

Carbon Dioxide Concentration and Atmospheric Flux in the Hudson River

PETER A. RAYMOND¹

NINA F. CARACO

JONATHAN J. COLE²

Institute of Ecosystem Studies

Box AB

Millbrook, New York 12545

ABSTRACT: We made direct measurements of the partial pressure of CO₂ (P_{CO_2}) in the tidal-freshwater portion of the Hudson River Estuary over a 3.5-yr period. At all times the Hudson was supersaturated in CO₂ with respect to the atmosphere. P_{CO_2} in surface water averaged 1125 ± 403 (SD) μatm while the atmosphere averaged 416 ± 68 μatm . Weekly samples at a single, mid-river station showed a pronounced and reproducible seasonal cycle with highest values (~ 2000 μatm) in mid-to-late summer, and lowest values (~ 500 μatm) generally in late winter. Samples taken along the length of the 190-km section of river showed a general decline in CO₂ from north to south. This decline was most pronounced in summer and very slight in spring. Diel and vertical variation were small relative to the standing stock of CO₂. Over six diel cycles, all taken during the algal growing season, the mean range was 300 ± 114 μatm . CO₂ tended to increase slightly with depth, but the gradient was small, about 0.5 $\mu\text{mol m}^{-1}$, or an increase of 190 μatm from top to within 1 m of the bottom. For a large subset of the samples ($n = 452$) we also calculated CO₂ from measurements of pH and total DIC. Calculated and measured values of CO₂ were in reasonably good agreement and a regression of calculated versus measured values had a slope of 0.85 ± 0.04 and an r_2 of 0.60 . Combining our measurements with recent experimental studies of gas exchange in the Hudson, we estimate that the Hudson releases CO₂ at a rate of $70\text{-}162$ $\text{g C m}^{-2} \text{yr}^{-1}$ from the river to the atmosphere.

Introduction

Large rivers tend to be heterotrophic ecosystems. That is, there is more organic matter oxidized within the river than is fixed by the photosynthesis of phytoplankton plus macrophytes (Vannote et al. 1980; Cummins et al. 1995). This simple balance implies that rivers in general should be net sources of carbon dioxide to the atmosphere or should transport excess CO₂ (as either CO₂ or total dissolved inorganic carbon [DIC]) into the coastal zone. Exchanges of CO₂ between the water and atmosphere have not been well studied in large rivers (Kempe 1982). Although several rivers have been shown to be supersaturated in CO₂ (or undersaturated in oxygen; Depetris and Kempe 1993; Quay et al. 1995), the data are often too sparse for a good estimate of atmospheric flux. That is, we do not know how CO₂ varies over space and time in sufficient detail to calculate flux to the atmosphere (Sellers et al. 1995). Further, estimating the exchange with the atmosphere is problematic even when the CO₂ gradient is well known because there have been few field measurements of gas ex-

change rates and the factors affecting these rates (Clark et al. 1994). Finally, most of the data to date on riverine CO₂ concentrations has been derived from measurements of pH and alkalinity. Other researchers have argued that pH is difficult to measure with sufficient accuracy to allow for accurate calculations of aqueous CO₂ (Herczeg and Hesselein 1984; Stauffer 1990).

In this paper we estimate the total amount of CO₂ the Hudson exchanges with its overlying atmosphere. The estimate is based upon a large dataset of direct measurements of the partial pressure of CO₂ in both the water and the atmosphere and on recent studies of gas exchange rates, based on the fates of added tracers (Clark et al. 1994).

Methods

STUDY SITE AND SAMPLING REGIME

We studied the tidal freshwater portion of the Hudson River Estuary from Albany, New York, to the Tappan Zee Bridge (Fig. 1). This 190-km stretch of river accounts for $\sim 84\%$ of the length of the tidal river, 85% of the volume of the river, and encompasses an area of 210 km^2 (Gladden et al. 1988). Over most of this stretch of the river the water is fresh, with conductivities near 200 μmhos and salinities of 0% . The bulk of the water in this stretch comes from upstream in the main stem; less

¹ Present address: Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, Virginia 23062

² Corresponding author; tele: 914-677-5343; fax 914-677-5976; email:76067.3033@compuserve.com.

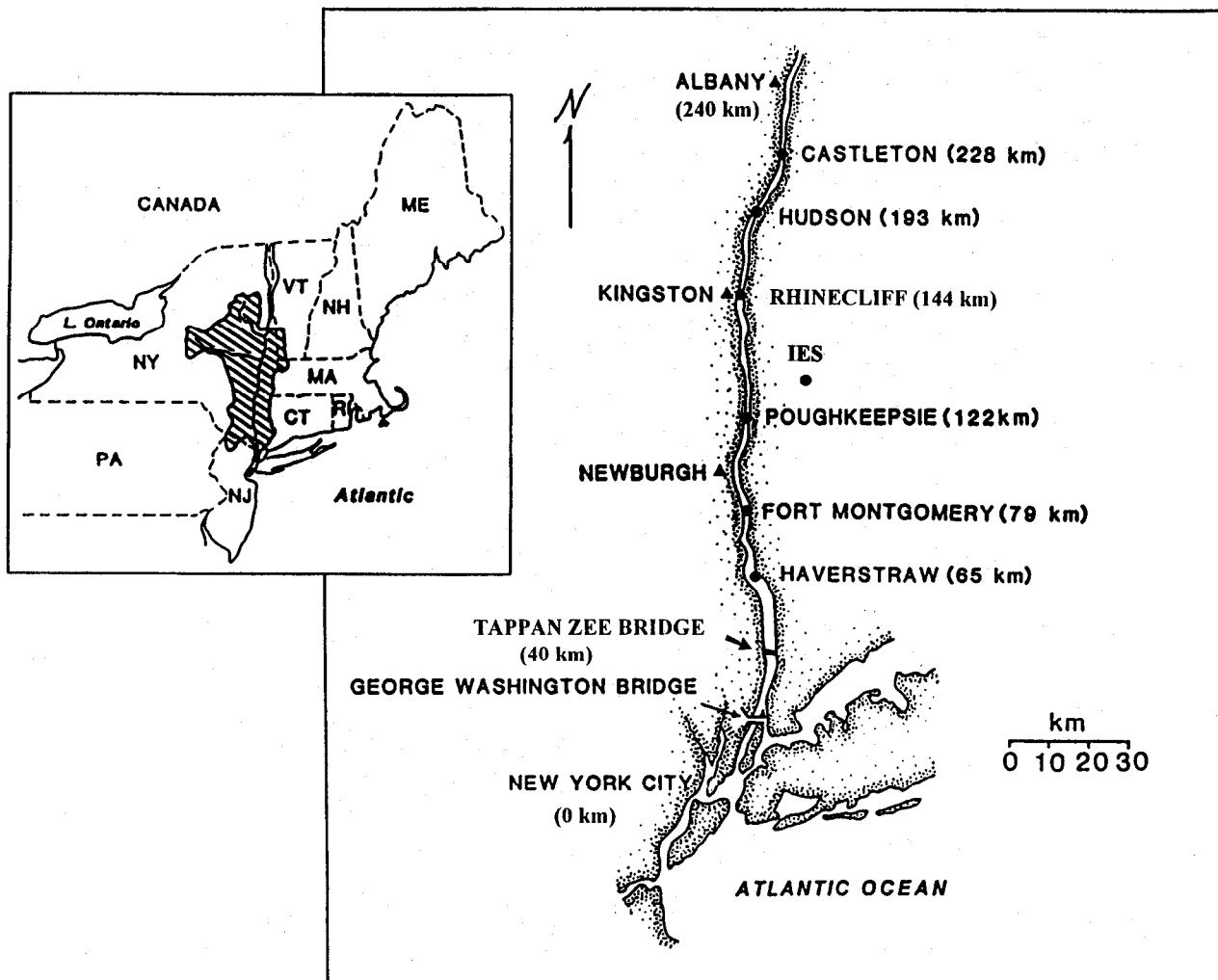


Fig. 1. Map of the Hudson River and its watershed (inset) showing some of the locations along its length. River km are measured as distance along the river from New York City (river km 0). Our study reach extended from river km 240 (at Albany) 190 km south to river km 50, at the Tappan Zee Bridge. The point labeled "IES" marks the location of the meteorological station at the Institute of Ecosystem Studies.

than 20% of the total discharge is added by tributaries along this stretch (Gladden et al. 1988). Total DIC concentrations are near 1000 μM and pH ranges from 7.4 to 8.0 (Cole et al. 1992). Toward the seaward end, the water becomes brackish with salinities reaching 5‰ at the extreme south, especially at times of low freshwater discharge. Due to tidal action, the Hudson River is generally well mixed, and turbid throughout the freshwater portion (Cole et al. 1992).

As in prior studies, we identify stations by river kilometer moving north from New York City (km 0) to Albany, New York (km 240, Fig. 1; see Findlay et al. 1991; Caraco et al. 1997). Using this scale, our reach extends from river km 240 (at Albany) to river km 50 (just north of the Tappan Zee Bridge; Fig. 1).

We examined the dynamics of aqueous CO_2 on four spatial and temporal scales:

Seasonal Cycles

Weekly samples were taken at one location for 1 yr (river km 121; 1 km south of Poughkeepsie) for 43 samples, and at a second location for 3.5 yr (at Rhinecliff, river km 144; Fig. 1) for 139 samples. Samples were taken at various times of day between 0530 h and 1800 h.

Longitudinal Profiles

To determine variation over the length of the river we sampled from Albany, New York, to the Tappan Zee bridge on six dates in 1994 and 1995. We made measurements at 38 or 39 stations on each transect, approximately 4 km apart, each sam-

pled just outside the main shipping channel. The longitudinal sampling generated 232 samples.

Diel Studies

During 1993 and 1994, we sampled the river over six 24-h periods to characterize diel variation in aqueous CO₂. During 1993, we sampled off the Rhinecliff public docks (river km 144) and samples were taken 8 to 10 times over each 24-h period. During 1994, we cruised a 20 km-length of river (from river km 120 to river km 148), taking samples at four stations 5 to 6 times over each 24-h period.

Vertical Profiles

Samples were taken over depth at three sites during 1993 and 1994 to characterize vertical stratification. Each profile consisted of samples from 3 to 5 depths, from top to bottom. Samples were taken from a boat using a peristaltic pump just outside the main shipping channel. The sites were at Kingston (river km 152), ~3 km south of Poughkeepsie (river km 119), and at river km 77, 2 km south of Fort Montgomery (Fig. 1).

CHEMICAL METHODS

Partial Pressure of CO₂

Aqueous CO₂ can be either directly measured or calculated from measurements of the total dissolved inorganic C pool and pH. In this study we used both approaches. Our results and discussion are based almost entirely upon the direct measurements; we use the calculated values to corroborate the direct measurements. With the exception of two longitudinal transects in 1995, all values we report here are based on direct measurements of P_{CO₂}.

In all cases (except the vertical profiles), samples were taken from the surface water at a depth of 0.1 m. The direct measurement of P_{CO₂} was accomplished by headspace equilibration (Cole et al. 1994). Briefly, a thermally-insulated, heavy-walled glass bottle (1.2 l) was filled with water and allowed to flush for several volumes by continuous pumping. The bottle was capped with a specially designed stopper with gas-tight syringe valves that allow the introduction and removal of gas or water phases. We immediately introduced a 50-ml headspace of ambient air and shook vigorously for 60 s. Prior tests demonstrated that this shaking was approximately twice the amount of time required to equilibrate the air and water phases. The temperature of the water was unchanged during this procedure. Samples of both the equilibrated gas headspace and ambient air (1 m above the river's surface) were transported to the laboratory in modified 20-ml nylon syringes. CO₂ was measured

by gas chromatography using a Shimadzu Model GC-AIT equipped with a thermal conductivity detector. For each sample we made duplicate equilibrations; for each equilibration we extracted duplicate gas samples. The coefficient of variation for this procedure (for the four measurements) averaged 8% of the mean.

We measured pH and total dissolved inorganic C (DIC) in order to calculate P_{CO₂}. From June 1992 to March 1994, DIC was measured using the syringe gas-stripping method of Stainton (1973) and the Shimadzu gas chromatograph (above). Using this procedure, the coefficient of variation was 1.2% of the mean for triplicates. Beginning in March 1994, we used a dedicated total inorganic C (TIC) analyzer (Shimadzu ASI-5050) equipped with an auto-sampler. Using this procedure, the coefficient of variation was 0.8% of the mean for triplicates. In both cases, samples were collected in gas-tight containers in the field and kept refrigerated until the time of analysis (within 24 h).

pH was measured with a Fisher Accumet 1001 meter using a gel-filled combination, temperature-compensating (ATC) electrode. Samples were either collected in gas-tight BOD bottles and transported in a cooler or measured directly in the field. Calibration was done using two buffers (7.00 and 10.00; Fisher). To measure pH accurately, after calibrating and thoroughly rinsing the electrode, we allowed the electrode to soak in a sample of river water for 30 min. After this initial soak we measured pH from the previously unopened BOD bottle (Stauffer 1990). Replicate determinations, using this procedure, agreed to within 0.03 pH units.

Calculated CO₂

As a check on the direct measurements of P_{CO₂}, P_{CO₂} was also calculated from measurements of DIC and pH, with appropriate corrections for temperature, altitude, and ionic strength (Kling et al. 1992). We estimated ionic strength from conductivity (Butler 1991), and activity coefficients for carbonate and bicarbonate were estimated using MINEQL version 2.1 (Schecher and McAvoy 1991) and complete anion and cation measurements for the Hudson River. Henry's constant (K_h) was corrected for temperature and salinity; aqueous CO₂ in equilibrium with the atmosphere ([CO₂]_{sat}) was calculated from Henry's law and the fugacity-pressure relationship from Weiss (1974).

Chlorophyll-*a* was measured on all samples for the seasonal cycle, longitudinal profiles, and diel studies. Samples were filtered through Whatman GF/F filters and frozen prior to analysis. We used the basic methanol procedure of Holm-Hansen

and Reimann (1978) and a Turner Designs Fluorometer.

CALCULATION OF CO₂ FLUX

The rate of exchange of a gas between surface waters and the atmosphere depends on two main factors: the concentration gradient between the water and the air, and the gas exchange coefficient for a given gas at a given temperature, k (see Wanninkhof 1992). The concentration gradient is expressed as the difference between the actual concentration of CO₂ in the water and the concentration that water would have, were it in equilibrium with the atmosphere. Thus:

$$\text{Flux} = k \times ((P_{\text{CO}_2} \times K_h) - [\text{CO}_2]_{\text{sat}}) \quad (1)$$

where $[\text{CO}_2]_{\text{sat}}$ is the concentration of CO₂ the water would have at equilibrium with the overlying atmosphere; K_h is Henry's constant for CO₂ at a given temperature and salinity; P_{CO_2} is the partial pressure of CO₂ in the surface water; and the product, $P_{\text{CO}_2} \times K_h$, is the actual concentration of CO₂ in the water. In all cases we used the directly measured value of P_{CO_2} in the calculations. The piston velocity (or gas exchange coefficient), k , was estimated from the experimental tracer work of Clark et al. (1994) who added deliberate gas exchange tracers (SF₆ and He) to the Hudson River and modeled k as a function of wind speed. The gas exchange coefficient depends on both the gas of interest and the temperature; if k is known for any one gas and temperature it can be calculated for any other gas and temperature by the ratio of the Schmidt numbers. The Schmidt number is the kinematic viscosity of the water divided by the diffusion constant, in water, of the gas of interest (see Wanninkhof 1992):

$$k_{\text{CO}_2}/k_{\text{SF}_6} = (S_{\text{CO}_2}/S_{\text{SF}_6})^n \quad (2)$$

where S_c is the Schmidt number for the respective gases evaluated for a particular temperature and water density (Wanninkhof et al. 1987; Wanninkhof 1992). Depending on the process which dominates the diffusion, this exponent, n , can vary from unity to -0.67 . We used -0.5 , a value consistent with direct measurements of n in the Hudson using dual gas additions (Clark et al. 1994). Additionally, we used a second estimate of k from the work of Marino and Howarth (1993), who used the floating helmet method to estimate oxygen exchange rates in the Hudson. We used wind speeds at 10-m height from the meteorological station at the Institute of Ecosystem Studies, located about 12 km from the Hudson River ("IES" on Fig. 1). Ice-cover is an irregular occurrence in the Hudson. During these periods of ice-cover (more than 2 mo in 1993, and 1 mo in other years), we assumed that

atmospheric exchange was reduced by the fraction of river area that was covered by ice ($\sim 75\%$).

Results

SEASONAL CYCLES

Relative to the atmosphere, P_{CO_2} was supersaturated on all dates sampled (Fig. 2A). Thus, there is always a concentration gradient between the water and the air and a net flux of CO₂ out of the water (Fig. 2C). For the 182 different sample dates, the overall mean (directly measured) P_{CO_2} for Hudson River water was $1147 \pm 387 \mu\text{atm}$ (SD) (Fig. 2A). The highest value, $2270 \mu\text{atm}$, occurred at Poughkeepsie on September 11, 1992; the lowest value, $503 \mu\text{atm}$, also occurred at Poughkeepsie on April 28, 1992. Over the same period P_{CO_2} in the air averaged $416 \pm 68 \mu\text{atm}$.

The seasonal patterns in P_{CO_2} across stations and years were highly consistent with each other. P_{CO_2} tended to be highest in summer and lowest in late autumn, and changed smoothly from week to week (Fig. 2A). During both winter periods we observed a secondary P_{CO_2} maximum with values near $1200 \mu\text{atm}$ that were associated with ice-cover. Ice-cover on the Hudson is erratic and is usually broken up quickly to keep shipping channels clear when it does form. In the winter of 1993, the ice cover was unusually persistent and lasted for about 2 mos in the mid-Hudson region.

LONGITUDINAL VARIATION

Measured values of P_{CO_2} varied along the length of the river in all six of our transects (Fig. 3). Among transects, the average range in P_{CO_2} was $968 \mu\text{atm}$, and the average cv was 39%. Because it takes two 8-h days to sample the length of the river, the longitudinal variation in P_{CO_2} combines true spatial variation with diel CO₂ cycling. We show (below) that diel cycling is not a major component of the observed spatial variation.

In 1994, P_{CO_2} was rather flat over the length of the river in early May. By June and July a great deal of structure had developed, especially in mid and upstream sections. The major trend was an overall increase in P_{CO_2} in upstream sections but the pattern was complex and far from monotonic, with many local increases and decreases (Fig. 3A). It is interesting that many of these local changes were stable over time and appeared in both the June and July transects. In 1995 there were drought conditions, and P_{CO_2} was somewhat higher and more variable over the length of the river (Fig. 3B).

The mean P_{CO_2} over the length of the river was extremely close to the value at Rhinecliff, our intensively sampled station, on the same dates (Fig. 4). In fact, on none of the three dates was the av-

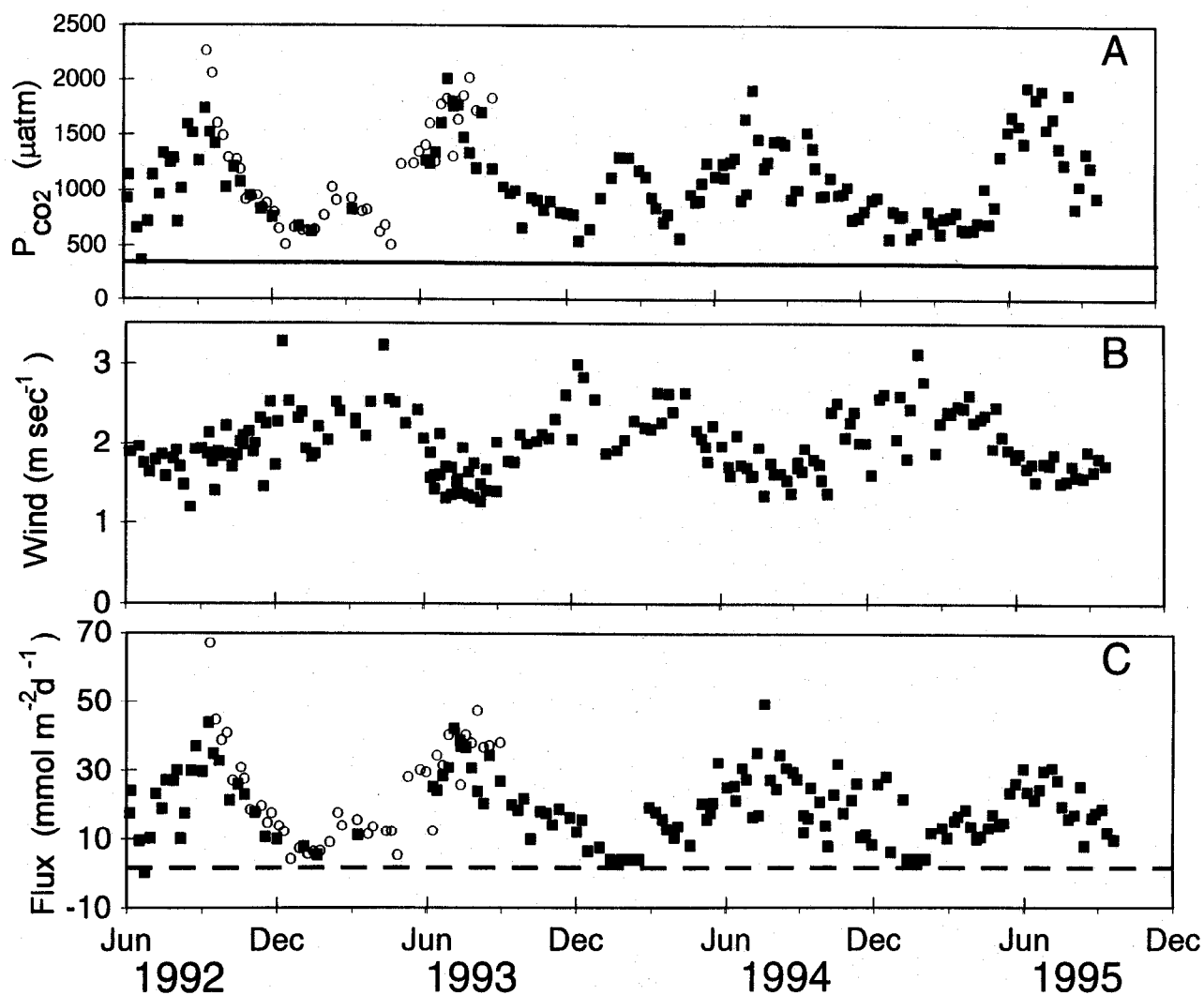


Fig. 2. Seasonal variation in measured P_{CO_2} , wind speed, and the net exchange of CO_2 with the atmosphere for a 3.5-yr period. A) Weekly, direct measurement of P_{CO_2} at river km 144 (solid squares) or river km 121 (open circles). The solid line represents the mean P_{CO_2} in the overlying atmosphere; B) Weekly mean wind speed at 10-m height from the weather station of the Institute of Ecosystem Studies; C) The exchange of CO_2 with the atmosphere was calculated for river km 144 (solid squares) or river km 121 (open circles), based on the weekly samples of P_{CO_2} , the mean weekly wind, and the SF_6 -derived relationship between k (the gas exchange coefficient) and wind-speed from Clark et al. (1994; see text). Positive values denote flux from the river to the atmosphere. The dotted line represents zero net flux.

erage for the river significantly different from the value at Rhinecliff (Fig. 4).

Total DIC did not show a large degree of longitudinal variation (Fig. 5A). DIC concentrations tended to decline slightly over the summer period, and during summer there was an increase of about 200 μM from north to south (Fig. 5B). Because DIC was relatively constant, pH tended to track, inversely, the longitudinal variations in P_{CO_2} (Fig. 5B).

DIURNAL VARIATION

The range in diel fluctuation in the Hudson River is small relative to both the seasonal and longitudinal scales (Fig. 6). Across the six diel cycles we

measured, the mean range in P_{CO_2} was 300 ± 114 μatm . This is less than 20% of the observed range for the seasonal measurements, and only one-third of the range in longitudinal variation. Further, the diel samplings were conducted during summer months, when phytoplankton were abundant and at maximal river temperature, when diel changes are expected to be at their highest (Cole et al. 1992).

A representative diel CO_2 cycle is shown in Fig. 6. In the dark (when respiration continues in the absence of photosynthesis), we observed an increase of P_{CO_2} in the surface water from 41 μatm to 297 μatm on different dates (78 μatm for the date shown). During the day, when both respira-

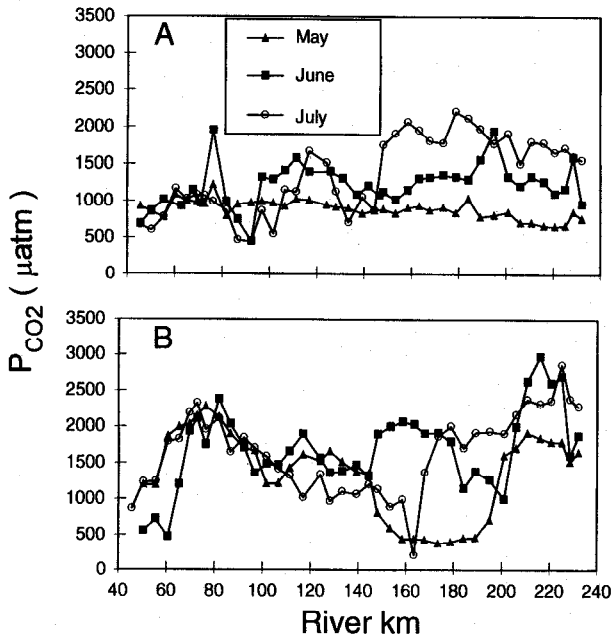


Fig. 3. Spatial variation in P_{CO_2} along the length of the river on three dates in 1994 (A) and three dates in 1995 (B). 1994 was a wetter than average year and 1995 had severe drought conditions. The values for 1994 and for July 1995 are directly measured; the values for May and June 1995 are calculated from pH and DIC (see text).

tion and photosynthesis are occurring, the build up of P_{CO_2} due to respiration is masked by photosynthetic uptake. During the hours of intense sunlight, from 10 am to 3 pm, there was an average decrease of $17 \mu\text{atm h}^{-1}$. Dissolved oxygen showed a corresponding inverse pattern. The daytime decrease in CO_2 ($0.6 \mu\text{mol C l}^{-1} \text{h}^{-1}$) is consistent with measurements of oxygen changes in the river (Fig. 6) and with estimates of algal plus macrophyte photosynthesis integrated over the Hudson

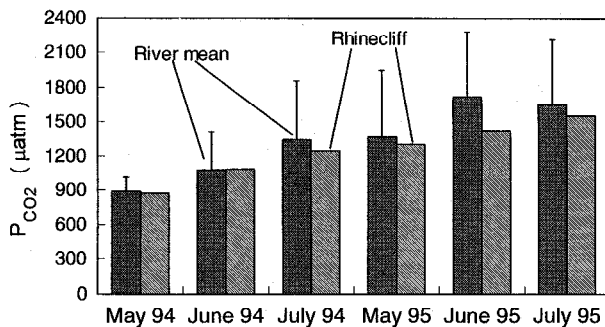


Fig. 4. A comparison of mean measured P_{CO_2} at Rhinecliff (river km 144, our long-term intensively sampled site; see Fig. 1) and the mean of measured P_{CO_2} over the length of the tidal-freshwater river, paired by dates. The error bars represent the standard deviation of the variation among sites along the length of the river (see Fig. 3). River mean = dark gray; Rhinecliff = light gray.

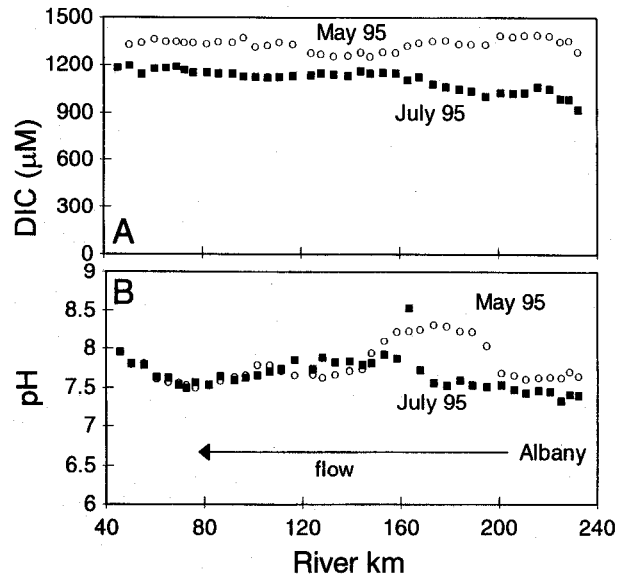


Fig. 5. Longitudinal variation in total DIC (A) and pH (B) on two dates.

water column during daylight hours (Caraco et al. in press).

VERTICAL VARIATION

Due to tidal current, the Hudson River is relatively well mixed, at least in the tidal-freshwater section. Not surprisingly, the vertical profiles varied little in P_{CO_2} and temperature. Although temperature differences from top to bottom were extremely small, $<1^\circ\text{C}$ over the entire profile, we did observe some evidence of stratification in CO_2 . P_{CO_2} was never constant over depth and, on most dates, increased slightly with increasing depth (Fig. 7). The gradient over depth ranged from $0.2 \mu\text{mol}$

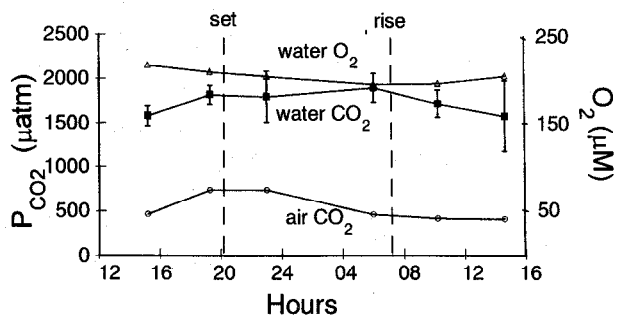


Fig. 6. A representative diel cycle of measured P_{CO_2} July 13–14, 1994. Samples were taken at four stations in the mid Hudson region (river km 155 to 130) at six times during a 24-h period. Plotted is mean (with SD of the four stations) of P_{CO_2} in the water (solid squares; left-hand axis); P_{CO_2} in the air (open circles), and dissolved oxygen (open triangles; right-hand axis) at the mean time the four stations were sampled. Time is plotted as hour day. The timing of sunset and sunrise are indicated with dashed lines.

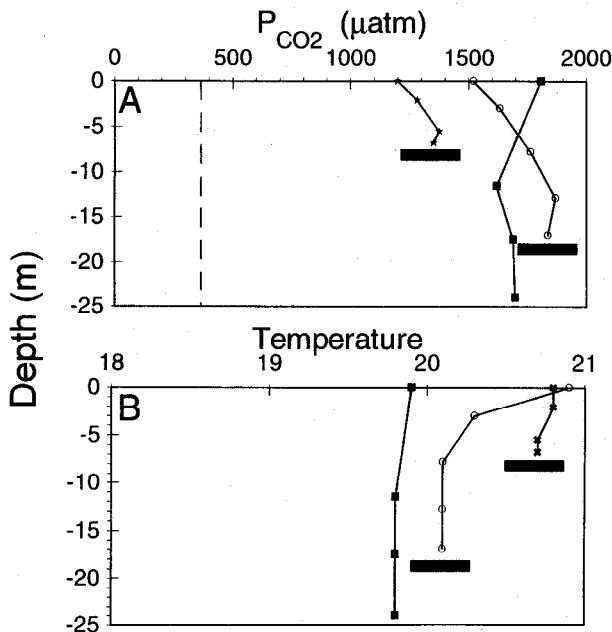


Fig. 7. Variation in directly measured P_{CO_2} (A) and temperature (B) over depth at three sites of different depths during June 1994. Solid triangles - Kingston (river km 144); open circles - Poughkeepsie (river km 110); solid squares - Fort Montgomery (river km 77). Atmospheric equilibrium for CO₂ is shown with the dotted line. The bottom at the two shallower stations is indicated with cross-hatching.

CO₂ m⁻¹ to 1.5 $\mu\text{mol CO}_2$ m⁻¹. Across all measurements, the average gradient was $0.7 \pm 0.45 \mu\text{mol CO}_2$ m⁻¹, or a range of $197 \pm 128 \mu\text{atm}$ from top to bottom. On some dates and sites, CO₂ decreased with increasing depth (Fig. 7).

MEASURED AND CALCULATED P_{CO_2}

To corroborate our results based on directly measured values of P_{CO_2} , we compared these direct measurements to calculated values of P_{CO_2} for a large subset of the samples for which we had both directly measured values and measurements of pH and DIC. Across this dataset ($n = 452$), measured P_{CO_2} averaged 1125 ± 403 (SD) μatm , while calculated values averaged 1096 ± 442 (SD) μatm . Although these means are statistically different (t -test; $p < 0.05$) from each other, this difference represents only 3% of the mean standing stock of CO₂. On the other hand, there is some variability between measured and calculated values for given individual samples. A regression of measured versus calculated P_{CO_2} by samples for the entire dataset has a slope of 0.85 and an r^2 of 0.60 (Fig. 8). Thus, in the Hudson, calculated values of CO₂ underestimate the true value by about 15% over the full range of P_{CO_2} .

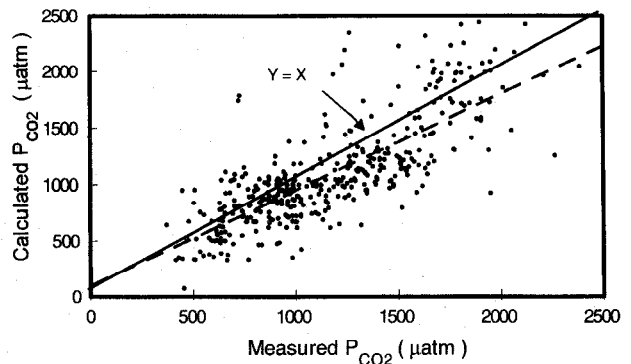


Fig. 8. Direct and indirect assessments of the partial pressure of CO₂ in the surface water of the Hudson River. Shown are 452 measurements for which we have both direct measurements of P_{CO_2} (by headspace equilibration; see text) and also calculated P_{CO_2} from measurements of pH and DIC, with corrections for temperature and salinity (see text). The equation for the regression line is $Y = 0.85 X + 109$; $r^2 = 0.60$; the dotted line represents $Y = X$.

Discussion

MEASURED AND CALCULATED P_{CO_2}

We observed imperfect agreement between calculated and directly measured values of P_{CO_2} . These errors are clearly not due to an incorrect assessment of the activity coefficients for CO₃²⁻ in the calculations. Activity coefficients for CO₃²⁻, based on complete ion chemistry and MINEQL, averaged 0.65. Recalculating P_{CO_2} using extreme activities of 0.1 or 0.99 changed the values of P_{CO_2} by only 2.5% on average, because CO₃²⁻ concentrations in the Hudson are such a small proportion of total DIC. Is it also unlikely that uncertainties in the activity coefficient for HCO₃⁻ were the cause of error. Based on MINEQL, the activity coefficient for HCO₃⁻ should have been near unity and not variable. Other researchers working in dilute freshwaters have suggested that calculated values tend to overestimate the true value of CO₂ due to a low bias in electrode based pH measurements (Herzceg et al. 1985; Stauffer 1990). In the Hudson, our calculated values slightly underestimate the directly measured value. Variation in the accuracy of the pH measurement is the most likely cause of the observed discrepancies between measured and calculated values of CO₂. At the mean conditions for the Hudson, a pH error of 0.05 units (0.6% error) results in a 10% error in estimated P_{CO_2} . With the exception of two of the longitudinal transects, our arguments below are based entirely on the directly measured values of P_{CO_2} .

CO₂ FLUX TO THE ATMOSPHERE

The exchange of gas between the water and the air depends on the concentration gradient between the water and air, and on the gas exchange

coefficient. For the gradient, we can use the weekly CO₂ measurements at Rhinecliff (Fig. 3A) to calculate the flux of CO₂ from the river to the atmosphere. The seasonal variation at this site is much larger than maximal diel variation (Fig. 7). The spatial variation is sometimes large, but the station at Rhinecliff appears to give a reasonable estimate of mean CO₂ for the entire tidal-freshwater section (Fig. 4).

The gas exchange coefficient, in theory, should be a function of wind speed, except possibly at low wind speeds (Wanninkhof 1992). In data from both the experimental additions of SF₆ to the Hudson of Clark et al. (1994) and the helmet reaeration experiments of Marino and Howarth (1993), *k* does appear to vary with wind speed. The SF₆ data of Clark et al. (1994) approximates the general power relationship suggested by Wanninkhof (1992) the best fit of Hudson data being:

$$k_{600} = 0.41 \times U^{1.94} \quad r^2 = 0.60 \quad (3)$$

where *k*₆₀₀ is the exchange coefficient (cm h⁻¹) for a gas with a Schmidt number of 600 (equivalent to the Schmidt number of CO₂ at about 20°C) and *U* is the wind at 10-m height (m s⁻¹). This relationship is quite close to that suggested by Wanninkhof (1992) in the modal wind range observed on the Hudson and only diverges at higher winds, >5 m s⁻¹. The relationship derived from floating helmet experiments gives somewhat different results. The relationship, corrected to *k*₆₀₀, used by Marino and Howarth (1993) to fit helmet-derived data from estuaries in general, including the Hudson, would be

$$k_{600} = 2.28 \times e^{(U \times 0.237)} \quad r^2 = 0.86. \quad (4)$$

This relationship gives a slightly higher value of *k* at the mid-range of wind on the Hudson (2–4 m s⁻¹) than the SF₆-derived data, but, due to the exponential form of the equation, is much higher at the very low wind speeds (3.6-fold greater at 1.5 m s⁻¹) that dominate the Hudson wind distribution. To bracket the most likely value for *k*, we calculated it according to both of the relationships above.

Based on the Hudson SF₆ additions, mean weekly *k*₆₀₀ would be 1.54 cm h⁻¹ and mean CO₂ fluxes would be 16.1 mmol m⁻² d⁻¹ or 70 g C m⁻² yr⁻¹; based on the helmet data mean *k*₆₀₀ would be 4.1 cm h⁻¹ and the flux would be 37 mmol m⁻² d⁻¹ or 162 g C m⁻² yr⁻¹. Both methods produced a nearly identical seasonal pattern. Flux is clearly driven more by the seasonal differences in the CO₂ gradient, which are large, than by differences in mean weekly wind speed, which are slight (Fig. 3B).

It may be that averaging the wind into weekly intervals obscures important high wind events of shorter duration (see Wanninkhof 1992). We recalculated the flux using mean daily wind speeds

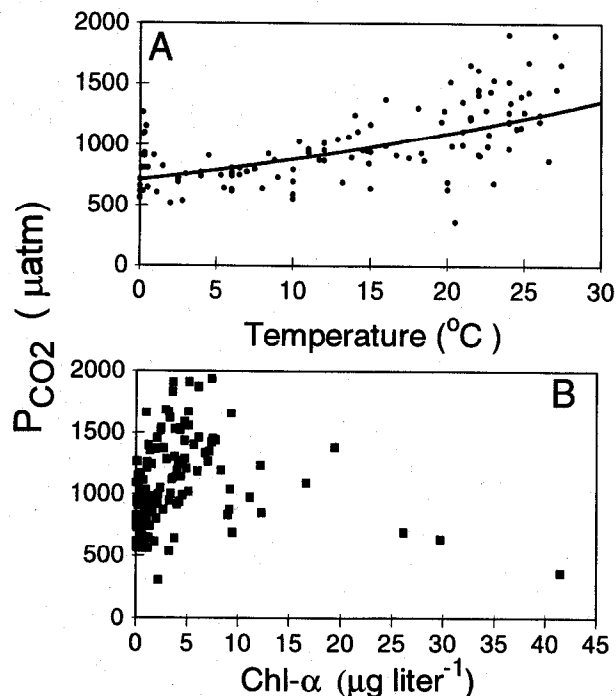


Fig. 9. (A) Relationship between temperature (in °C) and directly measured *P*_{CO₂} for all seasonal series samples at Rhinecliff. The equation for the line is $Y = 711 + e^{(0.022 \times \text{temp})}$; $r^2 = 0.4$. The slope is significant at $p < 0.01$. (B) Relationship between chlorophyll-*a* and directly measured *P*_{CO₂} for all seasonal series samples at Rhinecliff. The slope of regression is not significantly different from 0.

and arrived at slightly higher values. Based on the SF₆-derived relationship, the flux becomes 18.5 mmol m⁻² d⁻¹.

The Hudson is persistently supersaturated in CO₂ with respect to the atmosphere at all times of the year. This supersaturation is consistent with the Hudson being a net heterotrophic system (Findlay et al. 1991; Howarth et al. 1992). In lakes with a strong autotrophic component, algal and macrophyte growth can be a significant sink for CO₂ and depress concentrations below atmospheric equilibrium (Schindler et al. 1972; Emerson 1975; McConnaughey et al. 1994). In most lakes, CO₂ concentrations reach their lowest values during the summer growing season at the time of maximum temperature and algal biomass (Quay et al. 1986; Hesslein et al. 1991; Cole et al. 1994). In the Hudson, CO₂ peaks during the summer or early fall, near the time of maximum temperatures. *P*_{CO₂} is not well correlated to chlorophyll-*a* ($r^2 = 0.02$; $p > 0.5$), but does appear to decrease at times when chlorophyll is highest (Fig. 9B). *P*_{CO₂} is positively correlated with temperature (Fig. 9A). In the Hudson, as heterotrophy increases with increasing temperature (Findlay et al. 1991), CO₂ is probably added during the warmer weather. Similarly, the flux

TABLE 1. CO₂ efflux to the atmosphere in the context of other C fluxes in the tidal freshwater Hudson River. In the equations in the Reference column, the letters refer to the letters identifying components in the component column. Note the primary production of macrophytes, which may be large here.

Component	g C m ⁻² yr ⁻¹	Reference
A. CO ₂ efflux to atmosphere	70–162	This study
B. Net CO ₂ advection	<31	This study
C. Total CO ₂ lost as CO ₂	<101–193	C = A + B
D. Gross whole system respiration	665	Howarth et al. 1992
E. Net primary production of phytoplankton	~80	Cole et al. 1992
F. Respiration in excess of phytoplankton net primary production (= net CO ₂ input)	585	F = D - E (see Howarth et al. 1992)
G. CO ₂ unaccounted for	392–484	G = F - C
H. Net advective loss of DIC	?	

of CO₂ from the river to the atmosphere peaks in mid- to late summer.

Because the water column is well mixed and relatively deep, the water-column CO₂ pool is not very rapidly affected by atmospheric exchange. Assuming 20°C (which specifies K_h and $[CO_2]_{sat}$) and the mean P_{CO_2} of 1100 μ atm in the river (CO₂ concentration of 45 mmol m⁻³ or 423 mmol m⁻²), and using a gas exchange coefficient, k , of 2 cm h⁻¹ (e.g., using Eq. 3 at a wind speed of 3.25 m s⁻¹), it would take about 21 d for the total water-column CO₂ pool to be halved by efflux to the atmosphere, in the absence of any other processes. Looked at another way, at a steady-state concentration of 45 mmol m⁻³, only 4% of the water-column CO₂ must be added each day to maintain the atmospheric flux at the mean value. The large size of the pool relative to the flux is one of the reasons the CO₂ concentration changes smoothly from week to week (Fig. 2A) without abrupt ups and downs.

We observe fairly large changes in CO₂ along the length of the river (Fig. 3). These differences must be caused by difference in input or output of CO₂ at particular locations. Such differences need not be large to be expressed as differences in CO₂ concentration. The greatest longitudinal variation in CO₂ occurs during summer at low flow. During summer the residence time of water in the tidal-freshwater stretch is long, > 100 d (Gladden et al. 1988). Thus, whatever feature causes the longitudinal variation would have sufficient time to alter concentrations.

CO₂ EVASION IN RELATION TO SYSTEM METABOLISM

CO₂ added to the river water can have several fates. It can be evaded to the atmosphere, advected downstream as CO₂, or it can react with the inorganic C pool and be exported as bicarbonate. In this study we have dealt only with loss to the atmosphere, but it is useful to put this term into the perspective of what is currently known about the Hudson River carbon budget (Table 1). Based on an analysis of night-time oxygen declines, Howarth

et al. (1992) estimate that the total respiration of the tidal, freshwater Hudson is between 665 g C m⁻² yr⁻¹ to 984 g C m⁻² yr⁻¹ (Table 1). Since reported net primary production of phytoplankton is no higher than about 80 g C m⁻² yr⁻¹ (Cole et al. 1992), the analysis of Howarth et al. (1992) suggests that at least 585 g C m⁻² yr⁻¹ of allochthonous origin are respired within the river. This large net addition of CO₂ is apparently not balanced by CO₂ evasion, assuming both estimates are correct. Our estimate of CO₂ evasion (see above; 70–162 g C m⁻² yr⁻¹) is only from 13% to 27% of this 585 g C m⁻² yr⁻¹ amount. This leaves from 423–515 g C m⁻² yr⁻¹ unaccounted for. The CO₂ added from net respiration that was not evaded to the atmosphere must be advected as either CO₂ or DIC, or must have another or larger sink for CO₂ within the river. The following calculation demonstrates that the net advection of CO₂ is small. Net advection would be maximal if all of the CO₂ exported were produced within the river (e.g., no importation from upstream of excess CO₂). If we assume, then, that water entering upstream was at equilibrium with the atmosphere, the net advection of CO₂ equals flow times the difference between the downstream CO₂ concentration and the concentration of CO₂ at equilibrium with the atmosphere. Expressed per unit area of river, this transport can account for only an additional 31 g C m⁻² yr⁻¹. We do not yet know how large is the net advection of DIC, but we can calculate how large it would need to be to balance the budget. After accounting for CO₂ losses to the atmosphere and to advection downstream, the net advection of DIC would need to be a net export on the order of 393–484 g C m⁻² yr⁻¹ (Table 1). That is, hydrologic flow times the difference between upstream and downstream DIC concentration, divided by river area, would have to be near 393–484 g C m⁻² yr⁻¹ (Table 1). If this were the case, water leaving the river would need to be, on average, about 730 μ M greater in DIC than the water entering the river. We do not yet know the net export of DIC from the river (be-

cause we do not know all the inputs), but such a large net export seems unlikely. For example, the difference in DIC concentration from upstream to downstream ($<200 \mu\text{M DIC}$; Fig. 5A) is considerably smaller than what would be needed to balance this budget. A more detailed accounting of the inorganic C budget of the river is needed to resolve these discrepancies in the C budget.

Note added in proof. While this paper was in press, Howarth et al. (1996) revised downward their prior estimate of net respiration in the Hudson to $293 \text{ g C m}^{-2} \text{ y}^{-1}$ (Item F Table 1). While this closes the gap considerably it still leaves from 100 to $192 \text{ g C m}^{-2} \text{ y}^{-1}$ as CO_2 unaccounted for (Item G, Table 1), but makes the advective loss of DIC (Item H) more plausible.

ACKNOWLEDGMENTS

This research was supported by grants from the National Science Foundation (DEB-9317698), the Hudson River Foundation, the Polgar Fellowship Program, and the General Reinsurance Fund. This is a contribution to the Institute of Ecosystem Studies. We thank D. Foster and R. Miller for their help with the field and lab work, and S. Findlay for his comments on the manuscript. George Kling provided valuable advice throughout the work.

LITERATURE CITED

- BUTLER, J. N. 1991. Carbon Dioxide Equilibria and Their Applications. Lewis Publishers, Chelsea, Michigan.
- CARACO, N. F., J. J. COLE, P. A. RAYMOND, D. L. STRAYER, M. L. PACE, S. E. G. FINDLAY, AND D. T. FISCHER. 1997. Zebra mussel invasion in a large turbid river: Phytoplankton response to increased grazing. *Ecology* 78:588-602.
- CLARK, J. F., R. WANNINKHOF, P. SCHLOSSER, AND H. J. SIMPSON. 1994. Gas exchange rates in the tidal Hudson river using a dual tracer technique. *Tellus* 46B:264-285.
- COLE, J. J., N. F. CARACO, G. W. KLING, AND T. K. KRATZ. 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265:1568-1570.
- COLE, J. J., N. F. CARACO, AND B. PEIERLS. 1992. Can phytoplankton maintain a positive carbon balance in a turbid, freshwater, tidal estuary? *Limnology and Oceanography* 37:1608-1617.
- CUMMINS, K. W., C. E. CUSHING, AND G. W. MINSHALL. 1995. Introduction: An overview of stream ecosystems, p.1-8. In C. E. Cushing, K. W. Cummins, and G. W. Minshall (eds.), *River and Stream Ecosystems*. Elsevier, New York.
- DEPETRIS, P. J. AND S. KEMPE. 1993. Carbon dynamics and sources for the Parana River. *Limnology and Oceanography* 38:382-396.
- EMERSON, S. 1975. Gas exchange rates in Canadian Shield lakes. *Limnology and Oceanography* 20:754-761.
- FINDLAY, S., M. L. PACE, D. LINTS, J. COLE, N. CARACO, AND B. PEIERLS. 1991. Weak coupling of bacterial and algal production in a heterotrophic ecosystem: The Hudson River estuary. *Limnology and Oceanography* 36:268-278.
- GLADDEN, J. B., F. R. CANTELMO, J. M. CROOM, AND R. SHAPOT. 1988. Evaluation of the Hudson River Ecosystem in relation to the dynamics of fish populations. *American Fisheries Society Monographs* 4:37-52.
- HERCZEG, A. L., W. S. BROECKER, R. F. ANDERSON, S. L. SCHIFF, AND D. W. SCHINDLER. 1985. A new method for monitoring temporal trends in the acidity of fresh waters. *Nature* 315:133-135.
- HERCZEG, A. L. AND R. H. HESSLEIN. 1984. Determination of hydrogen ion concentration in softwater lakes using carbon dioxide equilibria. *Geochimica et Cosmochimica Acta* 48:837-845.
- HESSLEIN, R. H., J. W. M. RUDD, C. KELLY, P. RAMLAL, AND K. A. HALLARD. 1991. Carbon dioxide pressure in surface waters of Canadian Lakes, p.413-431. In S. G. Wilhelms and J. S. Gulliver (eds.), *Air Water Mass Transfer*. American Society of Civil Engineers, Boston, Massachusetts.
- HOLM-HANSEN, O. AND B. RIEMANN. 1978. Chlorophyll *a* determinations: Improvements in methodology. *Oikos* 30:439-447.
- HOWARTH, R. W., R. MARINO, R. GARRITT, AND D. SHERMAN. 1992. Ecosystem respiration and organic carbon processing in a large, tidally influenced river: The Hudson River. *Biogeochemistry* 16:83-102.
- HOWARTH, R. W., R. SCHNEIDER, AND D. SWANEY. 1996. Metabolism and organic carbon fluxes in the tidal freshwater Hudson River. *Estuaries* 19:848-865.
- KEMPE, S. 1982. Long-term records of CO_2 pressure fluctuations in fresh waters. *Mitteilungen Aus Dem Geologisch-Paleontologischen Institut Der Universitaet Hamburg* 52:91-332.
- KLING, G. W., G. W. KIPPHUT, AND M. C. MILLER. 1992. The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. *Hydrobiologia* 240:23-36.
- MARINO, R. AND R. W. HOWARTH. 1993. Atmospheric oxygen exchange in the Hudson River: Dome measurements and comparison with other natural waters. *Estuaries* 16:433-445.
- MCCONNAUGHEY, T. A., J. W. LABAUGH, D. O. ROSENBERY, R. G. STRIEGL, M. M. REDDY, P. F. SCHUSTER, AND V. CARTER. 1994. Carbon budget for a groundwater-fed lake: Calcification supports summer photosynthesis. *Limnology and Oceanography* 39:1319-1332.
- QUAY, P. D., S. R. EMERSON, B. M. QUAY, AND A. H. DEVOL. 1986. The carbon cycle for Lake Washington. *Limnology and Oceanography* 31:596-611.
- QUAY, P. D., D. O. WILBUR, J. E. RICHEY, A. H. DEVOL, R. BENNER, AND B. R. FORSBERG. 1995. The ^{16}O : ^{18}O of dissolved oxygen in rivers and lakes in the Amazon Basin: Determining the ratio of respiration to photosynthesis rates in fresh waters. *Limnology and Oceanography* 40:718-729.
- SCHECHER, W. D. AND D. C. MCAVOY. 1991. MINEQL: A chemical equilibrium program for personal computers. User's Manual Version 2.1. Procter and Gamble Company, Pittsburgh, Pennsylvania.
- SCHINDLER, D. W., G. J. BRUNSKILL, S. EMERSON, W. S. BROECKER, AND T. PENG. 1972. Atmospheric carbon dioxide: Its role in maintaining phytoplankton standing stocks. *Science* 177:1192-1194.
- SELLERS, P., R. H. HESSLEIN, AND C. A. KELLY. 1995. Continuous measurement of CO_2 for estimation of air-water fluxes in lakes: An in situ technique. *Limnology and Oceanography* 40:575-581.
- STANTON, M. P. 1973. A syringe gas-stripping procedure for gas-chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. *Journal of the Fisheries Research Board of Canada* 30:1441-1445.
- STAUFFER, R. E. 1990. Electrode pH error, seasonal epilimnetic pCO_2 , and the recent acidification of the Maine lakes. *Water Air and Soil Pollution* 50:123-148.
- VANNOTE, R. L., G. W. MINSHALL, K. W. CUMMINS, J. R. SEDELL, AND C. E. CUSHING. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37:130-137.
- WANNINKHOF, R. 1992. Relationship between gas exchange and wind speed over the ocean. *Journal of Geophysical Research* 97:7373-7382.
- WANNINKHOF, R., J. LEDWELL, W. S. BROECKER, AND M. HAMILTON. 1987. Gas exchange on Mono Lake and Crowley Lake, California. *Journal of Geophysical Research* 92:14567-14580.
- WEISS, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non ideal gas. *Marine Chemistry* 2:203-215.

Received for consideration, October 16, 1995
Accepted for publication, September 18, 1996