r}-4\right) C_{A}^{2}\right]^{0.5} \tag{5-14}
\end{equation*}
$$

and $K_{r}=K_{1} / K_{2}$. The results are plotted in Figure 5-3b. and show a $\sim 0.4 \%$ increase in $\left[\mathrm{CO}_{2}\right]$ for each ${ }^{\circ} \mathrm{C}$ in temperature increase due to shifts in $\mathrm{K}_{1}$ and $\mathrm{K}_{2}$. The fugacities for each value of $\left[\mathrm{CO}_{2}\right]$ between $0-25^{\circ} \mathrm{C}$ were calculated using equation $2-14$ and plotted in Figure 5-3c. A linear fit of the data gave a slope of $d \ln f \mathrm{CO}_{2} / d t=0.0377$. The change in fugacity due to a change in temperature was therefore calculated as:

$$
\begin{equation*}
\ln f \mathrm{CO}_{2 \text { NEW TEMP }}=\ln f \mathrm{CO}_{2 \text { OBS TEMP }}+0.0377 d . \tag{5-15}
\end{equation*}
$$

where $d t=$ the change in temperature in ${ }^{\circ} \mathrm{C}$. For example, for an initial fugacity of 350 $\mu \mathrm{atm}$ at $0^{\circ} \mathrm{C}$. a temperature increase of $20^{\circ} \mathrm{C}$ would cause the apparent fugacity to increase $\sim 112 \%$ to $744 \mu \mathrm{~atm}$. A closer look at the plot of $d \ln f \mathrm{CO}_{2} / d t$ versus temperature (Figure 5-3d) revealed the relationship was not quite linear, but the error
introduced using the linear assumption was small over the temperature range seen in Green Bay. Scaling the $d \ln f \mathrm{CO}_{2} / d t$ relationship at $\mathrm{T}_{\mathrm{A}} / \mathrm{C}_{\mathrm{T}}=1.028$ up to a ratio of $\mathrm{T}_{\mathrm{A}} / \mathrm{C}_{\mathrm{T}}$ typical of seawater $(\sim 1.1), d \ln f \mathrm{CO}_{2} / d \mathrm{t} \cong 0.042$ which. again, is typical in marine systems (see Millero 1995, Takahashi et al. 1993. Weiss et al. 1982).

Another $\mathrm{CO}_{2}$ parameter normally associated with marine systems is the Revelle or homogeneous buffer factor. The Revelle factor (B) is defined by Butler (1982) as:

$$
\begin{equation*}
\mathrm{B}=\Sigma \mathrm{CO}_{2} / f \mathrm{CO}_{2}\left(\partial f \mathrm{CO}_{2} / \partial \Sigma \mathrm{CO}_{2}\right)_{\mathrm{TA}}=\left(\partial \log f \mathrm{CO}_{2} / \partial \log \Sigma \mathrm{CO}_{2}\right)_{\mathrm{TA}} \tag{5-16}
\end{equation*}
$$

and describes the percent change in $f \mathrm{CO}_{2}$ caused by a $1 \%$ change in $\mathrm{\Sigma CO}_{2}$ at constant alkalinity (Lewis and Wallace 1998). The value of B is sensitive to both temperature and the ratio of total alkalinity to $\Sigma \mathrm{CO}_{2}$. In marine systems, B typically ranges from $\sim 8$ $\left(\mathrm{A}_{\mathrm{T}} / \Sigma \mathrm{CO}_{2} \sim 1.20\right)$ to $14\left(\mathrm{~A}_{\mathrm{T}} / \Sigma \mathrm{CO}_{2} \sim 1.06\right)$ (Takahashi et al. 1993). Interest in the Revelle factor has for the most part been related to estimating the ocean`s capacity to buffer anthropogenic increases in atmospheric $\mathrm{CO}_{2}$. However, for a given change in $f \mathrm{CO}_{2}$, the Revelle factor can also be used to estimate the change in $\Sigma \mathrm{CO}_{2}$ if direct measurements are lacking (Takahashi et al. 1993).

An estimate of the Revelle buffer factor in southern Green Bay was made under the assumption that $A_{T} \cong A_{C} \cong C_{A}$. Under these conditions, $B$ is simply defined as:

$$
\begin{equation*}
\mathrm{B}=\Sigma \mathrm{CO}_{2} /\left[\mathrm{CO}_{2}\right]+\left[\mathrm{CO}_{3}{ }^{2-}\right](\text { Butler } 1982) . \tag{5-17}
\end{equation*}
$$

Using the $\mathrm{pH} . f \mathrm{CO}_{2}$, and temperature data collected on August $29^{\text {th }} .1995$ and the values of $\Sigma \mathrm{CO}_{2},\left[\mathrm{CO}_{2}\right]$, and $\left[\mathrm{CO}_{3}{ }^{2-}\right]$ that were calculated using equations 2-14, 5-6, 5-7. 5-8, 5-9. and 5-10. estimates of $B$ were calculated using equation 5-17 and plotted in Figure 5-4 (gray circles) in relation to the $C_{A} / C_{T}$ ratio observed along the transect route between the Fox River $\left(\mathrm{C}_{\mathrm{A}} / \Sigma \mathrm{CO}_{2} \sim 1.05\right)$ and Sturgeon Bay $\left(\mathrm{C}_{\mathrm{A}} / \Sigma \mathrm{CO}_{2} \sim 0.99\right)$. Values of $B$ were also calculated using measured values of $f \mathrm{CO}_{2} . \mathrm{A}_{\mathrm{T}}$. and $\mathrm{C}_{\mathrm{T}}$ from October $10^{\text {th }} .1995$ (Figure 54. black circles) where $\left[\mathrm{CO}_{3}{ }^{-}\right]$was assumed to be approximately equal to:

$$
\begin{equation*}
\left[\mathrm{CO}_{3}{ }^{2-}\right] \cong \mathrm{A}_{\mathrm{T}}-\mathrm{C}_{\mathrm{T}}-\left[\mathrm{CO}_{2}\right] \tag{5-18}
\end{equation*}
$$

In both cases. estimates of the Revelle factor for the major basin of Green Bay (outside of Sturgeon Bay and the Fox River) generally fell between 25 and 35-meaning that a $1 \%$ change in $\mathrm{SCO}_{2}$ would result in a $\sim 30 \%$ change in $f \mathrm{CO}_{2}$.

## Surface water carbon dioxide

Over 1800 carbon dioxide measurements were made during the open water transects of 1994 and 1995. The concentrations of $\mathrm{CO}_{2}$ (expressed as fugacities) and

Figure 5-4. Homogeneous buffer factor as a function of alkalinity/ $\Sigma \mathrm{CO}_{2}$ in southern Green Bay. Gray circles were calculated from data collected on August 29 ${ }^{\text {th }}$. 1995. Black circles were calculated from data collected on October $10^{\text {th }} .1995$.

## homogeneous buffer factor


sampling sites are shown in Figure 5-5. Each of the concentrations. their coordinates. and the physical parameters relevant to calculating each concentration are also given in Appendix 3. Variations in $f \mathrm{CO}_{2}$ in surface waters were large with individual measurements ranging from greater than $900 \mu$ atm in the Fox River and Sturgeon Bay to less than $200 \mu \mathrm{~atm}$ over portions of southern Green Bay.

Average surface water $f \mathrm{CO}_{2}$ values ( $\pm 1 \mathrm{SD}$ ) in each of the seven zones of southern Green Bay revealed a more interesting spatial trend (Figure 5-6). In zone 1, the average fugacity of $\mathrm{CO}_{2}$ was $\sim 390 \mu \mathrm{~atm}$. This was slightly higher than the average fugacity of atmospheric $\mathrm{CO}_{2}$ as shown by the gray dotted line (see below for derivation). North of zone 1, the average surface water $f \mathrm{CO}_{2}$ dropped below atmospheric equilibrium and remained so till zone 5 (Sturgeon Bay). Though it appeared that zones 2.3 and 4 would import $\mathrm{CO}_{2}$ from the atmosphere on an annual basis, while the remaining zones would export $\mathrm{CO}_{2}$, bias in sampling dates and the coupling between changes in wind speed and surface water $f \mathrm{CO}_{2}$ preclude this assumption. Concentrations of surface water $\mathrm{CO}_{2}$ were measured under the ice on February 21 and 22, 1995 (Figure 5-7). While sampling sites were limited due to ice conditions, $f \mathrm{CO}_{2}$ values tended to be below atmospheric equilibrium and averaged $\sim 320 \mu \mathrm{~atm}$.

To simplify flux calculations and interpretations of large scale changes over space and time, $\mathrm{CO}_{2}$ fugacities measured over an entire cruise ( $\sim 3$ days) were spatially weight averaged in each of the seven zones of the study site. This was accomplished by interpolating the data over a grid of each zone using an exact inverse distance method (equation 2-19). Each grid was then integrated and divided by its base area. Grid nodes were spaced at 100 meter intervals in zone 5. 250 meter intervals in zone 1 , and 500 meter

Figure 5-5. Green Bay surface water $f \mathrm{CO}_{2}$ values measured during transect cruises of 1994 and 1995. The axis range is adjusted to the highest observed concentration for each day's cruise. The transect distance represents the cumulative distance traveled in kilometers. The location of each sample point is plotted with a circle. The area of each circle is proportional to the concentration of $\mathrm{CO}_{2}$.


03-Jun-94


13-Jul-94

14-Jul-94


15-Jul-94



## 03-Aug-94



## 23-Aug-94



13, 14, 15 Sep 94


## 25-Oct-94



26-Oct-94


## 18-Apr-95



19-Apr-95


20-Apr-95


## 22-May-95


5080000



24-May-95


## 18-Jul-95



25-Jul-95


## 26Jul-95



## 28-Jul-95



## 29-Aug-95



## 06-Oct-95


09-Oct-95


10-Oct-95



Figure 5-6. The mean fugacity of surface water $\mathrm{CO}_{2}$ in zones l-7 ( $\pm 1$ S.D.). The mean fugacity of atmospheric $\mathrm{CO}_{2}(357 \mu \mathrm{~atm})$ is shown as a gray dotted line.

## mean $\mathrm{fCO}_{2}$ in surface water

zones 1-7

... mean atmospheric $\mathrm{fCO}_{2}$

Figure 5-7. The fugacity of surface water $\mathrm{CO}_{2}$ under ice in southern Green Bay. See Appendix 1 for ice station coordinates.

## fCO2 under ice <br> 21-22 February 1995

5000000

$290,315,318{ }^{E}$
4940000

$420000 \quad 440000$| 460000 |
| ---: |
|  |
|  |
| meters UTM E |

intervals in zones 2. 3, 4, 6. and 7. The data set for each particular zone only included measurements made within the zone; measurements made outside of the zone were blanked. If no (or insufficient) measurements were made in a zone. the zone was excluded from consideration.

The fluctuations in surface water $\mathrm{CO}_{2}$ over time in each zone are presented in Figure 5-8. Concentrations in $\mathrm{CO}_{2}$ tended to increase toward the north with minima occurring during the summer and maxima occurring after destratification of the water column in October. While most of the change in aqueous $\mathrm{CO}_{2}$ was probably due to photoautotrophic uptake and heterotrophic respiration, changes in temperature and flux across the air-water interface must have significantly dampened the amplitude of fluctuation. On occasion. the effect of temperature may even have overridden the biological affect on $\mathrm{CO}_{2}$ concentrations. For example, values of $f \mathrm{CO}_{2}$ may actually have risen due to an increase in temperature in spite of net autotrophic conditions (i.e. a $\mathrm{P} / \mathrm{R}$ ratio $>1$ ). To determine if this was true, the effects of temperature on $f \mathrm{CO}_{2}$ in Green Bay were compensated for by normalizing each fugacity (shown in Figure 5-8) to an average surface water temperature of $12.5^{\circ} \mathrm{C}$ using equation $5-15$ (see Takahashi et al. 1993).

The temperature normalized fugacities are presented along with their in situ temperature values (from Figure 5-8) in Table 5-2. Comparing the normalized to in situ fugacities reveals the striking effect of temperature change. In zone 4, for example, the observed $f \mathrm{CO}_{2}$ rose $36 \%$ between June and July of 1994 while the normalized fugacities remained essentially unchanged. The fact that the temperature normalized fugacities were stable suggests that the other forces affecting $\mathrm{CO}_{2}$ concentrations were in balance. In zone

Figure $5-8(\mathrm{a}-\mathrm{g})$. The temporal variation of spatially weight-averaged surface water $\mathrm{CO}_{2}$ concentrations in zones 1-7 of southern Green Bay. Zones 1-7 appear as shaded areas within the Green Bay shoreline. Concentrations measured during the 1994 transects appear as light gray symbols; 1995 values are plotted as dark gray symbols. Ice cover is plotted as a thick line using the same color scheme. Atmospheric $f \mathrm{CO}_{2}$ is plotted as a thin black line. Note the change of scale on the Y axis in each zone. All relevant data is tabulated below each figure.








Table 5-2. Surface water $\mathrm{CO}_{2}$ fugacities at in situ water temperatures and their respective fugacities normalized to a mean annual temperature of $12.5^{\circ} \mathrm{C}$.

| ZONE 1 | date | day | $\begin{gathered} \text { temp } \\ C \end{gathered}$ | fCO2 (uatm) <br> in situ temp | $\begin{gathered} \mathrm{fCO2} \text { (uatm) } \\ 12.5 \mathrm{C} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 13-Jul-94 | 194 | 24.5 | 221 | 141 |
|  | 02-Aug-94 | 214 | 23.4 | 388 | 257 |
|  | 23-Aug-94 | 235 | 21.2 | 298 | 215 |
|  | 13-Sep-94 | 256 | 18.9 | 258 | 203 |
|  | 25-Oct-94 | 298 | 11.1 | 497 | 524 |
|  | 20-Apr-95 | 110 | 3.6 | 345 | 482 |
|  | 22-May-95 | 142 | 12.9 | 530 | 522 |
|  | 19-Jul-95 | 200 | 23.7 | 535 | 351 |
|  | 29-Aug-95 | 241 | 22.5 | 289 | 198 |
|  | 10-Oct-95 | 283 | 14 | 534 | 505 |
| ZONE 2 | date | day | $\begin{gathered} \text { temp } \\ C \end{gathered}$ | fCO2 (uatm) <br> in situ temp | $\begin{gathered} \text { fCO2 (uatm) } \\ 12.5 \mathrm{C} \end{gathered}$ |
|  | 03-Jun-94 | 154 | 17.7 | 282 | 232 |
|  | 13-Jul-94 | 194 | 23.7 | 462 | 303 |
|  | 02-Aug-94 | 214 | 22.7 | 255 | 174 |
|  | 23-Aug-94 | 235 | 20.8 | 242 | 177 |
|  | 13-Sep-94 | 256 | 18.5 | 261 | 208 |
|  | 25-Oct-94 | 298 | 11.7 | 360 | 371 |
|  | 20-Apr-95 | 110 | 3.1 | 334 | 477 |
|  | 22-May-95 | 142 | 12 | 342 | 348 |
|  | 19-Jul-95 | 200 | 23.2 | 318 | 212 |
|  | 29-Aug-95 | 241 | 22.5 | 201 | 138 |
|  | 10-Oct-95 | 283 | 14.8 | 470 | 431 |
| ZONE 3 | date | day | $\stackrel{t e m p}{C}$ | fCO2 (uatm) <br> in situ temp | $\begin{gathered} \mathrm{fCO2} \text { (uatm) } \\ 12.5 \mathrm{C} \end{gathered}$ |
|  | 03-Jun-94 | 154 | 16.5 | 293 | 252 |
|  | 13-Jul-94 | 194 | 22.4 | 456 | 314 |
|  | 02-Aug-94 | 214 | 21.7 | 300 | 212 |
|  | 23-Aug-94 | 235 | 20.2 | 233 | 175 |
|  | 13-Sep-94 | 256 | 18.1 | 229 | 185 |
|  | 25-Oct-94 | 298 | 12 | 446 | 454 |
|  | 20-Apr-95 | 110 | 2.7 | 329 | 477 |
|  | 22-May-95 | 142 | 10.8 | 352 | 375 |
|  | 19-Jul-95 | 200 | 22.5 | 291 | 200 |
|  | 29-Aug-95 | 241 | 22.5 | 239 | 164 |
|  | 10-Oct-95 | 283 | 15 | 431 | 392 |
| ZONE 4 | date | day | $\begin{gathered} \text { temp } \\ C \end{gathered}$ | fCO2 (uatm) in sity tomp | $\begin{gathered} \mathrm{fCO2}(\text { uatm }) \\ 12.5 \mathrm{C} \end{gathered}$ |
|  | 03-Jun-94 | 154 | 14.7 | 334 | 308 |
|  | 13-Jul-94 | 194 | 22.1 | 453 | 316 |
|  | 02-Aug-94 | 214 | 21.1 | 302 | 218 |
|  | 23-Aug-94 | 235 | 19.8 | 241 | 183 |
|  | 13-Sep-94 | 256 | 17.8 | 255 | 209 |
|  | 25-Oct-94 | 298 | 12.2 | 475 | 480 |
| ICE Station D | 22-Feb-95 | 53 | 0.2 | 311 | 494 |
|  | 20-Apr-95 | 110 | 2.2 | 349 | 514 |
|  | 22-May-95 | 142 | 9.7 | 367 | 408 |
|  | 19-Jut-95 | 200 | 22.3 | 301 | 208 |
|  | 29-Aug-95 | 241 | 22.3 | 236 | 163 |
|  | 10-Oct-95 | 283 | 15 | 475 | 432 |
|  | 09-Nov-95 | 313 | 8.6 | 367 | 425 |

$\left.\left.\begin{array}{lllccc}\text { ZONE 5 } & \text { date } & \text { day } & \text { temp } & \text { fCO2 (uatm) } & \text { fCO2 (uatm) } \\ \text { in situ temp }\end{array}\right] \begin{array}{c}\text { 12.5 C }\end{array}\right)$
3. however. the observed fugacity rose from $329 \mu \mathrm{~atm}$ on April $20^{\text {th }} .1995$ to $352 \mu \mathrm{~atm}$ on May $22^{\text {nd }}$ while the temperature normalized fugacities dropped from $477 \mu$ atm to 375 $\mu \mathrm{atm}$. Since the observed values of $f \mathrm{CO}_{2}$ were below atmospheric equilibrium (see below), an influx of $\mathrm{CO}_{2}$ from the atmosphere occurred. Assuming the alkalinity remained essentially constant, a decrease in the normalized fugacities could only have occurred through net autotrophy (i.e. a $\mathrm{P} / \mathrm{R}$ ratio greater than one).

The fluctuations in $f \mathrm{CO}_{2}$ observed in all zones between October 1994 and April 1995 were equally interesting. In zone 4 . normalized $f \mathrm{CO}_{2}$ values increased only slightly from October $25^{\text {th }} .1994$ to February $22^{\text {nd }} .1995$ to April $20^{\text {th }}, 1995$. Since ice covered the bay during much of that time. either the rates of photosynthesis and respiration decreased to levels that had little effect on the inorganic carbon pool or the $\mathrm{P} / \mathrm{R}$ ratio was close to one.

When the temperature normalized values of $f \mathrm{CO}_{2}$ (listed in Table 5-2) were plotted against time (Figure 5-9). one feature common to all zones stood out. The fugacity of $\mathrm{CO}_{2}$ decreased throughout the summer until autumn when the water column mixed. Some of the decrease in $f \mathrm{CO}_{2}$ could have been caused by a venting of $\mathrm{CO}_{2}$ from the bay to the atmosphere. However, because the observed values of $f \mathrm{CO}_{2}$ in each zone eventually dropped to levels below atmospheric equilibrium. the rate of carbon uptake through photosynthesis must have been higher than carbon release through heterotrophic respiration. In other words, while the water column was stratified. the mixed layer (epilimnion) of southern Green Bay appeared to have a $\mathrm{P} / \mathrm{R}$ ratio greater than one.

Figure 5-9. The temporal dynamics of dissolved $\mathrm{CO}_{2}$ in southern Green Bay normalized to $12.5^{\circ} \mathrm{C}$.





Though the epilimnion appeared to have a $\mathrm{P} / \mathrm{R}$ ratio greater than one. heterotrophic respiration occurring in the hypolimnion and sediment could have resulted in an areal $\mathrm{P} / \mathrm{R}$ ratio of less than one. Since $\mathrm{CO}_{2}$ produced through respiration below the mixed layer was essentially "hidden" from my surface water analyses until the water column destratified, estimates of the areal $\mathrm{P} / \mathrm{R}$ ratio could only be calculated on an annual time scale. Areal estimates of the $\mathrm{P} / \mathrm{R}$ ratio on an annual time scale required the calculation of air-water $\mathrm{CO}_{2}$ fluxes.

## Atmospheric exchange

Daily estimates of carbon dioxide flux across the air-water interface in each of the seven zones of southern Green Bay were calculated using equation 3-1. where $K$ equaled the $\mathrm{CO}_{2}$ specific transfer coefficients derived in Chapter 3 (Figure 3-7), and $\Delta \mathrm{C}$ equaled $\mathrm{C}_{\mathrm{w}}-\mathrm{C}_{\mathrm{a}} . \mathrm{C}_{\mathrm{w}}$ was equal to the dissolved $\mathrm{CO}_{2}$ concentrations of the mixed layer (epilimnion) and $\mathrm{C}_{\mathrm{a}}$ equaled the concentration of $\mathrm{CO}_{2}$ in the surface water micro-layer which was assumed to be in equilibrium with atmospheric $\mathrm{CO}_{2}$.

The atmospheric concentrations of $\mathrm{CO}_{2}$ over southern Green Bay were measured repeatedly during the field seasons of 1994 and 1995 and showed considerable variability ( $\sim 35 \mathrm{ppm}$ ) over very short time scales (Figure 5-10. bottom panel - open triangles). Sue Boehme (Rutgers University) collected and measured atmospheric $\mathrm{CO}_{2}$ in 1996 and found similar short-term variability in $\mathrm{xCO}_{2}$ over southern Green Bay (Figure 5-10, bottom panel - black triangles). The 1995 atmospheric $\mathrm{CO}_{2}$ mole fractions at Park Falls. Wisconsin ( $4556{ }^{\prime} \mathrm{N} 9016^{\prime} \mathrm{W}$ ) were measured by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) and also showed considerable variability (Figure 5-10.

Figure 5-10. Annual variation of atmospheric $\mathrm{CO}_{2}$ over southern Green Bay. Top) Average daily estimates of atmospheric $f \mathrm{CO}_{2}$ were determined by fitting a sinusoidal curve to a $2^{\text {nd }}$-order polynomial regression which in turn was fit to the measured fugacities of $\mathrm{CO}_{2}$ over Green Bay. Bottom) Variability in atmospheric $\mathrm{CO}_{2}$ over Green Bay appears to be real. The open triangles represent the mole fractions of $\mathrm{CO}_{2}$ measured in this study during the 1995 field season. The solid triangles show atmospheric $\mathrm{xCO}_{2}$ values in Green Bay samples that were collected and measured by Susan Boehme at the Lamont Doherty Earth Observatory using $\mathrm{CO}_{2}$ WMO calibrated standards.

## atmospheric carbon dioxide


O measured fugacity
2nd order polynomial regression
—— sinusoidal fit


$$
\begin{array}{ll}
\nabla & \text { Green Bay } 95 \text { (WAPLES) } \\
\text { A } & \text { Green Bay } 96 \text { (BOEHME) } \\
\circ & \text { Park Falls. WI } 94-95 \text { (NOAA) }
\end{array}
$$

bottom panel - gray circles). Since no clear pattern describing the daily fluctuations in $\mathrm{xCO}_{2}$ could be discerned. an average daily estimate of $f \mathrm{CO}_{2}$ for both 1994 and 1995 was calculated using the measured fugacities of 1995 (Figure 5-10, top panel). A sinusoidal curve was fit to a $2^{\text {nd }}$-order polynomial regression of the measured fugacities to give:

$$
\begin{equation*}
f \mathrm{CO}_{2 \mathrm{CD}}=9 \cos (2 \Pi / 365 \times \mathrm{CD})+1.5 \sin (2 \Pi / 365 \times \mathrm{CD})+357 \tag{5-19}
\end{equation*}
$$

where $\mathrm{CD}=$ calendar day.
The molarity ( $\cong$ molality) of $\mathrm{C}_{3}$ was taken as the product of the fugacity of $\mathrm{CO}_{2}$ (equation 5-19) and its solubility coefficient (equation 2-14) which was calculated using the surface temperatures derived in Chapter 3 (see Figure 3-5). Daily estimates of $\mathrm{C}_{\mathrm{w}}$ in each of the seven zones of southern Green Bay were based on linear interpolations between the spatially averaged concentrations measured during each of the transect cruises shown in Figure 5-8. The concentration of dissolved $\mathrm{CO}_{2}$ just prior to and after ice cover was taken as the mean of the last and first concentration measured during 1994 and 1995 respectively.

The net exchange of $\mathrm{CO}_{2}$ between each zone of southern Green Bay and the atmosphere is shown together with daily flux estimates of $\mathrm{CO}_{2}$ across the air-water interface in Figure 5-1 la (1994) and 5-11b (1995) where negative values indicate $\mathrm{CO}_{2}$ uptake by the bay. An " $M$ " shaped pattern in daily flux estimates appeared in many of the zones. The initial increase in $\mathrm{CO}_{2}$ flux to the atmosphere occurred due to rising surface water temperatures. As the rate of temperature increase slowed, the rate of photosynthetic

Figure 5-11. Carbon dioxide flux from Green Bay to the atmosphere based on the air colurnn stability corrected transfer coefficients derived in Chapter 3 and air-water $\mathrm{CO}_{2}$ concentration gradients derived in this chapter. a) 1994 flux estimates for southern Green Bay zones 1-7. b) 1995 flux estimates for southern Green Bay zones 1-7.




## $1995 \mathrm{CO}_{2}$ fux


b
uptake of $\mathrm{CO}_{2}$ overcame the rate of increase in $f \mathrm{CO}_{2}$ due to temperature change and respiration. This resulted in a decrease and (in some instances) sign change in air-water flux. In autumin. surface water temperatures cooled and the water column destratified. $\mathrm{CO}_{2}$ that had been produced through heterotrophic respiration below the surface layer mixed throughout the water column. In most instances, $\mathrm{CO}_{2}$ fluxes changed sign and the bay vented $\mathrm{CO}_{2}$ to the atmosphere. Finally, as surface water temperatures continued to fall. the resultant decrease in surface water $f \mathrm{CO}_{2}$ quickly reduced the positive flux of $\mathrm{CO}_{2}$ to the point where, just before ice cover. $\mathrm{CO}_{2}$ fluxes again changed sign.

The annual flux of $\mathrm{CO}_{2}$ across the air-water interface is given for each zone in southern Green Bay in Figure 5-12. Flux estimates from the first few days of 1995 (before the onset of ice cover) were included in the 1994 flux estimates. In 1994, approximately $180 \times 10^{7}$ moles of $\mathrm{CO}_{2}$ were vented to the atmosphere from southern Green Bay (zones 1-7) in spite of the fact that the southern most portion of the bay ( $\sim 1000 \mathrm{~km}^{2}$ ) actually imported $\mathrm{CO}_{2}$ from the atmosphere. In 1995, the net flux of $\mathrm{CO}_{2}$ to the atmosphere increased to $240 \times 10^{7}$ moles with most of the increase coming from the southern most portion of the bay (zones 1-4). The proportional increase in $\mathrm{CO}_{2}$ flux to the atmosphere in 1995 was quite similar to the proportional increase in methane flux observed in 1995 over 1994-thus strengthening the argument that wind direction significantly affected the rate of benthic bacterial respiration by altering the hydrodynamics of the bay and sediment temperatures (see Chapter 4).

## P/R ratios

To a first approximation, the sign (or direction) of the annual flux of $\mathrm{CO}_{2}$ across the air-water interface (Figure 5-12, top left) indicated whether the areal $\mathrm{P} / \mathrm{R}$ ratio in each

Figure 5-12. Carbon dioxide flux sums for Green Bay zones 1-7. Positive values indicate a net efflux of $\mathrm{CO}_{2}$ from Green Bay to the atmosphere. Negative values indicate a net influx of $\mathrm{CO}_{2}$ from the atmosphere to the bay. Top left) Annual $\mathrm{CO}_{2}$ flux sums in units of mmol $\mathrm{m}^{-2} \mathrm{yr}^{-1}$. Top right) Annual $\mathrm{CO}_{2}$ flux sums from each zone. Bottom) Tabulated $\mathrm{CO}_{2}$ flux sums for southern Green Bay zones 1-7 including area of each zone.

of the seven zones of the study site was greater or less than one. An annual flux of $\mathrm{CO}_{2}$ out of the bay and into the atmosphere in zones $1,4,5,6$ and 7 suggested that these areas had an areal $\mathrm{P} / \mathrm{R}$ ratio less than one. Zones 2 and 3, however. imported $\mathrm{CO}_{2}$ from the atmosphere and thus appeared to have areal $\mathrm{P} / \mathrm{R}$ ratios greater than one.

Specific $\mathrm{P} / \mathrm{R}$ ratios were calculated from annual air-water $\mathrm{CO}_{2}$ fluxes and measured rates of areal primary productivity (Sager and Richman 1990. 1991: Russell Cuhel. unpublished data). Sager and Richman (1990, 1991) measured primary production in Green Bay during the summers of 1986,1987 and 1988. Their average summertime productivity rates for each year and station were plotted against distance from the Fox River in Figure 5-13 (top, black symbols). Standard errors for each summertime average ( $\mathrm{n}=4$ ) were approximately $\pm 50 \%$ (not shown). Two measurements made by Russell Cuhel (University of Wisconsin - Milwaukee) were included to show that primary productivity was still significant in late autumn (November 1995. gray circle) but decreased to approximately $10 \%$ of summertime values when ice covered the bay (January 1996. gray square).

A conservative estimate of the annual areal primary productivity was calculated using the 3-year summertime averages of productivity given by Sager and Richman (1990) (Figure 5-13, bottom) and the under-ice value measured by Cuhel. A second-order polynomial regression was fit to the summertime data as a function of distance from the Fox River to give

$$
P_{\text {summer }}=1762.0-17.3 \mathrm{X}+0.1 \mathrm{X}^{2}
$$

Figure 5-13. Areal primary production rates in Green Bay. Top) Average summertime primary productivity rates measured by Sager and Richman (1990, 1991) during the summers of 1986, 1987 and 1988 (black symbols). Productivity was measured at three stations located approximately 13,66 and 120 kilometers from the mouth of the Fox River. Sampling consisted of four cruises per summer spaced at $\sim 2$ week intervals. Gray symbols represent additional productivity measurements (unpublished) made by Russell Cuhel from the University of Wisconsin - Milwaukee during November of 1995 and January of 1996. All productivity measurements were based on the ${ }^{14} \mathrm{C}$ method. Bottom) Average of all summertime productivity measurements made by Sager and Richman (1990).

where $\mathrm{X}=$ distance from the Fox River in kilometers and $\mathrm{P}_{\text {summer }}=$ photosynthetic uptake of carbon in units of $\mathrm{mg} \mathrm{C} \mathrm{m} \mathrm{m}^{-2}$ day ${ }^{-1}$. Summertime productivity rates were applied to 265 days of the year-the remaining 100 days were assigned a value of one tenth of $\mathrm{P}_{\text {summer }}$. Annual estimates of productivity were therefore taken as

$$
P=\left(265 * P_{\text {summer }}+100 *\left(P_{\text {summer }} / 10\right)\right) / 1200 .
$$

where $P$ was equal to $\mathrm{mol} \mathrm{Cm}^{-2} \mathrm{yr}^{-1}$. Using equation 5-1, relative estimates of annual areal respiration (R) were calculated as

$$
\mathrm{R}=\mathrm{P}+\mathrm{J}_{\mathrm{aw}}
$$

where $\mathrm{J}_{\mathrm{aw}}=$ the annual flux of $\mathrm{CO}_{2}$ to the atmosphere in units of mol $\mathrm{Cm}^{-2} \mathrm{yr}^{-1}$ (Figure 512). Estimates of $P$ and $R$ and their ratio were plotted for each of the six zones in southern Green Bay in terms of distance from the mouth of the Fox River in Figure 5-14 (zone 5 was excluded from consideration).

For much of the bay, photosynthesis and respiration were essentially in balance. In 1994. $\mathrm{P} / \mathrm{R}$ ratios measured $0.99,1.10,1.04,0.99,0.82$ and 0.83 in zones $1.2,3.4 .6$ and 7 respectively. In 1995, $\mathrm{P} / \mathrm{R}$ ratios measured $0.91,1.02,1.02,0.97,0.83$ and 0.87 in the same order. While gradients in the concentration of $\mathrm{CO}_{2}$ across the air-water interface were often large and easy to measure, annual fluxes between the bay and atmosphere appeared insignificant compared to biological exchange. In zone 1 for instance. the mass

Figure 5-14. Estimates of annual areal primary productivity (light gray bars) and heterotrophic respiration (dark gray bars), and their ( $\mathrm{P} / \mathrm{R}$ ) ratio (black circles) as a function of distance from the mouth of the Fox River. From left to right, each set of points correspond to conditions found in zones 1, 2, 3, 4. 6 and 7 (zone 5 excluded).

of total inorganic carbon $\left(\mathrm{\Sigma CO}_{2}\right)$ in the water column was only $\sim 5.5 \mathrm{~mol} \mathrm{C} \mathrm{m}{ }^{-2}$. Based on the rates of P shown in Figure 5-14, the biological turnover time for $\Sigma \mathrm{CO}_{2}$ was on the order of $\sim 50$ days. For the entire study site, the biological turnover time for $\Sigma \mathrm{CO}_{2}$ equaled $\sim 430$ days.

The pattern of rising then falling $P / R$ ratios may have been due to differences in light or nutrient limitation on primary productivity as well as differences in zooplankton grazing rates and bacterial respiration (Sager et al. 1984; Sager and Richman 1990. 1991; del Giorgio et al. 1997). The production of organic carbon in one zone followed by advection and respiration in another zone could have also influenced the observed ratios. If so, then estuaries. lakes and even the ocean may display patterns of rising and falling $\mathrm{P} / \mathrm{R}$ ratios much like those observed in lotic (river) systems (Cole 1983). These "ripples". over both time and space, could have varying amplitudes as well as wavelengths unique to each system. Inadequate temporal or spatial sampling could therefore lead to inaccurate estimates of the overall $\mathrm{P} / \mathrm{R}$ ratio.

There was also the possibility that $\mathrm{CO}_{2}$-in excess of the fugacity of atmospheric $\mathrm{CO}_{2}$-flowed into the study site where it eventually vented to the atmosphere. This "excess" $\mathrm{CO}_{2}$ would have been indistinguishable from $\mathrm{CO}_{2}$ respired inside of the study site and thus would have "artificially" lowered the $\mathrm{P} / \mathrm{R}$ ratio in the sense that the $\mathrm{P} / \mathrm{R}$ ratio would not have reflected in situ activity.

This last scenario may explain the relatively high $\mathrm{CO}_{2}$ fluxes (and low $\mathrm{P} / \mathrm{R}$ ratios) observed in zones 6 and 7. The largest contribution of excess $\mathrm{CO}_{2}$ from outside the study site was assumed to come from northern Green Bay. Based on current meter studies during the stratified season. water from the north flows into the hypolimnion of the
southern bay through the channel west of Chambers Island at a rate of $900 \mathrm{~m}^{3} \mathrm{sec}^{-1}$ (Miller and Saylor 1993). This translates to a total inflow volume of $9.3 \mathrm{~km}^{3}$ over 4 months. A profile of $f \mathrm{CO}_{2}$ values measured at station GB67 during late summer (14 September 1994) showed that the potential contribution of excess $\mathrm{CO}_{2}$ was large (Figure 5-15). Hypolimnetic $f \mathrm{CO}_{2}$ values averaged $\sim 2000 \mu$ atms at $\sim 10^{\circ} \mathrm{C}$. If the entire water mass entering the southern bay from the north eventually reached the surface layer and warmed $10^{\circ} \mathrm{C}$ in the process, then based on equation $5-15, f \mathrm{CO}_{2}$ would increase another $\sim 900$ $\mu \mathrm{atm}$ to $\sim 2900 \mu \mathrm{~atm}$. Bringing this water into equilibrium with the atmosphere would result in a loss of approximately $117 \mathrm{mmol} \mathrm{C} \mathrm{m}^{-3}$ based on equation 5-16 and a Revelle factor of 30 . Taking the product of $117 \mathrm{mmol} \mathrm{C} \mathrm{m}^{-3}$ and $9.3 \mathrm{~km}^{3}$ gave a total excess $\mathrm{CO}_{2}$ contribution of $\sim 110 \times 10^{7}$ mol C from northern Green Bay during the summer. Though the uncertainty in this number is large, it succeeds in demonstrating the potential contribution of $\mathrm{CO}_{2}$ from outside of the study site.

Integrating annual productivity rates over the entire study site gave a total productivity estimate of $4.4 \times 10^{10} \mathrm{~mol} \mathrm{C} \mathrm{yr}^{-1}$. Using the average annual $\mathrm{CO}_{2}$ flux to the atmosphere $\left(210 \times 10^{7} \mathrm{~mol} \mathrm{C} \mathrm{yr} ~\right) ~ a n d ~ e q u a t i o n ~ 5-1 . ~ t h e ~ P / R ~ r a t i o ~ f o r ~ a l l ~ o f ~ s o u t h e r n ~$ Green Bay equaled 0.95 . The sensitivity of this ratio to uncertainties in the terms used to calculate it are given in Table 5-3. To begin, the terms affecting the $\mathrm{P} / \mathrm{R}$ ratio were sorted into two categories: dampening terms and bias terms. Uncertainty in dampening terms could increase or decrease the $\mathrm{P} / \mathrm{R}$ ratio to a limit of one. Bias terms on the other hand had no limit. For example, in an autotrophic system with a $P / R$ ratio greater than one. error in a dampening term could increase or decrease the $\mathrm{P} / \mathrm{R}$ ratio-but only to a limit of one. Error in a bias term. however. could decrease the $\mathrm{P} / \mathrm{R}$ ratio to values below one. Examples

Figure 5-15. Water column profile of $f \mathrm{CO}_{2}$ values and temperature at station GB67 on September $14^{\text {th }} .1994$.




Table 5-3. Sensitivity of average $\mathrm{P} / \mathrm{R}$ ratio for southern Green Bay to uncertainties in the terms used to calculate it. "P" = annual areal primary productivity, "J(aw)" = average annual flux of $\mathrm{CO}_{2}$ across the air-water interface. " K " = average transfer coefficient. "delta $\mathrm{C} "=$ average concentration gradient of $\mathrm{CO}_{2}$ across the air-water interface, "excess $\mathrm{CO}_{2} "=$ $\mathrm{CO}_{2}$ respired outside of study site. "carbonate precip" = carbonate precipitation. "chemical uptake" = chemically enhanced $\mathrm{CO}_{2}$ flux and "sum" = sum of all bias terms.

## P/R SENSITMTY TABLE

|  | $\begin{gathered} \mathbf{P} \\ \mathrm{mol} \mathrm{C} \end{gathered}$ | J (aw) mol C | $\begin{aligned} & \mathbf{P} / \mathbf{R} \\ & \text { ratio } \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| Observed | 4.4E+10 | 2.1E+09 | 0.95 |
| dampening terms |  |  |  |
| 2 K | 4.4E+10 | 4.2E+09 | 0.91 |
| $0.5 K$ | $4.4 \mathrm{E}+10$ | 1E+09 | 0.98 |
| 2 delta C | $4.4 \mathrm{E}+10$ | 4.2E+09 | 0.91 |
| 0.5 delta C | $4.4 \mathrm{E}+10$ | 1E+09 | 0.98 |
| 2 P | $8.8 \mathrm{E}+10$ | 2.1E+09 | 0.98 |
| $0.5 P$ | $2.2 \mathrm{E}+10$ | 2.1E+09 | 0.91 |
| bias terms |  |  |  |
| excess CO2 | 4.4E+10 | 1E+09 | 0.98 |
| carbonate precip | $4.4 \mathrm{E}+10$ | 1.8E+09 | 0.96 |
| chemical uptake | $4.4 \mathrm{E}+10$ | 1.4E+09 | 0.97 |
| sum | $4.4 E+10$ | 0 | 1.00 |

of dampening terms include the transfer coefficient $(\mathrm{K})$, the concentration gradient of $\mathrm{CO}_{2}$ across the air-water interface $(\Delta \mathrm{C})$ and the rate of primary productivity $(\mathrm{P})$. Examples of bias terms include the advection of excess $\mathrm{CO}_{2}$ across the boundary of the study site, carbonate precipitation and chemically enhanced $\mathrm{CO}_{2}$ flux across the air-water interface. If the sign of $\Delta \mathrm{C}$ was incorrect. then this too could be considered a bias term. but $\mathrm{CO}_{2}$ concentration gradients in the bay were usually so large that this was not considered an issue.

Beginning with the dampening terms. an uncertainty in $\mathrm{K} . \Delta \mathrm{C}$ or P would have had little impact on the overall $P / R$ ratio. Doubling or halving $K$ or $\Delta C$ would have shifted the $\mathrm{P} / \mathrm{R}$ ratio $\pm \sim 3.5 \%$ to 0.91 and 0.98 respectively. Doubling or halving P would have increased or lowered the $P / R$ ratio to 0.98 and 0.91 respectively.

The bias terms also had little affect on the overall $\mathrm{P} / \mathrm{R}$ ratio. However. they all tended to have a positive bias-meaning they all tended to increase the $\mathrm{P} / \mathrm{R}$ ratio. Using the estimate of excess $\mathrm{CO}_{2}$ advection from above. an influx of $110 \times 10^{7} \mathrm{~mol} \mathrm{C}$ from northern Green Bay would have increased the $\mathrm{P} / \mathrm{R}$ ratio to a value of 0.98 .

Carbonate precipitation would have liberated an equivalent amount of $\mathrm{CO}_{2}$ and thus decreased the $\mathrm{P} / \mathrm{R}$ ratio (McConnaughey et al. 1994). The amount of carbonate permanently buried in the sediment of southern Green Bay has been estimated by Klump and Fitzgerald (1998) to be $\sim 30 \times 10^{7}$ moles per year. A cursory estimate of carbonate loss from southern Green Bay based on the observed decrease in alkalinity from the Fox River northward (see Figure 5-4) gives a similar value of

$$
\left(6 \% \times 2.3 \mathrm{~mol} \mathrm{C}_{\mathrm{A}} \mathrm{~m}^{-3}\right) / 2 \times 4 \times 10^{9} \mathrm{~m}^{3} \cong 28 \times 10^{7} \text { moles }\left[\mathrm{CO}_{3}^{2^{-}}\right] \text {year }^{-1}
$$

where the annual flow of the Fox River during 1994 was measured as $4 \times 10^{9} \mathrm{~m}^{3}$ (Figure $4-7 b)$. Subtracting the carbonate burial term from the net flux of $\mathrm{CO}_{2}$ to the atmosphere increased the $\mathrm{P} / \mathrm{R}$ ratio slightly from 0.95 to 0.96 .

Finally, additional $\mathrm{CO}_{2}$ could have entered the bay via the air-water interface due to chemical enhancement. Under conditions of low turbulence and high pH values. $\mathrm{CO}_{2}$ molecules can react with hydroxide ions and water to form bicarbonate ions (Butler 1982). As a result. $\mathrm{CO}_{2}$ flux due to chemical enhancement can more than double the rate of $\mathrm{CO}_{2}$ flux based on Fickian diffusion alone (Wanninkhof and Knox 1996). The conditions required for significant chemical enhancement were not generally found in Green Bay. However. the absence of chemical enhancement needs to be confirmed. An upper estimate of enhanced $\mathrm{CO}_{2}$ flux was made by doubling the flux estimates of $\mathrm{CO}_{2}$ into the bay in zones 2 and 3 . Doubling the uptake of $\mathrm{CO}_{2}$ in zones 2 and 3 would reduce the overall flux of carbon from the bay to the atmosphere by $70 \times 10^{7} \mathrm{~mol} \mathrm{C} \mathrm{yr}{ }^{-1}$ which in turn would increase the $\mathrm{P} / \mathrm{R}$ ratio to 0.97 .

Clearly. none of the factors alone had much influence on the average $\mathrm{P} / \mathrm{R}$ ratio for southern Green Bay. If all of the bias factors were summed, the $\mathrm{P} / \mathrm{R}$ ratio would only increase $5 \%$ to a value of 1.0 . Improving on the accuracy of this estimate would be difficult considering the dynamics of the system observed over two field seasons. Preliminary allochthonous carbon budget

Though many terms of the carbon budget for southern Green Bay are still unresolved. a suppositional budget for allochthonous carbon is presented in Figure 5-16.

Figure 5-16. Allochthonous carbon budget for southern Green Bay. A preliminary budget for allochthonous carbon entering southern Green Bay based on an assumed input of 360 $\times 10^{7}$ moles of particulate organic carbon (POC) per year. "Pin" = measured total phosphorus loading to southern Green Bay. $\mathrm{C}: \mathrm{P}=$ measured stoichiometry of carbon to phosphorus in particulate organic matter (POM) found at the sediment-water interface of Green Bay. See text for definition of other terms. All carbon fluxes are in units of $10^{7}$ moles year ${ }^{-1}$.

## southern Green Bay allochthonous carbon budget



| $\begin{aligned} & \text { Pin }= \\ & C: P= \end{aligned}$ | +07 (800 metric tons) surface sediment POM) | carbon flux* | formula | Klump et al. 1997 <br> Klump et al. 1997 <br> source |
| :---: | :---: | :---: | :---: | :---: |
| A | particulate organic C input | 360 | Pin $\times$ C:P | stoichiometry |
| 8 | particulate organic C sedimentation | 210 | measured | Klump and Fitzgerald (1998) |
| C | remineralized $\mathrm{CO2}$ (sediment) | 56 | measured | Klump and Fitzgerald (1998) |
| D | CO2 export to atmosphere | 210 | measured | this study |
| $E$ | carbonate burial | 30 | measured | Klump and Fitzgerald (1998) |
| $F$ | particulate organic carbon burial | 140 | measured | Klump and Fitzgerald (1998) |
| G | remineralized CO2 (water column) | 0-124 | D-C-E-1 | mass balance |
| H | particulate organic C export | 150-26 | A-B-G | mass balance |
| 1 | "excess" CO2 import | 124-0 | $D-C-E-G$ | mass balance |

check $\quad A=F+G+C+H+14(C H A)=360$
check
$D=C+E+G+I=210$

- units $=10^{7}$ moles year'

An upper estimate of $\sim 360 \times 10^{7}$ moles of particulate organic carbon (POC) are loaded into southern Green Bay from riverine sources each year based on an annual total phosphorus loading of $2.6 \times 10^{7}$ moles and an observed C:P stoichiometry of $141(\sim 140)$ for particulate organic matter (POM) at the Green Bay sediment-water interface (Klump et al. 1997).

This estimate of allochthonous POC assumes that all of the phosphorus entering the bay is already fixed in organic matter. It also assumes that the $\mathrm{C}: \mathrm{P}$ stoichiometry of 141 represents the average $\mathrm{C}: \mathrm{P}$ stoichiometry of POM entering the bay from riverine sources. In reality, both assumptions may be false. Some of the phosphorous entering the bay may be biologically unavailable. Another unknown fraction of the phosphorus input may stimulate new production within the bay.

Regardless. the fate of allochthonous POC can be constrained to some degree based on measurements of other terms in the carbon budget. To begin. Klump and Fitzgerald (1998) have measured a sedimentation rate of $210 \times 10^{7}$ moles of POC per year. Of that amount, approximately $140 \times 10^{7}$ moles are permanently buried while the remaining fraction returns to the water column as remineralized inorganic carbon ( $\sim 56 \mathrm{x}$ $10^{7}$ moles of $\mathrm{CO}_{2}$ and $\sim 14 \times 10^{7}$ moles of $\mathrm{CH}_{4}$ ) (Klump and Fitzgerald 1998). The amount of carbonate permanently buried each year is estimated to be $30 \times 10^{7}$ moles (Klump and Fitzgerald 1998; this study, see above). Finally, the flux of $\mathrm{CO}_{2}$ from the bay to the atmosphere averages $210 \times 10^{7}$ moles per year based on the observations of this study.

Based on an initial loading of $360 \times 10^{7}$ moles, a maximum of $58 \%$ of the POC settles to the sediments leaving a minimum of $42 \%$ of the POC (or $150 \times 10^{7}$ moles)
unaccounted for. Similarly, the amount of unaccounted for $\mathrm{CO}_{2}$ leaving the system via the air-water interface is equal to

$$
210 \times 10^{7}-56 \times 10^{7} \text { (from sediment) }-30 \times 10^{7} \text { (carbonate burial) }
$$

or $124 \times 10^{7}$ moles $\mathrm{CO}_{2}$ (i.e. $59 \%$ of the air-water $\mathrm{CO}_{2}$ flux). The subtraction of the carbonate term assumes that the carbonate precipitated within the bay-releasing an equal number of moles of $\mathrm{CO}_{2}$.

By mass balance, the amount of allochthonous POC exported out of southern Green Bay each year should equal $150 \times 10^{7}$ moles minus the amount respired within the water column of the southern bay. If all of the allochthonous POC is exported back out of the system, then approximately $124 \times 10^{7}$ moles of allochthonous "excess" $\mathrm{CO}_{2}$ must enter the southern bay in order to balance the flux of $\mathrm{CO}_{2}$ to the atmosphere. Likewise, a maximum of $124 \times 10^{7}$ moles of allochthonous POC could be respired within the water column of southern Green Bay. The remaining $26 \times 10^{7}$ moles of POC would have to be exported out of the study site in order to achieve mass balance.

If the allochthonous POC input was smaller (e.g. the average C:P stoichiometry of POM was equal to 116), then the export of POC would decrease and could change sign depending on the input of excess $\mathrm{CO}_{2}$. If some of the phosphorus stimulated new production within the bay, then an increase in the input of excess $\mathrm{CO}_{2}$ from outside of the system would be required the balance the budget.

Though the uncertainty in many of the terms of this carbon budget are large. it illuminates which terms are important and. on that account, the direction of future research.

## Conclusions

Based on over 1800 measurements of surface water $f \mathrm{CO}_{2}$ and the transfer coefficients derived in Chapter 3, southern Green Bay (south of Chambers Island) exported $180 \times 10^{7}$ moles of $\mathrm{CO}_{2}$ to the atmosphere in 1994 and $240 \times 10^{7}$ moles of $\mathrm{CO}_{2}$ in 1995. While the entire study site exported $\mathrm{CO}_{2}$ to the atmosphere, the southern most portion of the bay ( $\sim 1000 \mathrm{~km}^{2}$ ) imported $\mathrm{CO}_{2}$ over the year.

Heating of the water column during summer caused a $\sim 138 \%$ increase in $f \mathrm{CO}_{2}$ $\left(0^{\circ} \mathrm{C}: 320 \mu \mathrm{~atm} .23^{\circ} \mathrm{C}:-762 \mu \mathrm{~atm}\right.$, equation $\left.5-15\right)$ which was moderated to varying degrees throughout the bay by autotrophic $\mathrm{CO}_{2}$ uptake. Immediately after destratification of the water column. surface water $f \mathrm{CO}_{2}$ values rose sharply as $\mathrm{CO}_{2}$ produced through benthic bacterial metabolism spread throughout the water column. Rapidly dropping water temperatures quickly depressed $\mathrm{CO}_{2}$ fugacities to the point where. by ice cover. the surface waters of Green Bay were slightly below equilibrium with respect to atmospheric $\mathrm{CO}_{2}$.

The conclusions of this study can neither support nor refute Cole et al. (1994) who conclude that lakes, in general, export $\mathrm{CO}_{2}$ to the atmosphere. However. the observed spatial and temporal heterogeneity of surface water $f \mathrm{CO}_{2}$ in southern Green Bay points to the fact that decisions on whether or not a system imports or exports $\mathrm{CO}_{2}$ to the atmosphere cannot be made from single time or space point measurements. Of the 1835 lakes included in Cole's survey, less than 6\% (106) were surveyed over an entire seasonal
cycle. Nearly $88 \%$ (1612) of the lakes were sampled only once in the autumn when fluctuations in $f \mathrm{CO}_{2}$ due to falling temperatures and mixing of the water column are at their greatest. An additional $\sim 3 \%(60)$ of the lakes were only sampled during the summer when substantial increases in $f \mathrm{CO}_{2}$ caused by thermal effects alone could easily overwhelm the autotrophic depression of $f \mathrm{CO}_{2}$ in an oligotrophic system.

Estimates of the $\mathrm{P} / \mathrm{R}$ ratio in each of the six zones along the main axis of Green Bay rose from values below one at the mouth of the Fox River (zone 1) to values higher than one in zones 2 and 3. Further north. P/R ratios again dropped below one in zones 4,6 and 7. The physiological reasons for this were beyond the scope of this study but probably related to differences in light or nutrient limitation on primary productivity as well as differences in zooplankton grazing rates and bacterial respiration (Sager et al. 1984; Sager and Richman 1990, 1991; del Giorgio et al. 1997). Future research might focus on the relationship between heterotrophy and autotrophy at distances farther from the land-water interface. As the affects of terrestrial loading on community structure and activity should diminish with distance-so should the $\mathrm{P} / \mathrm{R}$ ratio eventually rise to a value of one or more.

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## Appendix 1

## Green Bay Stations

GREEN BAY SAMPLING STATIONS

| Station | latitude (N) degrees | longitude (W) degrees | UTM N meters | UTM E meters |
| :---: | :---: | :---: | :---: | :---: |
| FR | 44.520 | -88.012 | 4929949 | 419560 |
| -1 | 44.558 | -87.946 | 4934070 | 424867 |
| 0 | 44.558 | -88.008 | 4934129 | 419943 |
| 1 | 44.611 | -87.883 | 4939901 | 429935 |
| 2 | 44.611 | -87.946 | 4939957 | 424936 |
| 3 | 44.611 | -88.008 | 4940016 | 420016 |
| 4 | 44.658 | -87.758 | 4945022 | 439902 |
| 5 | 44.658 | -87.821 | 4945071 | 434907 |
| 6 | 44.658 | -87.883 | 4945122 | 429991 |
| 7 | 44.658 | -87.946 | 4945178 | 424996 |
| 8 | 44.706 | -87.758 | 4950354 | 439951 |
| 9 | 44.706 | -87.821 | 4950402 | 434961 |
| 10 | 44.706 | -87.883 | 4950454 | 430049 |
| 11 | 44.706 | -87.946 | 4950510 | 425058 |
| 12 | 44.750 | -87.758 | 4955242 | 439997 |
| 13 | 44.750 | -87.821 | 4955290 | 435010 |
| 14 | 44.750 | -87.883 | 4955341 | 430102 |
| 15 | 44.750 | -87.946 | 4955397 | 425115 |
| 16 | 44.794 | -87.696 | 4960085 | 444947 |
| 17 | 44.794 | -87.758 | 4960129 | 440043 |
| 18 | 44.794 | -87.821 | 4960178 | 435059 |
| 19 | 44.794 | -87.883 | 4960229 | 430155 |
| 20 | 44.839 | -87.663 | 4965062 | 447598 |
| 21 | 44.839 | -87.696 | 4965084 | 444990 |
| 22 | 44.839 | -87.758 | 4965128 | 440089 |
| 23 | 44.839 | -87.821 | 4965176 | 435110 |
| 24 | 44.883 | -87.508 | 4969862 | 459879 |
| 25 | 44.883 | -87.571 | 4969895 | 454904 |
| 26 | 44.883 | -87.633 | 4969931 | 450007 |
| 27 | 44.883 | -87.696 | 4969972 | 445031 |
| 28 | 44.883 | -87.758 | 4970016 | 440135 |
| 29 | 44.883 | -87.821 | 4970064 | 435159 |
| 30 | 44.928 | -87.446 | 4974832 | 464803 |
| 31 | 44.928 | -87.508 | 4974861 | 459911 |
| 32 | 44.928 | -87.571 | 4974894 | 454939 |
| 33 | 44.928 | -87.633 | 4974930 | 450046 |
| 34 | 44.928 | -87.696 | 4974971 | 445074 |
| 35 | 44.928 | -87.758 | 4975014 | 440181 |
| 36 | 44.928 | -87.821 | 4975063 | 435210 |
| 37 | 44.975 | -87.383 | 4980027 | 469800 |
| 38 | 44.975 | -87.446 | 4980053 | 464832 |
| 39 | 44.975 | -87.508 | 4980082 | 459943 |
| 40 | 44.975 | -87.571 | 4980115 | 454976 |
| 41 | 44.975 | -87.633 | 4980151 | 450087 |
| 42 | 45.021 | -87.383 | 4985137 | 469824 |
| 43 | 45.021 | -87.446 | 4985163 | 464860 |
| 44 | 45.021 | -87.508 | 4985192 | 459975 |
| 45 | 45.021 | -87.571 | 4985225 | 455012 |
| 46 | 45.067 | -87.321 | 4990226 | 474729 |

GREEN BAY SAMPLING STATIONS

| Station | latitude (N) degrees | longitude (W) degrees | UTM N <br> metars | UTM E motors |
| :---: | :---: | :---: | :---: | :---: |
| E39 | 45.065 | -87.378 | 4990023 | 470241 |
| 47 | 45.067 | -87.383 | 4990247 | 469848 |
| 48 | 45.067 | -87.446 | 4990273 | 464888 |
| 49 | 45.067 | -87.508 | 4990302 | 460007 |
| 50 | 45.067 | -87.571 | 4990335 | 455048 |
| 51 | 45.111 | -87.321 | 4995114 | 474748 |
| 52 | 45.111 | -87.383 | 4995135 | 469871 |
| 53 | 45.111 | -87.446 | 4995161 | 464915 |
| 54 | 45.111 | -87.508 | 4995189 | 460038 |
| 55 | 45.111 | -87.571 | 4995223 | 455082 |
| 56 | 45.156 | -87.258 | 5000095 | 479720 |
| 57 | 45.156 | -87.321 | 5000113 | 474768 |
| 58 | 45.156 | -87.383 | 5000134 | 469895 |
| 59 | 45.156 | -87.446 | 5000160 | 464943 |
| 60 | 45.156 | -87.508 | 5000188 | 460069 |
| 61 | 45.156 | -87.571 | 5000222 | 455117 |
| 62 | 45.200 | -87.133 | 5004959 | 489554 |
| 63 | 45.200 | -87.196 | 5004970 | 484606 |
| 64 | 45.200 | -87.258 | 5004983 | 479736 |
| 65 | 45.200 | -87.321 | 5005001 | 474788 |
| 66 | 45.200 | -87.383 | 5005022 | 469918 |
| 67 | 45.200 | -87.446 | 5005048 | 464970 |
| 68 | 45.200 | -87.508 | 5005076 | 460100 |
| 69 | 45.244 | -87.133 | 5009847 | 489562 |
| 70 | 45.244 | -87.196 | 5009858 | 484617 |
| 71 | 45.244 | -87.258 | 5009871 | 479752 |
| 72 | 45.244 | -87.321 | 5009889 | 474807 |
| 73 | 45.244 | -87.383 | 5009910 | 469941 |
| 74 | 45.244 | -87.446 | 5009936 | 464997 |
| 75 | 45.289 | -86.883 | 5014845 | 509175 |
| 76 | 45.289 | -86.946 | 5014839 | 504235 |
| 77 | 45.289 | -87.133 | 5014847 | 489570 |
| 78 | 45.289 | -87.196 | 5014857 | 484630 |
| 79 | 45.289 | -87.258 | 5014870 | 479768 |
| 80 | 45.289 | -87.321 | 5014888 | 474827 |
| 81 | 45.289 | -87.383 | 5014909 | 469965 |
| 82 | 45.333 | -87.008 | 5019726 | 499373 |
| 83 | 45.333 | -87.071 | 5019729 | 494436 |
| 84 | 45.333 | -87.133 | 5019735 | 489578 |
| 85 | 45.333 | -87.196 | 5019745 | 484641 |
| 86 | 45.333 | -87.258 | 5019758 | 479783 |
| 87 | 45.333 | -87.321 | 5019776 | 474847 |
| 88 | 45.333 | -87.383 | 5019797 | 469988 |
| 89 | 45.379 | -87.008 | 5024836 | 499374 |
| 90 | 45.379 | -87.071 | 5024839 | 494441 |
| 91 | 45.379 | -87.133 | 5024845 | 489587 |
| 92 | 45.379 | -87.196 | 5024855 | 484654 |
| 93 | 45.379 | -87.258 | 5024869 | 479800 |
| 94 | 45.379 | -87.321 | 5024886 | 474867 |

## GREEN BAY SAMPLING STATIONS

| Station | latitude (N) <br> degrees | longitude (W) <br> degrees | UTM $\boldsymbol{N}$ <br> meters | UTM $\boldsymbol{E}$ <br> metars |
| :---: | :---: | :---: | :---: | :---: |
| 95 | 45.425 | -86.758 | 5029975 | 518932 |
| 96 | 45.425 | -86.883 | 5029953 | 509153 |
| 97 | 45.425 | -86.946 | 5029948 | 504225 |
| 98 | 45.425 | -87.000 | 5029947 | 500000 |
| 99 | 45.425 | -87.071 | 5029949 | 494445 |
| 100 | 45.425 | -87.133 | 5029955 | 489595 |
| 101 | 45.425 | -87.196 | 5029965 | 484666 |
| 102 | 45.425 | -87.258 | 5029979 | 479816 |
| 103 | 45.425 | -87.321 | 5029997 | 474887 |
| 104 | 45.471 | -86.821 | 5035073 | 513992 |
| 105 | 45.471 | -86.883 | 5035064 | 509146 |
| 106 | 45.471 | -86.946 | 5035059 | 504221 |
| 107 | 45.471 | -87.008 | 5035057 | 499375 |
| 108 | 45.471 | -87.071 | 5035060 | 494450 |
| 109 | 45.471 | -87.133 | 5035066 | 489603 |
| 110 | 45.471 | -87.196 | 5035076 | 484679 |
| 111 | 45.471 | -87.258 | 5035089 | 479832 |
| 112 | 45.517 | -86.696 | 5040212 | 523744 |
| 113 | 45.517 | -86.821 | 5040183 | 513981 |
| 114 | 45.517 | -86.883 | 5040174 | 509138 |
| 115 | 45.517 | -86.946 | 5040169 | 504218 |
| 116 | 45.517 | -87.008 | 5040168 | 499375 |
| 117 | 45.517 | -87.071 | 5040170 | 494455 |
| 118 | 45.517 | -87.133 | 5040176 | 489612 |
| 119 | 45.517 | -87.196 | 5040186 | 484691 |
| 120 | 45.517 | -87.258 | 5040200 | 479849 |
| 111 | 45.561 | -86.696 | 504501 | 523726 |
| 122 | 45.561 | -86.758 | 5045084 | 518887 |
| 123 | 45.561 | -86.821 | 5045071 | 513970 |
| 124 | 45.561 | -86.883 | 5045062 | 509131 |
| 125 | 45.561 | -86.946 | 5045057 | 504214 |
| 126 | 45.561 | -87.008 | 5045056 | 499376 |
| 127 | 45.561 | -87.071 | 5045058 | 494459 |
| 128 | 45.561 | -87.133 | 5045064 | 489620 |
| 129 | 45.561 | -87.196 | 504074 | 484703 |
| 130 | 45.606 | -86.696 | 5050100 | 523707 |
| 131 | 45.606 | -86.758 | 5050084 | 518872 |
| 132 | 45.606 | -86.821 | 5050071 | 513959 |
| 133 | 45.606 | -86.883 | 5050062 | 509124 |
| 134 | 45.606 | -86.946 | 5050057 | 504211 |
| 135 | 45.606 | -87.008 | 5050055 | 499376 |
| 136 | 45.606 | -87.071 | 5050058 | 494463 |
| 137 | 45.606 | -87.133 | 5050064 | 489628 |
| 138 | 45.606 | -87.196 | 5050074 | 484715 |
| 139 | 45.650 | -86.758 | 5054972 | 518857 |
| 140 | 45.650 | -86.821 | 5054959 | 513948 |
| 141 | 45.650 | -86.883 | 5054950 | 509117 |
| 142 | 45.650 | -86.946 | 5054945 | 504208 |
| 143 | 45.650 | -87.008 | 5054944 | 499377 |
|  |  |  |  |  |

## green bay sampling stations

| Station | latitude ( $N$ ) <br> degrees | longitude (W) <br> dogrees | UTM $N$ <br> metors | UTM $E$ <br> metars |
| :---: | :---: | :---: | :---: | :---: |
| 144 | 45.650 | -87.071 | 5054946 | 494468 |
| 145 | 45.650 | -87.133 | 5054952 | 489636 |
| 146 | 45.696 | -86.696 | 5060099 | 523669 |
| 147 | 45.696 | -86.758 | 5060083 | 518842 |
| 148 | 45.696 | -86.821 | 5060070 | 513937 |
| 149 | 45.696 | -86.883 | 5060061 | 509109 |
| 150 | 45.696 | -87.008 | 5060054 | 499377 |
| 151 | 45.696 | -87.071 | 5060057 | 494472 |
| 152 | 45.742 | -86.696 | 5065210 | 523649 |
| 153 | 45.742 | -86.758 | 5065193 | 518826 |
| 154 | 45.742 | -86.821 | 5065180 | 513925 |
| 155 | 45.742 | -87.008 | 5065165 | 499378 |
| 156 | 45.786 | -86.633 | 5070119 | 528528 |
| 157 | 45.786 | -86.696 | 5070098 | 523631 |
| 158 | 45.786 | -8.758 | 5070082 | 518811 |
| 159 | 45.866 | -87.008 | 5070053 | 499378 |
| 160 | 45.831 | -86.571 | 5075142 | 533320 |
| 161 | 45.831 | -86.633 | 5075118 | 528505 |
| 162 | 45.831 | -86.696 | 5075098 | 523612 |
| 163 | 45.831 | -86.758 | 5075081 | 518796 |
| 164 | 45.831 | -87.008 | 5075053 | 499379 |
| 165 | 45.875 | -86.571 | 5080031 | 533294 |
| 166 | 45.875 | -86.977 | 5079942 | 501785 |

Ice Stations latitude (N) longitude (W)
degrees degrees

|  | degrees | degrees |  |  | aka |
| :---: | :---: | :---: | :---: | :---: | :---: |
| A | 45.028 | -87.292 |  |  | Egg Harbor |
| B | 45.020 | -87.341 |  |  | Horseshoe Point |
| C | 44.886 | -87.501 |  |  | Sand Bay |
| D | 44.828 | -87.732 |  |  | Ernjoys |
| E | 44.667 | -87.780 |  |  | Dyckesville |
| F | 44.520 | -88.014 |  |  | Fox River |
| G | 44.734 | -87.950 |  |  | Geano Beach |
| 17 | 44.794 | -87.758 | 4960129 | 440043 |  |
| 21 | 44.839 | -87.696 | 4965084 | 444990 |  |

## Appendix 2

## Expressing Gas Concentrations

Gas concentrations are commonly expressed as either mole fractions. partial pressures or fugacities. Mole fractions are designated with the notation $x$ (gas) and represent the ratio of moles of a particular gas to the total number of moles of all gases present (or the fraction of a particular gas in one mole of all gases present). For carbon dioxide and methane in air, the units are in parts per million (ppm).

Partial pressures and fugacities are both expressed in units of atmospheres or micro-atmospheres ( $\mu \mathrm{atm}$ ) and take the notation $p$ (gas) and $f$ (gas) respectively. A gas`s partial pressure is simply its mole fraction multiplied by atmospheric pressure. A gas's fugacity takes into account the non-ideal behavior of a real gas due to a slight attraction between the gas molecules and finite molecular volumes. The difference between ideal and real behavior depends somewhat on the gas itself. but more importantly on total pressure, temperature and its mole fraction.

At normal atmospheric pressure and temperature, gas behavior is nearly ideal. For example, for $350 \mathrm{ppm} \mathrm{CO}=$ in air at 1 atmosphere and $20^{\circ} \mathrm{C}$. the $p \mathrm{CO}_{2}$ equals $350 \mu \mathrm{~atm}$ and the $f \mathrm{CO}_{2}$ equals $348.8 \mu \mathrm{~atm}$ (approximately $0.3 \%$ lower than its partial pressure).

Gas concentrations are additionally designated as either wet or dry depending on whether or not water vapor is included in the atmospheric pressure. Atmospheric trace gas concentrations are generally expressed as mole fractions in dry air since both water vapor and total atmospheric pressure can vary significantly. Conversely, a dissolved gas equilibrates with its fugacity in water saturated (wet) air.

Concentrations of dissolved gases are given on both molarity and molality scales ( $M$ (mol/iter) and $M$ ( $\mathrm{mol} / \mathrm{kg}$ ) respectively). The latter scale has the advantage of not being affected by changes in water density due to variations in temperature or pressure. In Green Bay (and most other freshwater environments), the two scales differ by $-0.3 \%$ at the most. Given the accuracy of the measurements in this study, the scales may be considered equivalent (dissolved gas concentrations are given on both scales in the data tables of Appendix 3).

Dissolved gas concentrations are also expressed in terms of their apparent partial pressures or fugacities, especially in conjunction with atmospheric gas concentrations. This allows one to quickly determine the direction of gas flux across the air-water interface.

## Appendix 3 <br> Methane and Carbon Dioxide Data Tables

The following pages contain all measurements of Green Bay surface water methane and carbon dioxide made during the transect cruises of 1993, 1994 and 1995.

## Methane

The methane data tables have the following format:
1 Date (1993, 1994 or 1995)
2 Day - beginning with 1 on January 1
3 Time - of day in hours or transect in hours
4 Latitude
5 Longitude
6 UTM (E) - in meters, corresponding to Longitude
7 UTM (N) - in meters, corresponding to Latitude
8 Dist (km) - cumulative distance along transect
$9 \quad \mathrm{~T}_{\text {eq }}$ - equilibrator temperature in ${ }^{\circ} \mathrm{C}$
$10 \quad \mathrm{~T}_{\mathrm{w}}$ - in situ water temperature in ${ }^{\circ} \mathrm{C}$
$11 \quad \mathrm{x}\left(\mathrm{CH}_{4}\right)_{\text {eq }}$ - equilibrator mole fraction in units of ppm in wet air
$12 p\left(\mathrm{CH}_{4}\right)_{\mathrm{eq}}$ - equilibrator partial pressure in units of $\mu$ atm in wet air
$13\left[\mathrm{CH}_{4}\right]_{1}$ - in silu methane concentration in units of $\mu \mathrm{mol} / \mathrm{kg}$
$14\left[\mathrm{CH}_{4}\right]_{2}$ - in situ methane concentration in units of $\mu \mathrm{mol} / 1$
$15\left[\mathrm{CH}_{4}\right]_{\bmod }$ - corrected methane concentration (eq 2-3) in units of $\mu \mathrm{mol} / \mathrm{l}$
Note that for discrete sample analyses (1993, 23 August and September 1994), an asterisk appears in column 15. Time given in italics in column 3 represents the elapsed time along a particular leg of the day's transect. Generally. a day's transect was split into three legs with each leg beginning or ending at a profile station.

## Carbon Dioxide

The carbon dioxide data tables have the following format:
1 Date (1994 or 1995)
2 Day - beginning with 1 on January 1
3 Latitude
4 Longitude
$5 \quad$ UTM (E) - in meters, corresponding to Longitude

6 UTM (N) - in meters, corresponding to Latitude
7 Dist (km) - cumulative distance along transect
$8 \quad \mathrm{~T}_{\mathrm{eq}}$ - equilibrator temperature in ${ }^{\circ} \mathrm{C}$
$9 \quad \mathrm{~T}_{\mathrm{w}}$ - in situ water temperature in ${ }^{\circ} \mathrm{C}$
10 PSU - estimated salinity in \%o
$11 \quad \mathrm{PhPa}$-atmospheric pressure in hPa
$12 \mathrm{x}\left(\mathrm{CO}_{2}\right)_{\text {eq }}$ - equilibrator mole fraction in units of ppm in dry air
$13 \mathrm{x}\left(\mathrm{CO}_{2}\right)_{\mathrm{w}}$ - warming corrected in situ mole fraction in units of ppm in dry air
$14 f\left(\mathrm{CO}_{2}\right)_{\mathrm{w}}$ - warming corrected in situ fugacity in units of $\mu \mathrm{atm}$ in wet air
$15\left[\mathrm{CO}_{2}\right]$ - warming corrected in situ concentration in units of $\mu \mathrm{mol} / \mathrm{kg}$

## 1993 METHANE DATA




1994 METHANE DATA


































## 

## 

まoo







##  








##  <br> 웅웅 <br> 으릉 <br> 6St 0 Stg poulthol

唇



















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## Appendix 4

## Green Bay Temperature Profiles




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## Appendix 5

## Green Bay $\Sigma \mathrm{CO}_{2}$ Stable Isotope Ratios

The following pages contain all measurements of ${ }^{13} \mathrm{C}$ for $\Sigma \mathrm{CO}_{2}$ collected during the Green Bay transect cruises of 1995. Sampling, extraction and analysis methods are given in Chapter 2. The results are expressed using $\delta^{13} \mathrm{C}$ (\%) notation where

$$
\begin{equation*}
\delta^{13} \mathrm{C}\left(\%_{0}\right)=\left[\left(\mathrm{R}_{\text {sample }}-\mathrm{R}_{\text {standard }}\right) / \mathrm{R}_{\text {sandard }}\right] \times 10^{3} . \tag{A5-1}
\end{equation*}
$$

$R=$ the mass 44/45 ratio of the sample and standard relative to that of the PDB carbonate standard. The $\delta^{13} \mathrm{C}$ value of PDB is defined as $0 \%$ with an absolute ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}$ ratio (R RPDB ) of 0.0112372 (Boutton 1991).

The absolute ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}$ ratio of the sample can be calculated as:

$$
\begin{equation*}
R_{\text {sample }}=\left[\left(\delta^{13} \mathrm{C} / 1000\right)+1\right] \times R_{\text {PDB }} \tag{A5-2}
\end{equation*}
$$

The fractional abundance ( F ) of the ${ }^{13} \mathrm{C}$ isotope can be calculated as:

$$
\begin{equation*}
\mathrm{F}={ }^{13} \mathrm{C} /\left({ }^{13} \mathrm{C}+{ }^{12} \mathrm{C}\right)=\mathrm{R} /(\mathrm{R}+1) \tag{A5-3}
\end{equation*}
$$

The molarity of each $\Sigma \mathrm{CO}_{2}$ sample was determined manometrically on the isotope extraction line. Preliminary comparisons of the manometrically determined concentrations to concurrently measured samples using coulometry $(\mathrm{n}=6$ ) show a negative bias in the manometrically determined concentrations. A preliminary correction factor is given as:
$\Sigma \mathrm{CO}_{2 \text { CORRECTED }}(\mathrm{mM})=0.31057+0.90149\left[\Sigma \mathrm{CO}_{2 R A W}\right]\left(\mathrm{r}^{2}=0.998\right)$.

Station coordinates are given in Appendix 1.

| sample\# | station | depth m | collected | calendar day | del 13C ( $\mathrm{K}_{0}$ ) | DIC (raw) mM | DIC (corr) mM |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 73 | 6 | 1 | 22-May-95 | 142 | 0.03 | 2.11 | 2.21 |
| 79 | 6 | 7.2 | 22-May-95 | 142 | -0.23 | 2.08 | 2.19 |
| 102 | 6 | 2.2 | 19-Jut-95 | 200 | -0.56 | 2.23 | 2.32 |
| 125 | 6 | 2.1 | 29-Aug-95 | 241 | -0.87 | 2.18 | 2.27 |
| 124 | 6 | 7.3 | 29-Aug-95 | 241 | -1.26 | 2.22 | 2.31 |
| 150 | 6 | 2 | 10-Oct-95 | 283 | -1.05 | 2.24 | 2.33 |
| 160 | 6 | 5 | 10-Oct-95 | 283 | -1.06 | 2.21 | 2.30 |
| 68 | 17 | 2 | 20-Apr-95 | 110 | -1.17 | 2.19 | 2.29 |
| 64 | 17 | 2 | 20-Apr-95 | 110 | -1.25 | 2.31 | 2.39 |
| 90 | 17 | 0.7 | 23-May-95 | 143 | -0.42 | 2.09 | 2.19 |
| 74 | 17 | 0.7 | 23-May-95 | 143 | -0.93 | 2.15 | 2.25 |
| 80 | 17 | 11.3 | 23-May-95 | 143 | -0.6 | 2.07 | 2.18 |
| 104 | 17 | 2 | 19-Jul-95 | 200 | -0.64 | 2.22 | 2.31 |
| 103 | 17 | 2 | 19-Jut-95 | 200 | -0.69 | 2.22 | 2.31 |
| 105 | 17 | 5.1 | 19-Jut-95 | 200 | -0.74 | 2.22 | 2.31 |
| 106 | 17 | 10.2 | 19-Jul-95 | 200 | -0.99 | 2.21 | 2.30 |
| 107 | 17 | 13.2 | 19-Jut-95 | 200 | -2.73 | 2.31 | 2.39 |
| 123 | 17 | 2 | 29-Aug-95 | 241 | -0.97 | 2.14 | 2.24 |
| 133 | 17 | 5.3 | 29-Aug-95 | 241 | -0.3 | 2.11 | 2.21 |
| 138 | 17 | 8.2 | 29-Aug-95 | 241 | -0.49 | 2.15 | 2.25 |
| 139 | 17 | 12.1 | 29-Aug-95 | 241 | -1.36 |  |  |
| 149 | 17 | 2 | 10-Oct-95 | 283 | -0.61 | 2.16 | 2.26 |
| 155 | 17 | 10 | 10-Oct-95 | 283 | -0.7 | 2.16 | 2.26 |
| 126 | 21 | 0.5 | 22-Aug-95 | 234 | -0.33 | 2.14 | 2.24 |
| 127 | 21 | 3.1 | 22-Aug-95 | 234 | -0.2 | 2.14 | 2.24 |
| 141 | 21 | 3.1 | 22-Aug-95 | 234 | -0.27 | 2.15 | 2.25 |
| 128 | 21 | 6.2 | 22-Aug-95 | 234 | -0.47 | 2.16 | 2.26 |
| 140 | 21 | 9.1 | 22-Aug-95 | 234 | -0.39 | 2.15 | 2.25 |
| 137 | 21 | 12.1 | 22-Aug-95 | 234 | -1.26 | 2.23 | 2.32 |
| 136 | 21 | 15.2 | 22-Aug-95 | 234 | -3.08 | 2.30 | 2.38 |
| 108 | 25 | 2 | 28-Jut-95 | 209 | -0.35 | 2.21 | 2.30 |
| 109 | 25 | 22.5 | 28-Jut-95 | 209 | -2.12 | 2.37 | 2.44 |
| 56 | 32 | 1 | 19-Apr-95 | 109 | -0.19 | 2.13 | 2.23 |
| 57 | 32 | 21.2 | 19-Apr-95 | 109 | -0.02 | 2.14 | 2.24 |
| 75 | 32 | 0.9 | 23-May-95 | 143 | -0.18 | 2.04 | 2.15 |
| 86 | 32 | 5.1 | 23-May-95 | 143 | -0.24 | 2.00 | 2.12 |
| 87 | 32 | 10 | 23-May-95 | 143 | 0.09 | 2.01 | 2.12 |
| 81 | 32 | 21.6 | 23-May-95 | 143 | -0.55 | 2.10 | 2.21 |
| 120 | 32 | 2.3 | 20-Aug-95 | 232 | -0.33 | 2.10 | 2.20 |
| 121 | 32 | 5.2 | 20-Aug-95 | 232 | -0.35 | 2.12 | 2.22 |
| 143 | 32 | 5.2 | 20-Aug-95 | 232 | -0.39 | 2.11 | 2.21 |
| 134 | 32 | 7.8 | 20-Aug-95 | 232 | -0.64 | 2.12 | 2.22 |
| 132 | 32 | 10.1 | 20-Aug-95 | 232 | -0.6 | 2.05 | 2.16 |
| 142 | 32 | 12.7 | 20-Aug-95 | 232 | -0.72 | 2.12 | 2.22 |
| 130 | 32 | 15.1 | 20-Aug-95 | 232 | -0.92 | 2.15 | 2.25 |
| 135 | 32 | 17.7 | 20-Aug-95 | 232 | -1.58 | 2.20 | 2.29 |
| 131 | 32 | 20.3 | 20-Aug-95 | 232 | -2.89 | 2.26 | 2.35 |


| sample\# | station | depth m | collected | calendar day | del 13C (\%) | DIC (raw) mM | DIC (corr) mM |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 151 | 32 | 2 | 06-Oct-95 | 279 | -0.76 | 2.13 | 2.23 |
| 168 | 32 | 5 | 06-Oct-95 | 279 | -0.59 | 2.13 | 2.23 |
| 156 | 32 | 10 | 06-Oct-95 | 279 | -0.72 | 2.11 | 2.22 |
| 164 | 32 | 20 | 06-Oct-95 | 279 | -0.6 | 2.09 | 2.20 |
| 170 | 32 | 2 | 09-Nov-95 | 313 | -1.15 | 2.18 | 2.28 |
| 172 | 32 | 5 | 09-Nov-95 | 313 | -1.15 | 2.15 | 2.25 |
| 175 | 32 | 10 | 09-Nov-95 | 313 | -1.16 | 2.17 | 2.27 |
| 171 | 32 | 20.7 | 09-Nov-95 | 313 | -1.36 | 2.17 | 2.27 |
| 112 | 33 | 2 | 26-JuL-95 | 207 | -0.34 | 2.20 | 2.30 |
| 113 | 33 | 12.2 | 26-Jut-95 | 207 | -1.72 | 2.31 | 2.39 |
| 58 | 43 | 1 | 19-Apr-95 | 109 | -0.6 | 2.20 | 2.30 |
| 59 | 43 | 28.1 | 19-Apr-95 | 109 | -0.11 | 2.20 | 2.29 |
| 78 | 43 | 0.9 | 24-May-95 | 144 | -0.66 | 2.21 | 2.30 |
| 88 | 43 | 14.8 | 24-May-95 | 144 | 0.08 | 2.06 | 2.17 |
| 82 | 43 | 28 | 24-May-95 | 144 | -0.89 | 2.25 | 2.34 |
| 148 | 43 | 2 | 06-Oct-95 | 279 | -0.56 | 2.14 | 2.24 |
| 157 | 43 | 10 | 06-Oct-95 | 279 | -0.58 | 2.12 | 2.22 |
| 163 | 43 | 15 | 06-Oct-95 | 279 | -0.56 | 2.14 | 2.24 |
| 159 | 43 | 20 | 06-Oct-95 | 279 |  | 2.13 | 2.23 |
| 162 | 43 | 27 | 06-Oct-95 | 279 | -0.46 | 2.13 | 2.23 |
| 60 | 64 | 1 | 19-Apr-95 | 109 | 0.56 | 2.14 | 2.24 |
| 61 | 64 | 24.2 | 19-Apr-95 | 109 | -0.03 | 2.14 | 2.24 |
| 89 | 64 | 1.2 | 24-May-95 | 144 | -1.26 | 2.15 | 2.25 |
| 76 | 64 | 1.2 | 24-May-95 | 144 | -1.58 | 2.30 | 2.39 |
| 84 | 64 | 19 | 24-May-95 | 144 | -0.09 | 2.09 | 2.19 |
| 146 | 64 | 2 | 09-Oct-95 | 282 | -0.27 | 2.15 | 2.24 |
| 167 | 64 | 5 | 09-Oct-95 | 282 | -0.06 | 2.10 | 2.20 |
| 154 | 64 | 10 | 09-Oct-95 | 282 | 0.3 | 2.03 | 2.14 |
| 166 | 64 | 20 | 09-Oct-95 | 282 | -0.59 | 2.11 | 2.21 |
| 169 | 64 | 23 | 09-Oct-95 | 282 | -0.06 | 2.10 | 2.21 |
| 62 | 67 | 0.8 | 19-Apr-95 | 109 | -0.56 | 2.16 | 2.26 |
| 63 | 67 | 27.7 | 19-Apr-95 | 109 | -0.5 | 2.16 | 2.26 |
| 77 | 67 | 1 | 24-May-95 | 144 | 0.54 | 2.09 | 2.19 |
| 91 | 67 | 1 | 24-May-95 | 144 | -0.13 | 2.10 | 2.21 |
| 85 | 67 | 15 | 24-May-95 | 144 | 0.19 | 2.18 | 2.27 |
| 83 | 67 | 27.7 | 24-May-95 | 144 | 0.36 | 2.06 | 2.16 |
| 161 | 67 | 2 | 09-Oct-95 | 282 | -0.27 | 2.12 | 2.22 |
| 147 | 67 | 2 | 09-Oct-95 | 282 | -0.35 | 2.18 | 2.27 |
| 158 | 67 | 10 | 09-Oct-95 | 282 | -0.32 | 2.12 | 2.22 |
| 165 | 67 | 20 | 09-Oct-95 | 282 | 0.06 | 2.08 | 2.18 |
| 152 | 67 | 27 | 09-Oct-95 | 282 | -0.05 | 2.11 | 2.21 |
| 34 | D | 1 | 21-Feb-95 | 52 | -1.8 | 2.58 | 2.64 |
| 38 | D | 7 | 21-Feb-95 | 52 | -5.99 | 3.24 | 3.23 |
| 43 | D | 7 | 21-Feb-95 | 52 | -6.09 | 3.28 | 3.27 |
| 114 | E39 | 2 | 25-Jut-95 | 206 | 0.13 | 2.18 | 2.27 |


| sample\# | station | depth m | collected | calendar day | del 13C (\%) | DIC (raw) mM | DIC (corr) mM |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 115 | E39 | 10 | 25-Jut95 | 206 | -0.29 | 2.22 | 2.31 |
| 116 | E39 | 14.9 | 25-Jut95 | 206 | -1.62 | 2.29 | 2.38 |
| 117 | E39 | 20.2 | 25-Jut-95 | 206 | -1.77 | 2.29 | 2.38 |
| 119 | E39 | 27.1 | 25-Jul-95 | 206 | -2.23 | 2.31 | 2.39 |
| 35 | EJ | 1 | 22-Feb-95 | 53 | -1.4 | 2.37 | 2.45 |
| 40 | EJ | 7 | 22-Feb-95 | 53 | -1.1 | 2.27 | 2.36 |
| 39 | EJ | 7 | 22-Feb-95 | 53 | -0.96 | 2.22 | 2.31 |
| 46 | EJ | 11 | 22-Feb-95 | 53 | -1.63 | 2.33 | 2.41 |
| 45 | EJ | 15 | 22-Feb-95 | 53 | -2 | 2.47 | 2.54 |
| 55 | FR | 1 | 14-Mar-95 | 73 | -7.7 | 2.91 | 2.93 |
| 53 | FR | 1 | 14-Mar-95 | 73 | -7.53 | 2.89 | 2.91 |
| 50 | FR | 1 | 14-Mar-95 | 73 | -6.31 | 2.71 | 2.75 |
| 65 | FR | 2 | 20-Apr-95 | 110 | -5.83 | 3.27 | 3.25 |
| 72 | FR | 1 | 22-May-95 | 142 | -5.96 | 3.16 | 3.15 |
| 101 | FR | 2 | 19-Jut95 | 200 | -5.65 | 3.41 | 3.39 |
| 100 | FR | 2 | 19-Jul-95 | 200 | -5.61 | 3.39 | 3.37 |
| 122 | FR | 1 | 29-Aug-95 | 241 | -5.07 | 3.00 | 3.02 |
| 153 | FR | 2 | 10-Oct-95 | 283 | -4.92 | 2.78 | 2.82 |
| 51 | GB | 1 | 14-Mar-95 | 73 | -0.65 | 1.86 | 1.99 |
| 52 | GB | 1 | 14-Mar-95 | 73 | -0.61 | 1.70 | 1.84 |
| 37 | H | 1 | 21-Feb-95 | 52 | -0.63 | 2.30 | 2.38 |
| 44 | H | 7 | 21-Feb-95 | 52 | 0.44 | 1.89 | 2.01 |
| 42 | H | 7 | 21-Feb-95 | 52 | -0.17 | 2.14 | 2.24 |
| 36 | SB | 1 | 22-Feb-95 | 53 | -1.41 | 2.38 | 2.45 |
| 41 | SB | 7 | 22-Feb-95 | 53 | -1.34 | 2.31 | 2.39 |
| 129 | SB | 5.1 | 23-Aug-95 | 235 | -0.51 | 2.12 | 2.22 |
| 145 | T2 | 2 | 28-Jut-95 | 209 | -0.18 | 2.11 | 2.22 |
| 110 | T3 | 2 | 28-Jut95 | 209 | 0.05 | 2.18 | 2.27 |
| 111 | T4 | 2 | 28-Jut-95 | 209 | 0.05 | 2.16 | 2.26 |

## Appendix 6

## Wind Speed Computer Program

by Arlindo da Silva
(reprinted with permission)

* file: density.for - last update: 2/14/93 $\begin{array}{ll}\text { (c) } 1993 \text { A. da Silva }\end{array}$
* This program computes converts wind and temperature observations
* from a given height $z$ to the standard 10 m reference level.
* The full stability of the surface layer is taken into consideration.
* 
* 
* *** COPY FREELY BUT DO NOT SELL **
* 
* ALGORITHM: Based on surface layer similarity theory. For details
* see Large \& Pond (1981).
program Z_to_10m
*.
print *
print *. ( ( Observations Convertion to 10 m$))^{\prime}$
print *
print * , 'Options: '
print *' I. Dew-point (Td) as moisture variable'
print ** 2. Relative humidity ( RH ) as moisture variable'
print *. 'Which?'
read *, iopt
print *, iopt
print *. 'Enter nz. zl \& z2 (m) for profile: '
read *. nz, zl, z2
print *, nz, zl, z2
$d z=(z 2-z 1) /(n z-1)$
* Initialize L\&P package
call INILP
$i u=10$
$\mathrm{mu}=20$
open(iu, file='z_to_10m.out',form='formatted',status='unknown')
open(mu,file='profile.out',form='formatted',status='unknown')
write(iu.*)
$\therefore W(10 \mathrm{~m}) \mathrm{Z} / \mathrm{L}$ Ts_ta $\mathrm{Qs}-\mathrm{Q}$ CD CT CE (x1000)'
1 continue
* Read observations
* -------------
if ( iopt .eq. 1 ) then

```
print *
print *, 'Enter z(m),W (m/s), p (mb), Ta, Ts, Td (C): '
read(*,*,end=999) z. W. p. Ta, Ts, Td
print *, z, W, p, Ta, Ts, Td
else
    print *
    print *, 'Enter z(m),W (m/s), p (mb), Ta. Ts (C), RH (%):'
    read(*,*.end=999) z. W, p, Ta,Ts, rh
    print *, z, W, p, Ta, Ts, RH
    Td = DEWPT (Ta. RH )
end if
```

* Do the calculation
* 

$\mathrm{TaK}=\mathrm{Ta}+273$.
$\mathrm{dT}=\mathrm{Ts}-\mathrm{Ta}$
$\mathrm{Qa}=\mathrm{SSH}(\mathrm{p}, \mathrm{Td})$
$Q s=S S H(p, T s)$
$\mathrm{dQ}=\mathrm{Qs}-\mathrm{Qa}$
call LPZ (CD, CT, CE, zdl, wlo, tal0, dth 10, dq10.
z, w, TaK, dT, dQ)

* print out results
* 

write(iu, 100) wl0, zdl, dth 10, dq 10.
1000 * CD, $1000^{*} \mathrm{CT}, 1000^{*} \mathrm{CE}$
100 format( $1 \mathrm{x}, \mathrm{f8} .2, \mathrm{f8} .4 .5 \mathrm{f8} .2$ )

```
print *
print*,' Wind speed at 10 m: '. wl0
print *.' Z/L at 10 m:', zdl
```



```
print*.' Qs-Q at 10 m:', dql0
print *,' CD. CT & CE (xl000) at 10 m: ',
    1000*CD, 1000*CT, 1000*CE
```

print *
do $20 \mathrm{i}=1, \mathrm{nz}$
$z=z l+d z^{*}(i-1)$
$z \ln z=\operatorname{alog}(z / 10$.
$\mathrm{Wz}=\mathrm{wl} 0^{*} \mathrm{RM}$ (cd, zdl, z, zlnz)
write(mu,*) z, Wz
20 continue

## go to 1

999 continue
close(iu)
close(mu)
stop
end

* large-pond.f - last update: 09/13/92 (ams/ccy)
* This file contains routines for computation of transfer
* coefficients and other surface layer quantities using Large
* \& Pond formulation.
subroutine INILP
include 'lp.h'
deltaz $=(z d \mathrm{db}-\mathrm{zdla})$ float(nzdl -1$)$
* Calculate psi's
* --------
do $10 i=1$. nzd
zfit $(\mathrm{i})=$ float $(\mathrm{i}-\mathrm{i})^{*}$ deltaz + zdla
$z \mathrm{fit}(\mathrm{i})=\mathbf{z f t}(\mathrm{i})$
$\operatorname{psim}(i)=\operatorname{EXPSIM}(z \operatorname{zfit}(i))$
psit(i) $=\operatorname{EXPSIT}(\mathbf{z f i t}(\mathrm{i}))$
10 continue
* Calculate spline fit
* 

call SPLINE ( bbm, ccm, ddm, nzdl, zfit, psim )
call SPLINE ( bbt. cct, ddt. nzdl. zfit. psit )
return
end
*.
subroutine LPZ ( CD, CT, CE, zdl, wlo, tal0, dth10, dq10, z. w, ta, dth, dq )

* This routine calculates the corrected values for
* CD, CT, CE, w, ta, dth, and dq from height $z$ to 10 m .
* The routine assumes that dth is theta(sea) - theta(air).
* Upon input, however, dth may be $t$ (sea) - $t$ (air) if one
* does not need the accuracy that the theta values provide.
* Units for input/output: $w$ in $\mathrm{m} / \mathrm{s}$, ta in K . dth in $\mathrm{K}, \mathrm{dq}$
* in $\mathrm{g} / \mathrm{kg}$. Upon output zdl is actually $10 / \mathrm{L}$.
* 
* Notice that $C D=C D(z=10), C T=C T(z=10)$, etc...
* 
* No. of iteration and tolerance

parameter $($ itmax $=100$, eps $=1 . E-4$, gamma $=0.01)$
common / Ipneut / CDN, fofzdl
real $z \ln z$

```
\(z \ln z=\operatorname{alog}(z / 10\).
\(\mathrm{m}=0\)
```

* First guess
* ---------
$\mathrm{w} 10=\mathrm{w}$
tal0 $=$ ta
$\mathrm{dth} 10=\mathrm{dth}$
$\mathrm{dq} 10=\mathrm{dq}$
Ts = dth $+\mathrm{ta}+$ gamma * $z$
Tsg $10=$ Ts - gamma* 10 .
* NOTE: zdl below actually means 10 / L

* Trivial case: $z=10$. No height adjustment
if ( z .eq. 10. ) then call LPIO (CD, CT, CE, zdl, w, ta, dth, dq ) return
end if
* Otherwise, iterations are needed
* Find first guess zdl
call LPIO ( CD, CT, CE, ozdI, w10, ta10, dth 10, dq10)
* Adjust values

```
wl0 =w /RM(CD, ozdl, z, zlnz)
```

dth $10=$ dth $/ R T(C D, C T$. ozdl, z, zlnz $)$
$\mathrm{dq} 10=\mathrm{dq} / \mathrm{RE}(\mathrm{CD}, \mathrm{CE}$, ozdl$, ~ z, ~ z \operatorname{lnz})$
ta $10=\operatorname{Tsg} 10-\mathrm{dth} 10$

* Iterate...
* -------do $10 \mathrm{i}=1$, itmax
* Calculate a $\quad \mathrm{z} /$
* -------------
call LP10( CD, CT, CE, zdl, w10, tal0, dth 10, dq10)
* Find adjusted values
* -----------------
$w 10=w / R M(C D, \quad z d l, z, z \ln z)$
fofzdl $=C D / C D N$
dth $10=$ dth $/ R T(C D, C T, z d l, z, z \operatorname{lnz})$
$\mathrm{dq} 10=\mathrm{dq} / \operatorname{RE}(C D, C E, z d l, z, z \operatorname{lnz})$
tal0 $=$ Tsgl0-dth 10
$\mathrm{m}=\mathrm{m}+1$
* If zdl and ozdl are close enough. we're done

```
    if ( abs( zdl -ozdl ) .le. abs(eps* ozdl) ) then
        return
    end if
```

* If not. we must iterate again
* 

$\mathrm{ozdl}=\mathbf{z d l}$

10
continue

* Failure to converge

print *, 'zdl didnt converge after 100 iter: $w$, wl0, $\mathrm{dt}=$ ', w, w10, dth
if ( $\mathrm{w}^{*}$ wlo.lt. 0.) then
print *,'bad correction:w wlo dth dth 10 dq dq 10 ta tal $0^{\prime}$
print *, w, wl0, dth, dth 10, dq, dq10, ta, tal0
end if
return
end
*.
subroutine LP10 ( CD, CT, CE, ZDL, Winput, Ta, DT, DQ )
real $C D, C T, C E$, ZDL. Winput. Ta. DT, DQ
* This subroutine returns the drag coefficient computed using
* the Large and Pond $(1981,1982)$ formulation. This version
* iterates the drag coefficients/stability correction.
* Units: Winput in $\mathrm{m} / \mathrm{s}$, Ta in K, DT in K, DQ in $\mathrm{g} / \mathrm{kg}$
* 

parameter ( cappa $=0.4, g=9.81, Z=10 ., \operatorname{cg} Z=$ cappa ${ }^{*} g * Z$ )
parameter $\left(\mathrm{pi}=3.1415926, \mathrm{pid} 2=0.5^{*} \mathrm{pi}\right)$

* maximum number of iterations and fractional error

parameter $(I T M A X=15, E P S=1 . e-4)$
common / lpneut / CDN, fofzdl
* lower bound on $W(1 \mathrm{~m} / \mathrm{s})$ to avoid singularities
* (consistent with Tremberth et al., 1989)
* 

$\mathrm{W}=\operatorname{amaxl}$ ( $1 .$, Winput )

* first compute neutral drag coefficient
* (for now uses L\&P original formula; same as
* Harrison 1989). The number below also
* comes from Harrison's paper.

```
ccc if (W.ge. 11.) then
ccc \(\quad \mathrm{CDN}=\left(0.49+0.065^{*} \mathrm{~W}\right) *\) l. \(\mathrm{E}-3\)
ccc else
ccc \(\quad \mathrm{CDN}=1.205 * 1 . \mathrm{E}-3\)
ccc
    end if
```

* Trenberth et al. dependence.
* if ( W .ge. 10. ) then
$\mathrm{CDN}=(0.49+0.065 * W) * 1 . E-3$
else if ( $W$.ge. 3. ) then
$\mathrm{CDN}=1.14$ * $1 . \mathrm{E}-3$
else
$\mathrm{CDN}=(0.62+1.56 / \mathrm{W}) * \mathrm{I} . \mathrm{E}-3$
end if
* Neutral Dalton number
* ---n-_-
$\mathrm{CEN}=1.2 * 1 . \mathrm{E}-3$
* neutral Stanton number (Pond's notes)
* 

```
sguess = - DT
```

iter $=0$

1000 continue if ( sguess .It. 0.) then

```
        CTN = 1.2* 1. E-3
```

    else
        \(C T N=0.75 * 1 . E-3\)
    end if
    * stability independent part of ZDL

```
    S = - (cgZ/( W**2.*Ta ) )
    *(DT + (1.72 E -6)* (Ta**2.)* DQ )
```

* first guess for ZDL
*     - oZDL $=S^{*}$ CTN $/ C D N^{* *} 1.5$
* now iterate to find stability parameter
* 

do $10 \mathrm{it}=1, I \mathrm{TMAX}$

* CD/CT with previous ZDL
* 

call FORMCD ( CD, f, oZDL, CDN )
call FORMCT (CT, oZDL, CTN, CDN, f) call FORMCE ( CE, oZDL, CEN, CDN, f)

* update ZDL
$\mathrm{ZDL}=\mathrm{S}^{*} \mathrm{CT} / \mathrm{CD}^{* *} 1.5$
* good enough?
if ( abs(oZDL-ZDL) .le. abs(EPS*oZDL) ) go to 11
oZDL $=$ ZDL
10 continue
print *. 'CDLP: W, Ta, DT, DQ, Z/L: ', W, Ta, DT, DQ, ZDL print *, 'CDLP: ZDL iteration did not converge.'

II continue

* consistency check (the first guess is $\operatorname{sign}(Z / L)=\operatorname{sign}(-D T)$,
* if not, iterate just once)
* 

if ( ZDL * sguess .lt. 0.) then
iter $=$ iter +1
if ( iter .gt. 1 ) stop 'CDLP: too many steps.'
sguess = ZDL
go to 1000
end if

* compute CD with final ZDL estimate
* call FORMCD ( CD, f, ZDL, CDN )
call FORMCT ( CT, ZDL, CTN, CDN, f)
call FORMCE ( CE, ZDL, CEN, CDN, f)
cec print *, 'W CDCDN $\mathrm{f}^{\prime}, \mathrm{W}, \mathrm{f}^{*} \mathrm{CDN}, \mathrm{CDN}, \mathrm{f}$, it
return
end
* 

subroutine FORMCD ( $C D, f, Z D L, C D N$ )

* Given the stabilitility parameter ZDL and the neutral
* drag coefficient CDN, this function returns the full CD
* and the stability correction $f$.
parameter $($ cappa $=0.4)$
* compute stability correction
* --------------------------
$\mathrm{psi}=\operatorname{SPSIM}(Z D L)$
$\mathrm{f}=1 . /(1 .-\operatorname{sqrt}(\mathrm{CDN}) * \mathrm{psi} / \text { cappa })^{* *} 2$.
* form the drag coefficeint
* 

$C D=C D N * f$
return
end
*
subroutine FORMCT ( CT, ZDL, CTN, CDN, f)

* Given the stabilitility parameter ZDL. the neutral
* drag coefficient CDN. this subroutine returns the full CT
* including the stability correction.
parameter $($ cappa $=0.4)$
* compute stability correction
* 

psi = SPSIT( ZDL )
$g=f /\left(1 .-\mathrm{psi}^{*} \mathrm{CTN} /\left(\right.\right.$ cappa $\left.\left.\left.^{*} \operatorname{sqrt(CDN}\right)\right)\right)$

* form the coefficeint
* 

$\mathrm{CT}=\mathrm{CTN} * \mathrm{~g}$
return
end
*
subroutine FORMCE ( CE, ZDL, CEN, CDN, f)

* Given the stability ZDL, CDN, CEN, and the ratio $f$.
* this routine returns CE with stability correction.
parameter $($ cappa $=0.4)$
* compute stability correction
* 

psi $=\operatorname{SPSIT}($ ZDL $)$
$\mathrm{g}=\mathrm{f} /\left(\mathrm{I} .-\mathrm{psi}{ }^{*} \mathrm{CEN} /(\right.$ cappa * $\left.\left.\operatorname{sqrt(CDN})\right)\right)$

* Form the coefficient
* 

$C E=C E N * g$
return
end
*.
function RM (CD, z10dl, z, zlnz )

```
    real zlnz
    cappa = 0.4
    s=zlnz - SPSIM (z/10.* z10dl ) + SPSIM(z10dl )
    RM=I.+(sqrt(CD )/cappa )*s
    return
    end
*
    function RT ( CD, CT, z10dl, z, zlnz )
    real zlnz
    sig = zlnz - SPSIT( z/10.* zl0dl ) + SPSIT( zl0dl )
    RT = 1. + (CT / sqr(CD ) )* sig
    return
    end
*
```

    function RE (CD, CE, z10dl, z zinz )
    real zlnz
    \(\operatorname{sig}=z \operatorname{lnz}-\operatorname{SPSIT}(z / 10 . * z 10 d l)+\operatorname{SPSIT}(z 10 d l)\)
    \(R E=1 .+(C E / s q r(C D)) *\) sig
    return
    end
    *.
function SPSIM ( zdl )
include 'lp.h'
if ( zdl .le. zdla .or. zdl .ge. zdlb ) then
SPSIM $=$ EXPSIM ( 2 dl )
else
SPSIM = SEVAL( zdl. zfit. psim, nzdl, bbm, ccm, ddm )
end if
return
end
*.
function SPSIT ( zdl )

```
    include 'lp.h'
    if( zdl .le. zdla .or. zdl .ge. zdlb ) then
        SPSIT = EXPSIT ( zdl )
    else
        SPSIT = SEVAL( zdl, zfit. psit, nzdl, bbt, cct, ddt )
    end if
    return
    end
*.
    function EXPSIM (zdl )
    parameter (pid = 3.14159 / 2.0)
    if ( zdl .gt. 0. ) then
        EXPSIM = -7. * zdI
    else
        x = (1. - 16.* zdl )**0.25
        EXPSIM = 2. * alog(0.5*(1. + x ))
            + alog(0.5*(1.0+ x**2. ) )
            -2.0*}\operatorname{atan(x)}+\mathrm{ pid
    end if
    return
    end
*.
    function EXPSIT(zdl )
    if ( zdl .gt. 0.) then
        EXPSIT = -7.* zdl
    else
        x = (1. - 16.* zdl )**0.25
        EXPSIT =2.0* alog(0.5*(1.0+x**2. ))
    end if
    return
    end
```


## C Software for calculation of moisture variables in COADS 14 Jun 1991

## C

## C

$=$
C
C The following is excerpted from "Comprehensive Ocean-Atmosphere Data Set:
C Release I." pg. Al8.
C
C
C 4.4 Moisture Variables
C
C The derived moisture variables ( $Q, R$, and $Q S$ ) are computed using the C FORTRAN functions that are given in [10] and referenced as follows:
C $\quad \mathrm{Q}=\operatorname{SSH}(\mathrm{P}, \mathrm{A}-\mathrm{DP})$
C $\quad \mathrm{R}=\operatorname{HUM}(\mathrm{A}, \mathrm{A}-\mathrm{DP})$
C $\quad \mathrm{QS}=\mathrm{SSH}(\mathrm{P}, \mathrm{S})$
C Inside SSH the mixing ratio is approximated by function WMR. The method
$C$ of computing vapor pressure differs in the untrimmed and trimmed
C summaries. Function ESLO was used in the untrimmed summaries.
C Unfortunately, ESLO is unreliable at physically unrealistic conditions,
C although tests have demonstrated that, at least, no R exceeded $100 \%$.
C Function ES was used instead in the trimmed summaries. These algorithms
C were chosen because of their accuracy and computational efficiency. For
C more detailed information including the original source of these
C techniques see [10].
C
C [10] Schlatter, T. W., and D. V. Baker, 1981: Algorithms for thermodynamic
C calculations. NOAA/ERL PROFS Program Office, Boulder, CO, 34 pp.
C
C
$=-$
$=$
C
C The following text and code is extracted from a later version of [10],
C which differs for these routines only in that some comment lines have
$C$ been updated. In addition, the original code used functions ESAT and
C ESW in HUM and WMR, respectively. The COADS (trimmed) implementation C substituted ES for ESAT or ESW.

## C

C These algorithms were collected, edited, commented, and tested by Thomas W. C Schlatter and Donald V. Baker from August to October 1981 in the PROFS Program C Office, NOAA Environmental Research Laboratories, Boulder, Colorado. Where C possible, credit has been given to the original author of the algorithm and a C reference provided.
C
*.

FUNCTION ESLO(T)
C INCLUDE 'LIB_DEV:[GUDOC]EDFVAXBOX.FOR/LIST'
C Baker, Schlatter 17-MAY-1982 Original version.

C THIS FUNCTION RETURNS THE SATURATION VAPOR PRESSURE OVER LIQUID
C WATER ESLO (MILLIBARS) GIVEN THE TEMPERATURE T (CELSIUS). THE
C FORMULA IS DUE TO LOWE, PAUL R., 1977: AN APPROXIMATING POLYNOMIAL
C FOR THE COMPUTATION OF SATURATION VAPOR PRESSURE. JOURNAL OF APPLIED
C METEOROLOGY, VOL 16, NO. I (JANUARY), PP. 100-103.
C THE POLYNOMIAL COEFFICIENTS ARE A0 THROUGH A6.
DATA A0,A1,A2,A3,A4,A5,A6
$1 / 6.107799961,4.436518521 \mathrm{E}-01,1.428945805 \mathrm{E}-02$,
$22.65064847 \mathrm{IE}-04,3.031240396 \mathrm{E}-06,2.034080948 \mathrm{E}-08$,
3 6.136820929E-11/
$E S=A 0+T^{*}\left(A 1+T^{*}\left(A 2+T^{*}\left(A 3+T^{*}\left(A 4+T^{*}\left(A 5+A 6^{*} T\right)\right)\right)\right)\right.$
IF (ES.LT.0.) $\mathrm{ES}=0$.
ESLO $=\mathrm{ES}$
RETURN
END
*.

FUNCTION ES(T)
C THIS FUNCTION RETURNS THE SATURATION VAPOR PRESSURE ES (MB) OVER
C LIQUID WATER GIVEN THE TEMPERATURE T (CELSIUS). THE FORMULA APPEARS
C IN BOLTON, DAVID, 1980: "THE COMPUTATION OF EQUIVALENT POTENTIAL
C TEMPERATURE." MONTHLY WEATHER REVIEW, VOL. 108, NO. 7 (JULY).
C P. 1047, EQ.(10). THE QUOTED ACCURACY IS 0.3\% OR BETTER FOR
C $-35<T<35 C$.
C INCLUDE 'LIB DEV:[GUDOC]EDFVAXBOX.FOR/LIST'
C Baker, Schlatter 17-MAY-1982 Original version.
C ESO = SATURATION VAPOR PRESSURE OVER LIQUID WATER AT OC
DATA ES0/6.1121/
$\mathrm{ES}=\mathrm{ES} \mathbf{0}^{*} \operatorname{EXP}\left(17.67^{*} \mathrm{~T} /(\mathrm{T}+243.5)\right)$
RETURN
END
*.

FUNCTION HUM(T,TD)
C INCLUDE 'LIB_DEV:[GUDOC]EDFVAXBOX.FOR/LIST'
C G.S. Stipanuk 1973 Original version.
C Reference Stipanuk paper entitled:
C "ALGORITHMS FOR GENERATING A SKEW-T, LOG P
C DIAGRAM AND COMPUTING SELECTED METEOROLOGICAL
C QUANTITIES."
C ATMOSPHERIC SCIENCES LABORATORY
C U.S. ARMY ELECTRONICS COMMAND
C WHITE SANDS MISSILE RANGE, NEW MEXICO 88002
C 33 PAGES
C Baker. Schlatter 17-MAY-1982

C THIS FUNCTION RETURNS RELATIVE HUMIDITY (\%) GIVEN THE
C TEMPERATURE T AND DEW POINT TD (CELSIUS). AS CALCULATED HERE, C RELATIVE HUMIDITY IS THE RATIO OF THE ACTUAL VAPOR PRESSURE TO
C THE SATURATION VAPOR PRESSURE.

HUM $=100 . *(\mathrm{ES}(\mathrm{TD}) / \mathrm{ES}(\mathrm{T}))$
RETURN
END
*

FUNCTION SSH(P,T)
C INCLUDE 'LIB_DEV:[GUDOC]EDFVAXBOX.FOR/LIST
C Baker, Schlatter 17-MAY-1982 Original version.
C THIS FUNCTION RETURNS SATURATION SPECIFIC HUMIDITY SSH (GRAMS OF
C WATER VAPOR PER KILOGRAM OF MOIST AIR) GIVEN THE PRESSURE P
C (MILLIBARS) AND THE TEMPERATURE T (CELSIUS). THE EQUATION IS GIVEN
C IN STANDARD METEOROLOGICAL TEXTS. IF T IS DEW POINT (CELSIUS), THEN
C SSH RETURNS THE ACTUAL SPECIFIC HUMIDITY.
C COMPUTE THE DIMENSIONLESS MIXING RATIO.
$\mathrm{W}=.00 \mathrm{I}^{*} \mathrm{WMR}(\mathrm{P}, \mathrm{T})$
C COMPUTE THE DIMENSIONLESS SATURATION SPECIFIC HUMIDITY.

$$
Q=W /(1 .+W)
$$

$\mathrm{SSH}=1000 .{ }^{*} \mathrm{Q}$
RETURN
END
*

FUNCTION WMR(P,T)
C THIS FUNCTION APPROXIMATES THE MIXING RATIO WMR (GRAMS OF WATER
C VAPOR PER KILOGRAM OF DRY AIR) GIVEN THE PRESSURE P (MB) AND THE
C TEMPERATURE T (CELSIUS). THE FORMULA USED IS GIVEN ON P. 302 OF THE
C SMITHSONIAN METEOROLOGICAL TABLES BY ROLAND LIST (6TH EDITION).

C INCLUDE 'LIB_DEV:[GUDOC]EDFVAXBOX.FOR/LIST'
C Baker. Schlatter 17-MAY-1982 Original version.
C $E P S$ = RATIO OF THE MEAN MOLECULAR WEIGHT OF WATER (18.016 G/MOLE)
C TO THAT OF DRY AIR ( $28.966 \mathrm{G} / \mathrm{MOLE}$ )

DATA EPS/0.62197/
C THE NEXT TWO LINES CONTAIN A FORMULA BY HERMAN WOBUS FOR THE
C CORRECTION FACTOR WFW FOR THE DEPARTURE OF THE MIXTURE OF AIR
C AND WATER VAPOR FROM THE IDEAL GAS LAW. THE FORMULA FITS VALUES
C IN TABLE 89. P. 340 OF THE SMITHSONIAN METEOROLOGICAL TABLES.

## C BUT ONLY FOR TEMPERATURES AND PRESSURES NORMALLY ENCOUNTERED IN <br> C IN THE ATMOSPHERE.

```
X=0.02*(T-12.5+7500./P)
WFW = 1.+4.5E-06*P+1.4E-03*X*X
FWESW = WFW*ES(T)
R = EPS*FWESW/(P-FWESW)
```

C CONVERT R FROM A DIMENSIONLESS RATIO TO GRAMS/KILOGRAM.
$W M R=1000 . * R$
RETURN
END
*

* Routines below added by Arlindo da Silva - November 1993.
* 
* Routines to obtain dew point temperature from air temperature
* and relative humidity. Uses COAS termodynamic package.
* 
* 

function DEWPT ( $\mathrm{T}, \mathrm{RH}$ )
*

* Given the temperature (in C ) and the relative humidity in $\%$,
* this function returns the dew point temperature (in C).
* 

external ZHUM
parameter ( $\mathrm{tol}=0.0001$ )
common / dewprm / rhum, Ta
rhum $=$ rh
$\mathrm{Ta}=\mathrm{T}$
$\mathrm{Tdl}=\mathrm{T}$
$\mathrm{T} \dot{\mathrm{d}} \mathrm{Z}=-200$.
DEWPT $=$ ZBRENT ( ZHUM. TdI, Td2. tol $)$
return
end
*
*
function ZHUM ( Td )
common / dewprm / rhum. Ta
ZHUM = rhum $-\operatorname{HUM}(T a, T d)$
return
end
*.
function ZBRENT (func, $\mathrm{x} 1, \times 2$, tol )

```
parameter (itmax=100,eps=3.e-8)
a=xl
b=x2
fa=func(a)
fb=func(b)
if(fb*fa.gt.0.) then
    print *,'Root must be bracketed for ZBRENT.'
    call exit(1)
end if
fc=fb
do 11 iter=1,itmax
if(fb*fc.gt.0.) then
    c=a
    fc=fa
    d=b-a
    e=d
endif
if(abs(fc).lt.abs(fb)) then
    a=b
    b=c
    c=a
    fa=fb
    fb}=\textrm{fc
    fc=fa
endif
toll=2.*eps*abs(b)+0.5*tol
xm=.5*(c-b)
if(abs(xm).le.toll .or. fb.eq.0.)then
    zbrent=b
    return
endif
if(abs(e).ge.toll .and. abs(fa).gt.abs(fb)) then
    s=fb/fa
    if(a.eq.c) then
        p=2.*xm*s
        q=1.-s
    else
        q=fa/fc
        r=fb/fc
        p=s*(2.*xm*q*(q-r)-(b-a)*(r-l.))
        q=(q-I.)*(r-I.)*(s-1.)
    endif
    if(p.gt.0.) q=-q
    p=abs(p)
    if(2.*p .It. min(3.*xm*q-abs(toll*q),abs(e*q))) then
        e=d
        d=p/q
    else
        d=xm
        e=d
    endif
else
    d=xm
    e=d
```

endif
$a=b$
$f a=f b$
if(abs(d).gt. toll ) then
$b=b+d$
else
$\mathrm{b}=\mathrm{b}+\operatorname{sign}(\mathrm{tol} 1, \mathrm{xm})$
endif
fb=func(b)
11 continue
print *, 'ZBRENT exceeding maximum iterations.'
call exit(1)
zbrent=b
return
end

```
** FILE SPLINE - LAST CHANGE: 06/06/88 (AMS)
**
** THIS FILE CONTAINS ROUTINES TO COMPUTE CUBIC SPLINES. THE *
** ROUTINES ARE BASED ON:
**
* * FORSYTHE. G. E., M. A. MALCOLN AND C. B. MOLER (1977): *
** "COMPUTER METHODS FOR MATHEMATICAL COMPUTATIONS". Prentice-Hall.
**
```


subroutine spline (b, c, d, n, x, y)
integer $n$
real $b(n), c(n), d(n), x(n), y(n)$
** FIRST VERSION: 02/13/86 (AMS) CURRENT VERSION: 02/13/86 (AMS) *

** *
** THIS ROUTINE COMPUTES THE COEFFICIENTS B(I).C(I), D(I),
** $I=1, \ldots$. N FOR A CUBIC INTERPOLATING SPLINE.
** *
** $\mathrm{S}(\mathrm{X})=\mathrm{Y}(\mathrm{I})+\mathrm{B}(\mathrm{I})^{*}(\mathrm{X}-\mathrm{X}(\mathrm{I}))+\mathrm{C}(\mathrm{I})^{*}(\mathrm{X}-\mathrm{X}(\mathrm{I}))^{* * 2} \quad *$
** $\quad-\mathrm{D}(\mathrm{I}) *(\mathrm{X}-\mathrm{X}(\mathrm{I}))^{* *} 3$
**

** ORDER
** Y --- THE ORDINATES OF THE KNOTS
** ON OUTPUT
** -
** B.C,D -- ARRAYS OF SPLINE COEFFICIENTS AS DEFINED ABOVE.

** *
** INTERPRETAION:
**
** Y(I) -- S (X(I))
*
** $\mathrm{B}(\mathrm{I})$--- $\mathrm{S}^{\prime}(\mathrm{X}(\mathrm{I}))$ *
** C(I) -- S" (X(I))/2
** D(I) -- S"' (X(I) )/6 (DERIVATIVE FROM THE RIGHT) *
** *
** WHERE ' DENOTES DIFFERENTIATION. THE ACCOMPANYING SUBPROGRAM *

*     * FUNCTION SEVAL CAN BE USED TO EVALUATE THE SPLINE.
**

```
*
    integer nml,ib.i
    real t
*
    nm1=n-1
    if(n.lt. 2) return
    if(n.lt. 3) go to 50
*
* SET UP TRIDIAGONAL SYSTEM
*
* B = DIAGONAL, D = DIAGONAL, C = RIGHT HAND SIDE
*
    d(1)=x(2)-x(1)
    c(2) = (y(2)-y(1))/d(1)
    do 10i=2,nml
        d(i) = x(i+1)-x(i)
        b(i) = 2.0* (d(i-1) + d(i))
        c(i+1)=(y(i+l)-y(i))/d(i)
        c(i) = c(i+l)-c(i)
    10 continue
*
* END CONDITIONS. THIRD DERIVATIVES AT X(I) AND X(N)
* OBTAINED FROM DIVIDED DIFFERENCES
*
    b(l)=-d(1)
    b(n)=-d(n-I)
    c(1)=0.0
    c(n)=0.0
    if(n .eq. 3) go to 15
    c(1) = c(3) /( x(4)-x(2) )
    1-c(2)/(x(3)-x(1) )
    c(n)}=c(n-1)/(x(n)-x(n-2)
    1-c(n-2)/(x(n-1)-x(n-3))
    c(1) = c(1)* d(1)**2 / (x(4)-x(1))
    c(n)=-c(n)*d(n-I)**2 / (x(n)-x(n-3))
*
* FORWARD ELIMINATION
15 do 20 i=2,n
        t = d(i-1)/b(i-1)
        b(i)=b(i) - t* d(i-1)
        c(i)=c(i) - t* c(i-l)
20 continue
* BACK SUBSTITUTION
*
    c(n)=c(n)/b(n)
    do 30 ib = 1. nml
        i=n-ib
        c(i)=(c(i)-d(i)* c(i+1))/b(i)
    30 continue
* C(I) NOW CONTAINS SIGMA(I)
```

```
*
*
* COMPUTE POLYNOMIAL COEFFICIENTS
```



```
    b(n)=(y(n)-y(nml))/d(nml)
    l + d(nml)*(c(nml)}+2.\mp@subsup{0}{}{*}\textrm{c}(\textrm{n})
    do 40i=1, nm I
        b(i)=(y(i+1)-y(i))/d(i)
    1 -d(i)* (c(i+1) +2.0* c(i))
        d(i)=(c(i+l)-c(i))/d(i)
        c(i)=3.0* c(i)
40 continue
    c(n)=3.0* c(n)
    d(n)}=d(n-1
*
    return
*
50 b(1)=(y(2)-y(1))/(x(2)-x(1))
    c(I) = 0.0
    d(1)=0.0
    b(2)=b(1)
    c(2)}=0.
    d(2)}=0.
*
    return
*
* LAST CARD OF SPLINE
*
    end
    real function seval ( u,x,y,n,b,c,d)
*
    integer n
    real u,x(n),y(n),b(n),c(n),d(n)
*
*
*************************************************************************
** FIRST VERSION: 02/l3/86 (AMS) CURRENT VERSION: 02/13/86 (AMS) *
* *----------------------------------------------------------------
** *
** THIS ROUTINE RETURNS THE CUBIC SPLINE FUNCTION
** *
** SEVAL = Y(I) + B(I)*(U-X(I))+C(I)*(U-X(I) )**2
** +D(I)*(U-X(I))**3
****
** WHERE X(I).LT. U.LT. X(I+1), USING HORNER'S RULE. *
* * IF U.LT. X(1) THEN I=1 IS USED, IF U .GE. X(N) THEN I=N *
** IS USED.
**
* *-------------------------------------------------------------------
**
** ON INPUT
** _-_-_
** N -- NUMBER OF DATA POINTS OR KNOTS (N.GE. 2)
* * U --- ABSCISSA AT WHICH THE SPLINE IS TO BE EVALUATED *
```

```
** X,Y -- THE ARRAYS OF ABSCISSAS AND ORDINATES.
** B, C, D - ARRAYS OF SPLINE COEFFICIENTS AS DEFINED ABOVE. *
**
** IF U IS NOT IN THE SAME INTERVAL AS THE PREVIOUS CALL.
** THEN A BINARY SEARCH IS PERFORMED TO DETERMINE THE PROPER
** INTERVAL.
*
    save i
    integer i, j. k
    real dx
*
    data i/1/
*
    if(i.ge. n ) i=1
    if (u.lt. x(i) ) go to 10
    if( u .le. x(i+1)) go to 30
*
* BINARY SEARCH
10 i=1
    j=n+1
20 k=(i+j)/2
    if(u.lt. x(k)) j=k
    if(u .ge. x(k)) i=k
    if(j gt. i+1) go to 20
*
* EVALUATE SPLINE
*
30 dx =u-x(i)
    seval = y(i)
        +dx*(b(i)+dx*(c(i)+dx*d(i)))
*
    return
*
* LAST CARD OF SEVAL
*
    end
    subroutine spevall ( s, sp, spp,u, x, y, n, b, c,d )
*
    integer n
    real s,sp,spp,u,x(n),y(n),b(n),c(n),d(n)
*
*
********************************************************************************
** FIRST VERSION: 02/17/87 (AMS) CURRENT VERSION: 02/17/87 (AMS) *
**
**
** THIS ROUTINE RETURNS THE CUBIC SPLINE FUNCTION *
** *
** S(U)=Y(I)+B(I)*(U-X(I))+C(I)*(U-X(I) )**2
** +D(I)*(U-X(I) )**3
* * AND ITS RESPECTIVE FIRST AND SECOND DERIVATIVES:
** \(\quad S P=S^{\prime}(U)\) AND \(\quad S P P=S^{\prime \prime}(U)\)
AND Spp \(=\) * * *
* * WHERE X(I).LT. U.LT. X(I+1), USING HORNER'S RULE.
** IF U.LT. X (I) THEN I=1 IS USED. IF U.GE. X(N) THEN I=N *
** IS USED.
\(\qquad\)

** ON INPUT
**
** N - NUMBER OF DATA POINTS OR KNOTS (N .GE. 2 )
** U - ABSCISSA AT WHICH THE SPLINE IS TO BE EVALUATED *
** X.Y --- THE ARRAYS OF ABSCISSAS AND ORDINATES.
** B. C. D - arrays of SPLINE COEFFICIENTS AS DEFINED ABOVE. *
** B.C.D - ARRAYS OF SPINE *
** IF U IS NOT IN THE SAME INTERVAL AS THE PREVIOUS CALL.
** THEN A BINARY SEARCH IS PERFORMED TO DETERMINE THE PROPER
** INTERVAL.
* *

*
integer \(\mathrm{i} . \mathrm{j}\). k
real dx
*
data i/ I/
*
if ( \(i\).ge. \(n \quad\) ) \(i=1\)
if ( \(u\). It. \(x(i)\) ) go to 10
if ( \(u\).le. \(x(i+1)\) ) go to 30
*
* BINARY SEARCH
10 i=1
10 i=1
    \(j=n+1\)
\(20 \mathrm{k}=(\mathrm{i}+\mathrm{j}) / 2\)
    if ( u .lt. \(x(k)\) ) \(j=k\)
    if (u.ge. \(x(k))\) i \(=k\)
    if ( j .gt. \(\mathrm{i}+1\) ) go to 20
*
* EVALUATE SPLINE
\(30 \mathrm{dx}=\mathrm{u}-\mathrm{x}(\mathrm{i})\)
    \(s=y(i)+d x *(b(i)+d x *(c(i)+d x * d(i)))\)
    \(\mathrm{sp}=\mathrm{b}(\mathrm{i})+\mathrm{dx} *\left(2.0 * \mathrm{c}(\mathrm{i})+3.0^{*} \mathrm{~d}(\mathrm{i}) * \mathrm{dx}\right)\)
    \(\mathrm{spp}=2.0^{*} \mathrm{c}(\mathrm{i})+6.0^{*} \mathrm{~d}(\mathrm{i})^{*} \mathrm{dx}\)
*
    return
*
* LAST LINE OF SEVALI
    end
```

    subroutine bicspl(al, xl, yl, nxl, nyl.
    l a2, x2, y2, nx2, ny2.
    2 b, c,d)
    * 
* A2 contains input array; Al receives output
* dim ( A2 ): max(NXI,NX2) x max(NY1,NY2)
* dim (Al ): max(NX1,NX2) x max(NYI,NY2)
real al(*),a2(*)
real xl(nxl), x2(nx2), yl(nyl), y2(ny2)
* 
* these vectors must have dimension
* >= max ( nx2, ny2)
real b(*), c(*),d(*)
*     * FIRST VERSION: 06/06/88 CURRENT VERSION: 06/06/88

```

```

** *

*     * THIS ROUTINE COMPUTES INTRPOLATES THE BI-DIMENSIONAL FIELD A2 *
*     * GIVEN ON A GRID X2 x Y2 TO A FIELD AI DEFINED ON A GRID
** XlxYl.
** *
*     * Al, A2 should not share storage. No attempt is made to *
** save storage. A2 is overwritten.
**
*****************************************************************************

```
* X-INTERPOLATION
* - --analo
do \(10 \mathrm{j}=1\), ny2
    \(11 \mathrm{j}=(\mathrm{j}-1)^{*} \mathrm{n} \times 2+1\)
    call spline ( \(b, c, d, n \times 2, x 2, a 2(11 j)\) )
    do \(20 \mathrm{i}=1, \mathrm{nxl}\)
        \(\mathrm{lij}=(\mathrm{j}-\mathrm{l}) * \mathrm{nxl}+\mathrm{i}\)
        \(\mathrm{al}(\mathrm{lij})=\operatorname{seval}\left(\mathrm{xl}(\mathrm{i}), x_{2}, \mathrm{a}_{2}(\mathrm{llj}), \pi \mathrm{x} 2, \mathrm{~b}, \mathrm{c}, \mathrm{d}\right)\)
    20 continue
    10 continue
* TRANSPOSITION
* -----------
    do \(30 \mathrm{i}=1, \mathrm{nxl}\)
    do \(30 \mathrm{j}=1, \mathrm{ny} 2\)
        \(\mathrm{lij}=(\mathrm{j}-\mathrm{l}) * \mathrm{nxl}+\mathrm{i}\)
        \(\mathrm{lji}=(\mathrm{i}-\mathrm{l})^{*} n y 2+j\)
        \(\mathrm{a} 2(\mathrm{lji})=\mathrm{al}(\mathrm{lij})\)
    30 continue
    * Y-INTERPOLATION
    * --------------
```

    do 40i=1.nx l
    IIT=(i-1)* ny2 + I
    call spline (b, c, d, ny2. y2, a2(11i))
    do 50 j = 1, nyl
        lij = (j-1 )* nxI +i
        al(lij) = seval (yl(j), y2, a2(lli), ny2, b. c.d )
    50 continue
40 continue

```
    return
* LAST LINE OF BICSPL
    end

\section*{Air-water gas exchange and the carbon cycle of Green Bay. Lake Michigan}
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\end{tabular} \\
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\end{tabular}

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Major Department: Committee Directed Ph.D. Program in Biogeochemistry

Signed:


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