

The Use of Direct Carbon Dioxide Measurements on the Hudson
River

Peter Raymond
Polgar fellow

Jon Cole
Supervisor
Institute of Ecosystem Studies
Box AB, Millbrook New York 12545

ABSTRACT

A new method for directly measuring the concentration of aqueous carbon dioxide (CO₂) was employed on the Hudson River over different temporal and spatial scales from September 1992 to September of 1993. Over this time frame the Hudson River's CO₂ concentrations ranged from 30-80 *umol/L*, with an average of 55 *umol/L*, roughly three-fold greater than the water would have had at equilibrium with the atmosphere. There was very little variation of CO₂ over the length of the river or with depth. Diurnal fluctuations in CO₂ confirmed that the Hudson River was a heterotrophic system with a negative net production of 0.6 grams of C/m²/day during the month of July. On all sampling dates, the Hudson River was supersaturated with CO₂ compared with the atmosphere. The flux of CO₂ to the atmosphere was estimated with three different data sets, using the stagnant boundary layer model, and was found to be about 59 grams of C/m²/year.

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INTRODUCTION

Because of the link that major rivers form between terrestrial ecosystems and the ocean, understanding the carbon dynamics of the earth's major rivers is crucial. One component of carbon in rivers, dissolved inorganic carbon (DIC), can exist in the following four forms: H₂CO₃, CO₂, HCO₃⁻, and CO₃²⁻. Of the four, CO₂ is the only gaseous constituent, and the most dynamic. The dynamics of CO₂ in major rivers has received some attention. Richey et al. (1990) studied [CO₂] in the Amazon, Depetris and Kempe looked at [CO₂] in the Panara (1993), while Kempe (1982) constructed a impressive data base of pCO₂ (the partial pressure of CO₂) for a number of the world's rivers.

In all of these studies the authors relied on an indirect approach to calculate CO₂ concentrations. The indirect methods rely on the pH meter and alkalinity or DIC to calculate [CO₂] (Herczeg and Hesslein 1984, Kempe 1982, Richey et al. 1990, Depetris and Kempe 1993). Because of the uncertainty of the pH meter (Mcquaker et al. 1983, Herczeg and Hesslein 1984, Galloway et al. 1979, Raymond 1993), and the significant errors in alkalinity or DIC measurements, the indirect method is sometimes questionable. It would therefore prove valuable to report CO₂ concentrations which were based on direct measurements.

To properly study CO₂ dynamics for the Hudson River, the

sources and sinks of CO₂ must be well defined, and therefore, CO₂ must be measured on all possible spatial and temporal scales. In the Hudson River, the actual range of concentrations and some of the internal fluctuations may be distinctive to the system, yet they will provide constructive insight towards understanding internal processes and are useful in comparison with other river systems.

The four objectives of my study were to: introduce a method for the direct measurement of dissolved CO₂; to report the CO₂ levels and fluctuations on four different spatial and temporal scales in the Hudson River; to analyze what controls CO₂ concentrations in the Hudson River over a one year time period; and to consider the sources and sinks for CO₂ in the Hudson River.

METHODS

Sample sites and schedule

The Hudson River extends 248 kilometers from its mouth at Manhattan, New York, to the dam located at Troy. On average, the tidal freshwater portion of the river is nine meters deep and one kilometer wide (Limburg 1986), and its channel is deep enough to be navigated by ocean going ships. The river's mean discharge for 1992-1993 was 13,000 cubic feet per second with 90% coming from the joining of the Hudson and Mohawk Rivers, and about 10% being added by tributaries north of Poughkeepsie (USGS 1992-1994). The river is heterotrophic (Findlay et al.

1992, Howarth et al. 1992), with a large portion of the allochthonous organic materials originating from runoff from forest ecosystems (Howarth et al. 1991).

Carbon dioxide, DIC, chlorophyll a, pH, dissolved oxygen (DO), and temperature were measured on a weekly basis from September of 1992 to September of 1993 at the Marist College docks in Poughkeepsie NY, 130 km north of the mouth of the river.

Three diurnal studies were performed in July at the Rhinecliff docks, 148 km north of the mouth of the river. Carbon dioxide, DIC, chlorophyll a, and temperature were measured every three hours. The amount of time between sampling periods and number of samples were defined after two preliminary diurnal studies in which measurements were made every two hours. The number of samples and time of sampling were defined to ensure an accurate measurement and to ensure that the nighttime hours, and daytime hours used in metabolic calculations were properly bracketed.

Three vertical profiles were conducted at buoy R20 located at Kingston NY, during the summer and fall of 1993. Carbon dioxide, and temperature were measured at the surface, bottom, and middle of the water column.

Carbon dioxide

The concentration of a gas in water is expressed by its partial pressure and is defined by Henry's Law:

$$[\text{CO}_2] = K_h * p\text{CO}_2 \quad (1)$$

where K_h is the Henry's constant applicable to a particular gas at a specific temperature and ionic strength, $[\text{CO}_2]$ is the concentration in moles/liter of dissolved carbon dioxide, and $p\text{CO}_2$ is the partial pressure of CO_2 .

The method I used for obtaining CO_2 concentrations (Jon Cole, unpublished) involves measuring directly, the partial pressure of CO_2 ($p\text{CO}_2$) using gas chromatography, and utilizing equation (1) to compute the concentration. The theory behind the method is simple. A one liter glass bottle is filled with Hudson River water (Figure 1) and 50 ml of water is displaced with air. Next a headspace equilibration is performed (the bottle is shaken 100 times to ensure equilibration) with the assumption that there is an "infinitely" large volume of water (950 ml) and an "infinitely" small volume of air (50 ml). Sampling the air headspace after equilibration results in a representative sample of CO_2 concentrations in the water. Note that during the time frame of the headspace equilibration, the temperature is kept constant.

In the laboratory, samples were analyzed using a Shimadzu GC-8A thermal conductivity gas chromatograph with an auto injector and a Hewlett Packard Hd 3394 integrator. The settings were as follows: injection temperature 110°C , column temperature isothermal at 44°C , and current 160 mA with a positive polarity. Samples were run within five hours of when they were taken from the river. Carbon dioxide 1000 ppm

FIGURE 1

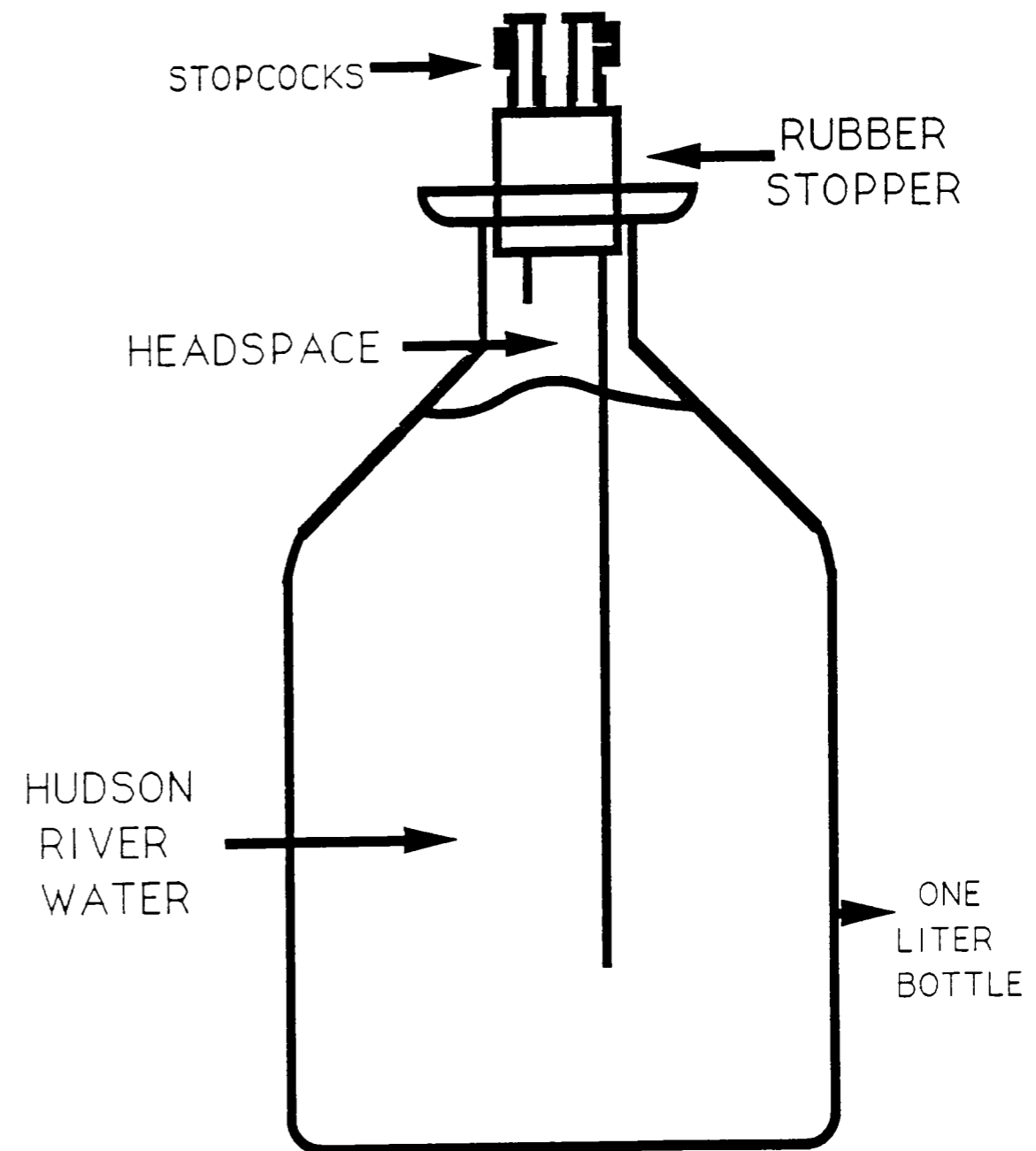


Figure 1 - Bottle used to measure the $p\text{CO}_2$ in the Hudson River.

standards were run with every sample set to obtain a concentration and adjust for the gas chromatograph's daily variation. To obtain a concentration in ppm's the average area of the standards is found and correlated with the area of the samples:

$$[\text{CO}_2]\text{ppm} = \frac{\text{avg. area sample} * 1000}{\text{avg. area standard}} \quad (2)$$

Henry's law (1) was used to find the concentration of dissolved carbon dioxide in $\mu\text{mol/L}$ of CO_2 .

DIC

DIC was measured using the method described by Stainton (1973). Water was collected in 60 ml glass dissolved oxygen bottles outfitted with a glass stopper and plastic top. Samples were analyzed by gas chromatography, with the same settings as above.

Electrode based pH

Water pH was measured using a Fisher Accumet pH meter model 610A, with a Fisher 13-620-51 probe. River water was sampled with 300 ml glass DO bottles equipped with glass stoppers and plastic caps to avoid contact with air. Samples were transported in a cooler and measured upon arrival. In the lab, care was taken to use the same procedure every time. The pH meter was calibrated with every use with pH 7 and 10 standards. The probes were then rinsed thoroughly with

deionized water and allowed to acclimate with Hudson River water for a period of approximately twenty minutes. Next, the probes were rinsed for another ten minute interval with fresh Hudson River water, and finally the probes were placed in river water from an unopened DO bottle and a reading was taken when the meter stabilized (within three minutes).

Chlorophyll a

Chlorophyll a was measured fluourometrically by the method of Holm-Hansen and Rieman (1978). Water was collected in one liter polycarbonate containers, returned to the laboratory in a cooler, filtered through Whatman GFF filters; the filters were then placed in a freezer. The filters were next extracted with five ml of basic methanol for 24 hours and read on the fluorometer. Samples were spiked with 0.05 ml of 0.3N H_2SO_4 , and after one hour, read again to correct for phaeopigments.

Conductivity

On the long river cruises, conductivity was measured using a YSI model 3000 T-L-C meter. The probe was placed in the river at 0.5m and allowed to stabilize.

Dissolved Oxygen

Dissolved oxygen was measured by Winkler titration. Water was sampled in 60 ml DO bottles and stored in the dark.

Upon titration, 50 ml Hudson River water was titrated.

Atmospheric flux

Atmospheric CO₂ flux was calculated using the thin film layer model (Bower and McCorkle 1980, Emerson 1975, Etceto 1991, Garritt 1990, Howarth et al. 1992, Kling et al. 1991 Liss 1973, Murphy et al. 1993, Richey et al. 1990) :

$$\text{Flux} = \frac{D}{Z} * ([\text{CO}_2]^{\text{atm}} - [\text{CO}_2]^{\text{water}}) \quad (3)$$

where D is the diffusivity for CO₂, Z is the stagnant boundary layer thickness, CO₂^{atm} is the concentration of CO₂ in water in equilibration with the atmosphere, and CO₂^{water} is the concentration of CO₂ in the water. Using equation (3), a positive flux is invasion from, and a negative flux is evasion to the atmosphere.

Z was estimated using wind speed data (Howarth et al. 1992, Garritt 1990) from the environmental monitoring station at the Cary Arboretum, Millbrook NY, at 10 meters and an equation formulated by Kling et al (1991).

Respiration/Production estimates

Metabolism was estimated using the changes of CO₂ concentrations over a diurnal time scale (Smith 1975, Howarth 1992, Schindler 1982). The first estimate is a 24-hour

respiration estimate. Note that all sample points for all calculations were corrected for flux to the atmosphere. Twenty four hour respiration estimates were calculated during nighttime hours between sunset and sunrise, and were estimated as follows:

$$24\text{hr Respiration} = (\text{night CO}_2 / \text{night hr's}) * 24\text{hr} \quad (4)$$

where night CO₂ is the amount of CO₂ produced in the river during an allotted time frame. The respiration rate is normalized to a 24-hour period assuming that day time respiration is equal to night time respiration.

Net daytime primary production was calculated in a similar manner. In order to get a maximum estimate, net daytime production was estimated during the most intense daylight hours, between 11 am and 2 pm, and was calculated as follows:

$$\text{Net Daytime Production} = (\text{CO}_2 \text{ consumption/day hours}) * 12 \quad (5)$$

where CO₂ consumption is the amount of CO₂ being consumed during the three hour time period. Net daytime production was normalized to 12-hours assuming production occurs at the same rate over a 12 hour daylight time period (remember, diurnal estimates were done in summer month's when the sun is present for more than twelve hours).

Once these two metabolism calculations were made other estimates were obtainable:

$$\text{Gross Prod.} = \text{Net daytime Prod.} + \text{daytime Respiration} \quad (6)$$

$$\text{Net Prod.} = \text{Gross Prod.} - 24\text{hr Respiration} \quad (7)$$

where daytime respiration is equal to the respiration rate normalized for the twelve hour daylight time period. Table 1 summarizes the metabolism results, and Table 2 compares it with previous studies.

RESULTS

Figure 2 displays dissolved CO₂ concentrations from September of 1992 to September of 1993. On every sampling date the Hudson River was supersaturated with CO₂ with respect to the atmosphere. It reached its highest concentration, 79 $\mu\text{mol/L}$, on September 11, 1992, and June 2, 1993; subsequently it was lowest, 30 $\mu\text{mol/L}$, on April 28, 1993.

It is quite evident that there are certain trends observed during the year (Figure 2). During the fall (September 11 to December 18) a steady decline of 35 $\mu\text{mol/L}$ was witnessed, driving the dissolved CO₂ concentrations down to 30 $\mu\text{mol/L}$. From December 18 to February 19, a marked increase in dissolved CO₂ concentrations was measured, with levels reaching 74 $\mu\text{mol/L}$, an increase of 44 $\mu\text{mol/L}$ in two months. This increase was immediately followed by a sharp

TABLE 1
DIURNAL RESULTS

grams of C/m²/day
JULY 6 JULY 20 JULY 27 AVERAGE

24h Resp.	2	3.1	2	2.4
Net Day Prod.	0.41	0.50	0.58	0.50
Gross Prod.	1.4	2.0	1.6	1.7
Net Prod.	-0.58	-1.0	-0.42	-0.67

TABLE 2
HUDSON RIVER JULY ESTIMATES

grams of C/m₂/day
STUDY METHOD 24hr RESP. GROSS PROD.

THIS STUDY	FREE WATER CO ₂	2 - 3	1.4 - 2
HOWARTH et al. (1992)	FREE WATER O ₂	4 - 5	NO DATA
GARRITT(1990)	FREE WATER O ₂ (MACROPHY TE)	3 - 5	3 - 8 (MACROPHY TE)
COLE et al. (1992)	¹⁴ C INCUBATION	NO DATA	1.2 (ALGAE)
FINDLAY et al. (1992)	OXYGEN DEMAND BOTTLES	4.7	NO DATA

Table 1 - Results from metabolic studies for July 1993.

Table 2 - Comparison of Table 1 with previous Hudson River metabolic studies.

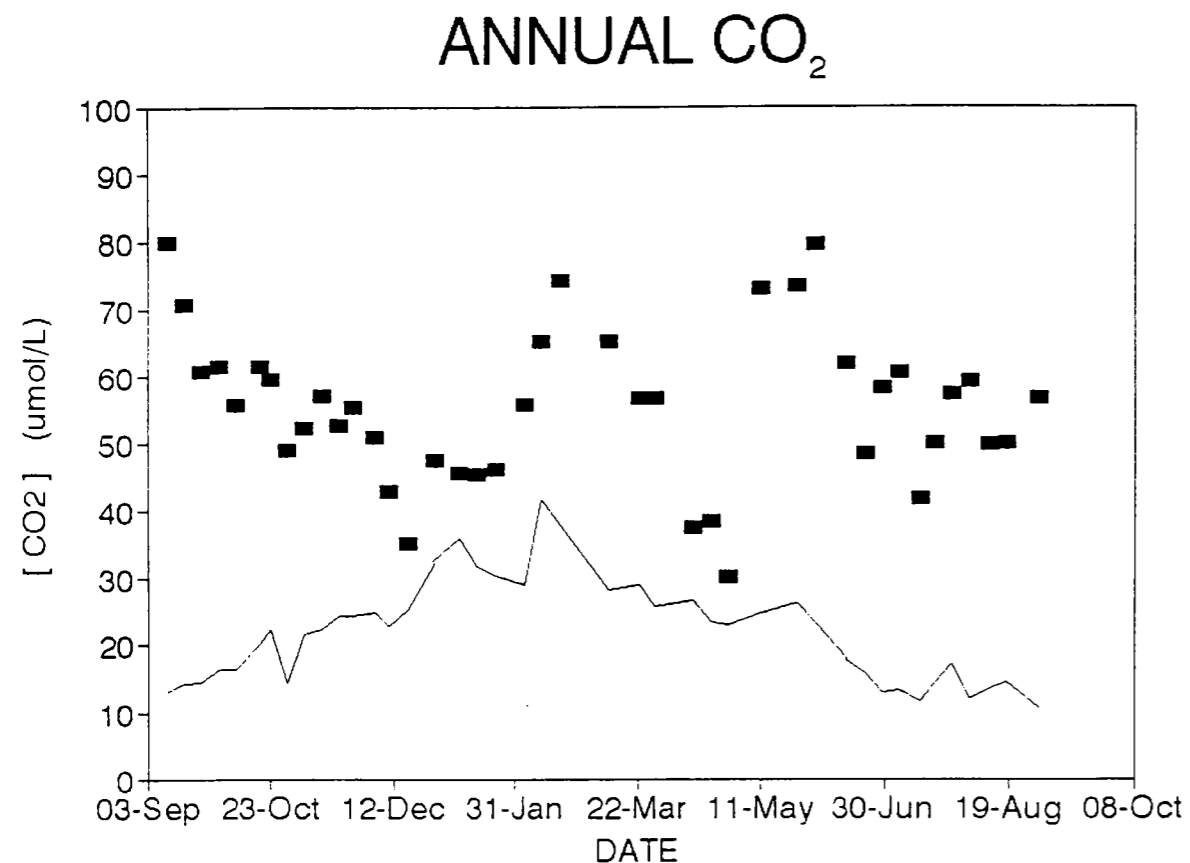


Figure 2 - Aqueous CO₂ for the 1992-1993 year at Poughkeepsie NY. The solid line is the concentration of CO₂ in water if it were in equilibrium with the atmosphere. The symbols represent aqueous CO₂. All CO₂ concentrations are reported in *umol/L*.

decline in dissolved CO₂, with concentrations falling to 30 *umol/L* by April 28. The last obvious trend occurred from April 28 to June 2 when the river's aqueous concentrations jumped to a level of 70 *umol/L* and remained there for three weeks. Finally, during the summer of 1993, the Hudson River's dissolved CO₂ fluctuated at around 50 *umol/L*.

The three diurnal studies performed on the Hudson River in the summer of 1993 are summarized in Figure 3. It should be noted that on a diurnal time scale, atmospheric evasion has little effect on CO₂ concentrations in the water. During intense sunlight hours (11 am to 2 pm) there was consumption of CO₂ due to photosynthesis. Photosynthesis during this three hour time period consumed 1.1-2.6 *umol* of CO₂ per liter. During nighttime hours, when photosynthesis is absent, there was production of CO₂ due to respiration. Nighttime respiration from 8 pm to 5 am led to the production of 6.8-10 *umol* of CO₂ per liter.

Figure 4 summarizes the three spatial studies (long river cruises) performed during the summer and fall of 1993. Except for the July cruise, there was little change in CO₂ on the longitudinal gradient (especially at 144 km where Rhinecliff is located), with concentrations changing by only around 10 *umol/L*. Previously, the effect of water advection on diurnal variations in CO₂ has been questioned (Howarth et al. 1992, Garritt 1990). It is possible that when sampling at a fixed location, the advection of water could bias results on a

DIURNAL CO₂

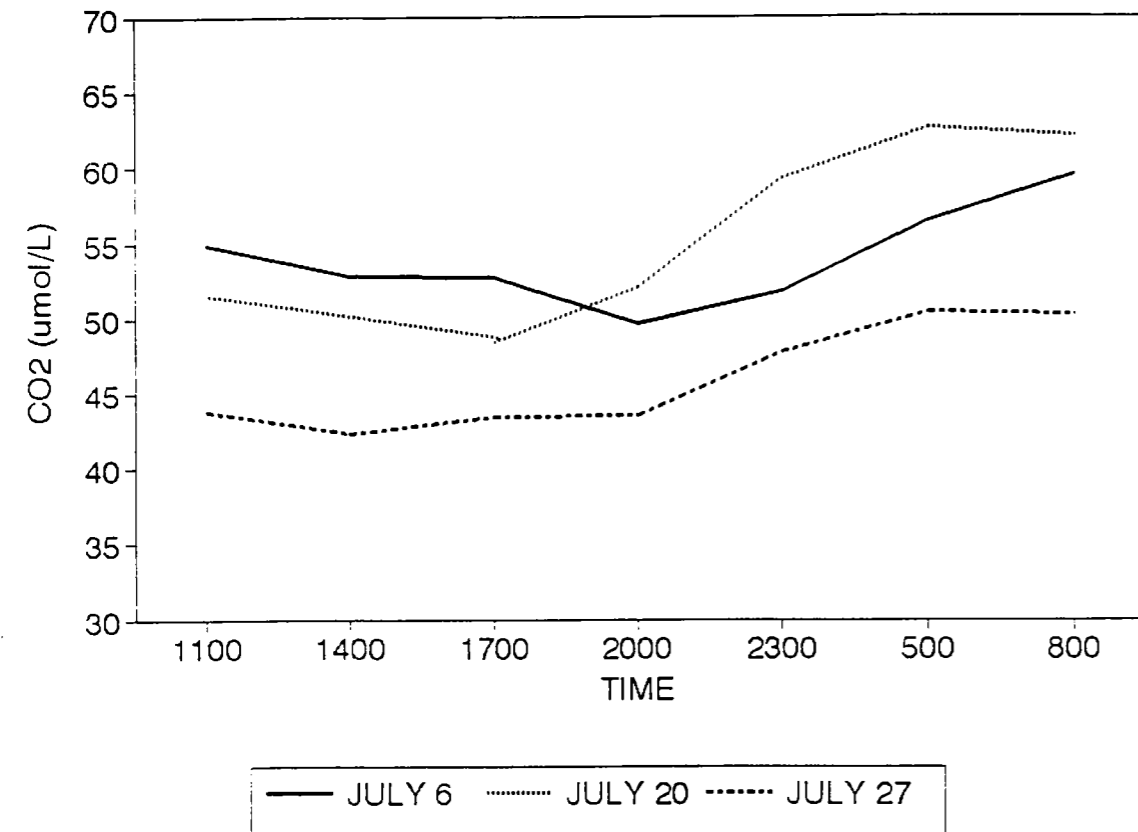


Figure 3 - Carbon dioxide on a diurnal time scale for three dates in July of 1993. On the x-axis is military time with 2000 equaling sunset and 500 sunrise. [CO₂] is reported on the y-axis in *umol/L*

LONG RIVER CRUISES

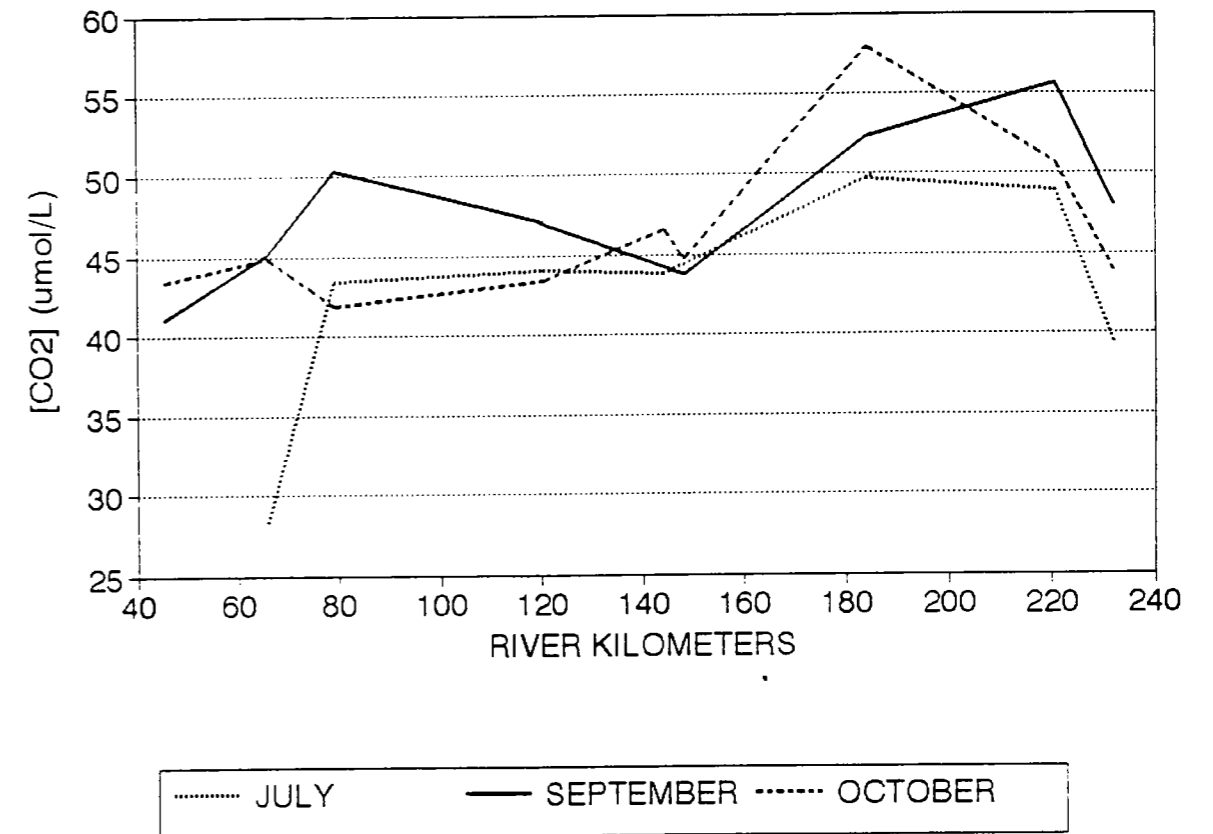


Figure 4 - Carbon dioxide measurements on a longitudinal scale as measured from the long river cruises. On the x-axis is river kilometers where 0 kilometers is the mouth, on the y-axis is the [CO₂]

diurnal time scale. The slight changes in CO₂ around the sample site (Figure 4) rules out large changes in CO₂ due to advection.

The final scale which will be addressed is vertical variation of [CO₂] in the Hudson River water column. On three dates in the summer and fall of 1993 the river was sampled during slack tide, at the surface, at mid-depth, and at one half meter off the bottom. On all dates there was a gradual, but slight increase in [CO₂] with depth on the scale of 0.9-2.9 $\mu\text{mol/L}$. This is a very small increase, most likely due to photosynthesis and evasion occurring at the surface and being absent at depth.

DISCUSSION

What controls CO₂ in the Hudson River?

At all times, and for every type of sample I took (seasonal, diurnal, spatial, and vertical) the Hudson River was supersaturated in CO₂ with respect to the atmosphere. This persistent CO₂ gradient implies that the river is a continuous source of CO₂ to the overlying atmosphere. I examine the magnitude of this source below.

A number of factors produce the persistent supersaturation in the river and the striking seasonal patterns we observe. First of all, the river is net heterotrophic. This means that the amount of organic materials being respired is in excess of the amount of organic

materials being generated by the autotrophs in the river. This is important because if carbon dioxide generated from respiration is in excess of CO₂ being consumed by photosynthesis, a situation can occur in which this excess CO₂ is building up in the system.

So what are causing these annual fluctuations and trends in dissolved CO₂ in the Hudson River? I propose that during the year, CO₂ is controlled mainly by four factors in the Hudson River: temperature, amounts of available organic carbon, river flow rates, and exchange with the atmosphere. The first two can be grouped together because they both are actually limiting factors of respiration, a source of CO₂. Anything which limits or controls respiration, controls a source of CO₂.

Temperature is directly related to the respiration rate (Odum 1956). This correlation has been demonstrated previously for the Hudson River (Howarth 1992), yet only during times of sharp temperature changes in the spring and fall can temperature regulate aqueous CO₂ concentrations. In fact, when water temperature was regressed against [CO₂] for the fall period, a significant relationship (r^2 of 0.58) was obtained (Figure 5). Yet this relationship does not hold for the entire year.

In the summer months the river temperature levels off at around 20° to 25°C. During these months CO₂ concentrations were not stable; CO₂ concentrations fluctuated as

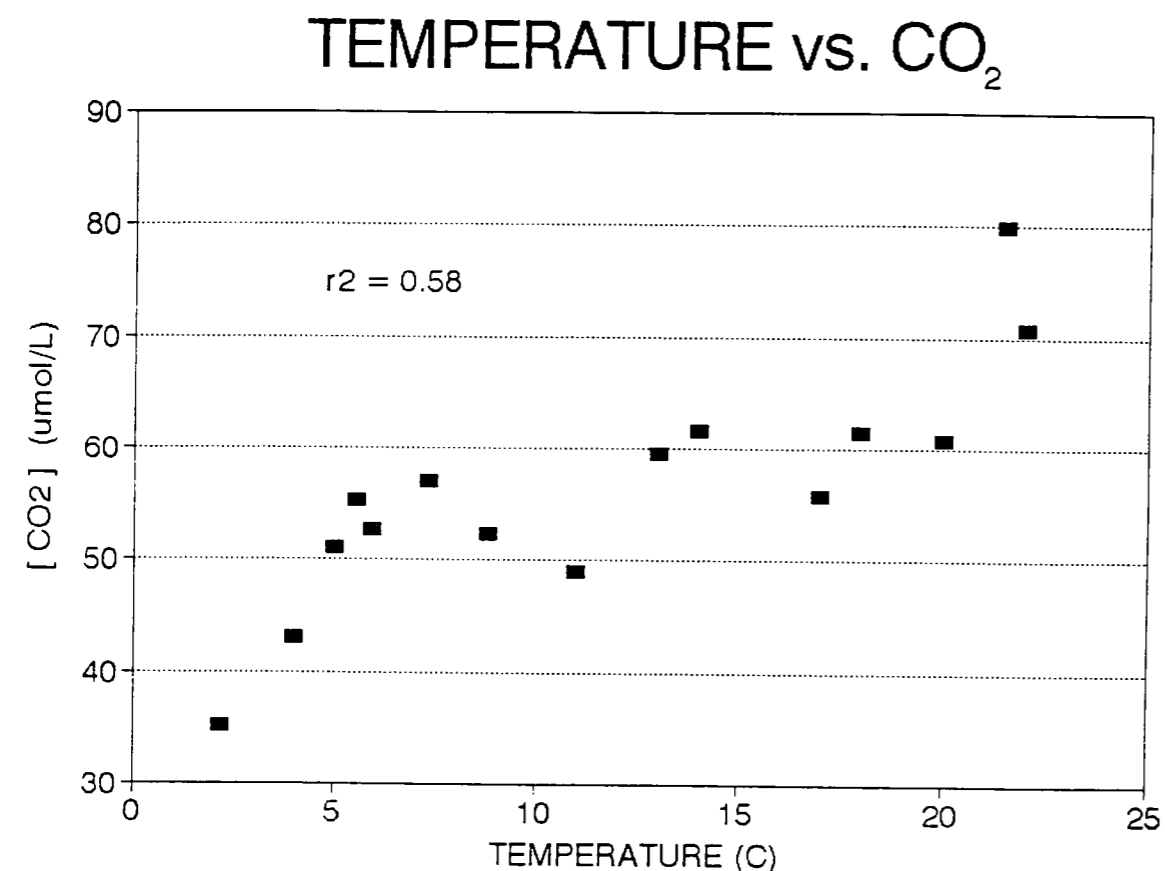


Figure 5 - Regression between temperature and [CO₂] during the fall of 1992. On the x-axis is temperature. and on the y-axis is [CO₂].

much as 20 $\mu\text{mol/L}$. One factor which can be ruled out for controlling CO₂ during this time frame is river flow rate. Flow rates increase the amount of time it takes for a section of river to reach the sample site in Poughkeepsie from the Dam at Troy. If flow rates are low it will take a longer time for a given section of water to reach Poughkeepsie, allowing a longer period for in situ processes. Therefore, varying flow rates could affect CO₂ concentrations at Poughkeepsie. But during the summer of 1993, rainfall was low and flow rates remained rather constant and low (Figure 6). During this period particulate, organic carbon (POC) was measured by David Fischer of IES. Figure 7 displays a regression between [POC] and [CO₂] from May through October of 1993: the regression has an r^2 of 0.80. This suggests that during this period of relatively constant temperature and flow rates, respiration rates controlled CO₂ concentrations. Furthermore, the amount of particulate organic carbon may have controlled respiration.

One indicator that river flow rate played a part in controlling CO₂ concentrations occurred in the spring of 1993. Melting snow and early rain resulted in increased discharge (Figure 6). In theory, this reduce down the time for in situ processes and atmospheric equilibration, and it should and introduce larger amounts of "fresh waters". The major process being slowed down is respiration, and this should leave less time for the build up of CO₂. Measurements from this period support this hypothesis.

FLOW AT GREEN ISLAND (1992-3)

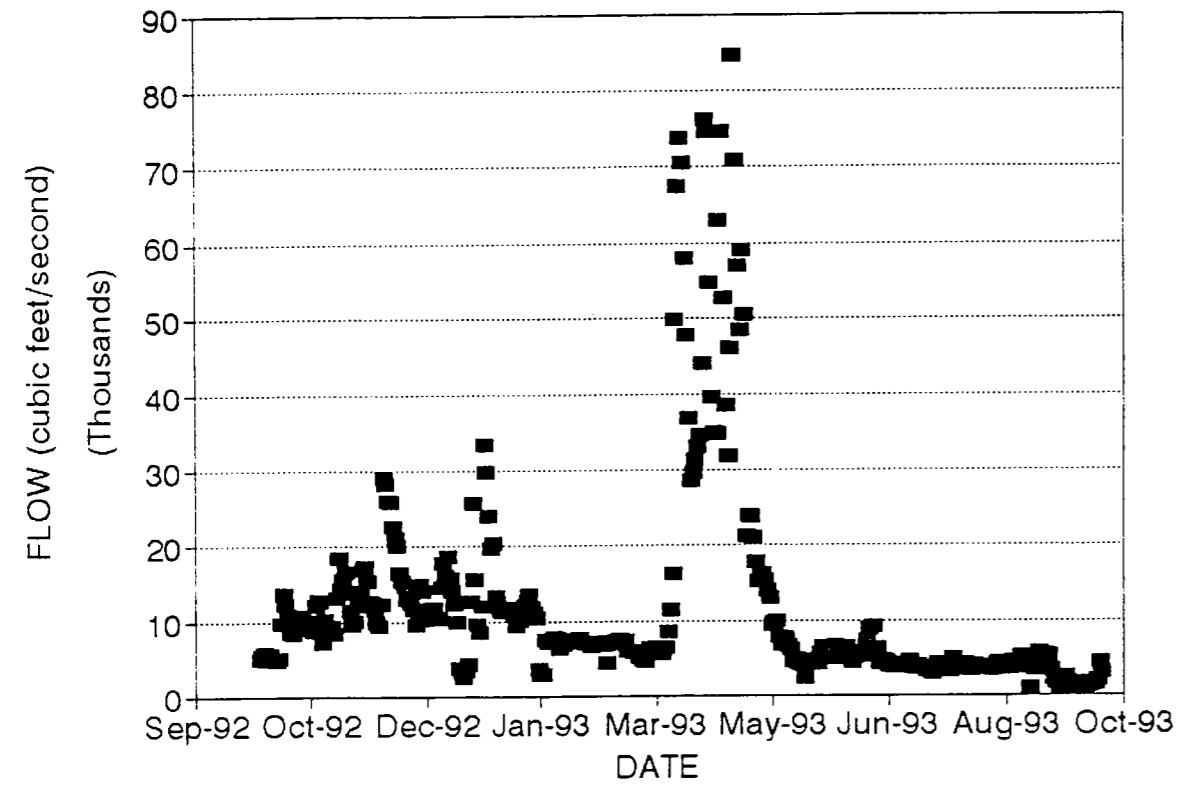


Figure 6 - The discharge at Green Island, located just above Albany, for the 1992-1993 year. Discharge is compiled from USGS data and is reported in cubic feet per second.

POC vs. CO₂

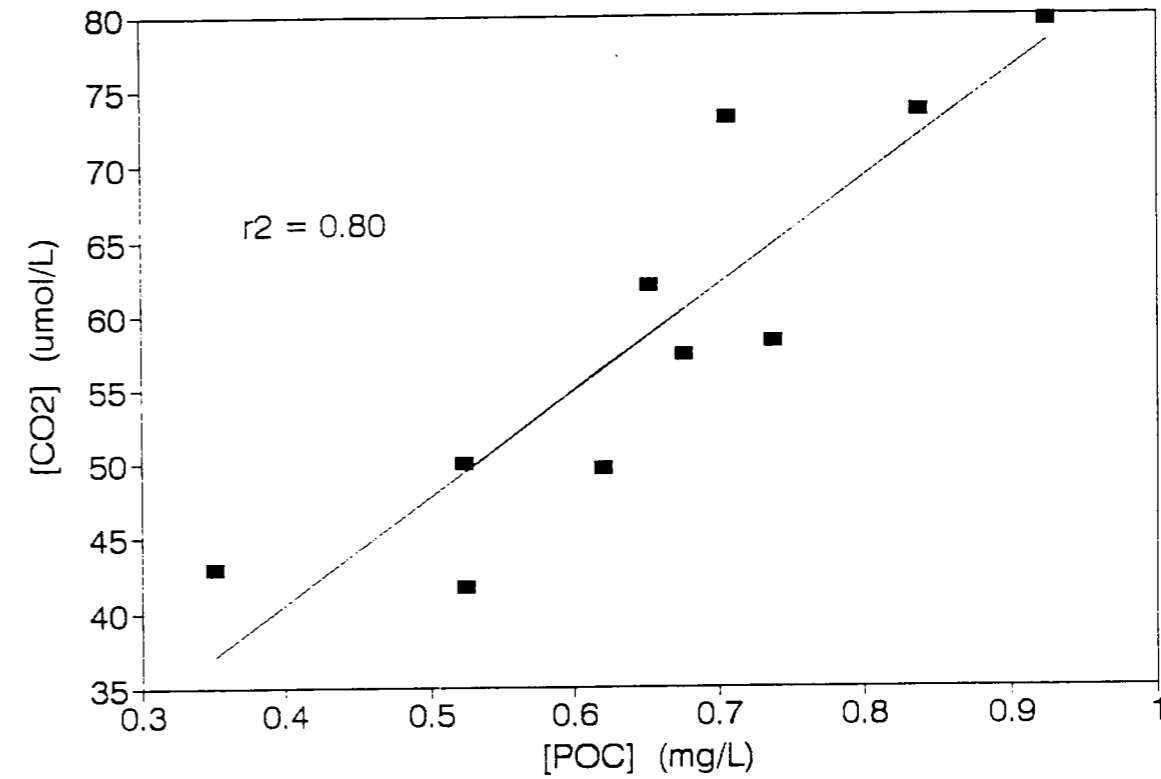


Figure 7 - A regression of [poc] and [CO₂] for the summer of 1993. On the x-axis is [POC] in mg/L on the y-axis is [CO₂] in *umol/L*

For the period studied, the Hudson River was a net source for atmospheric CO₂. The river is "exhaling", or degassing CO₂ to the atmosphere. In the winter of 1992-1993, the Hudson River was often fully or partially covered with ice; this ice creates a barrier which cuts off exchange with the atmosphere and allows for CO₂ to build up in the waters of the Hudson River. There is a distinct increase of CO₂ beginning in mid-January and ending in early March (Figure 2). These dates correspond exactly with the dates in which ice cover appears and disappears on the Hudson River.

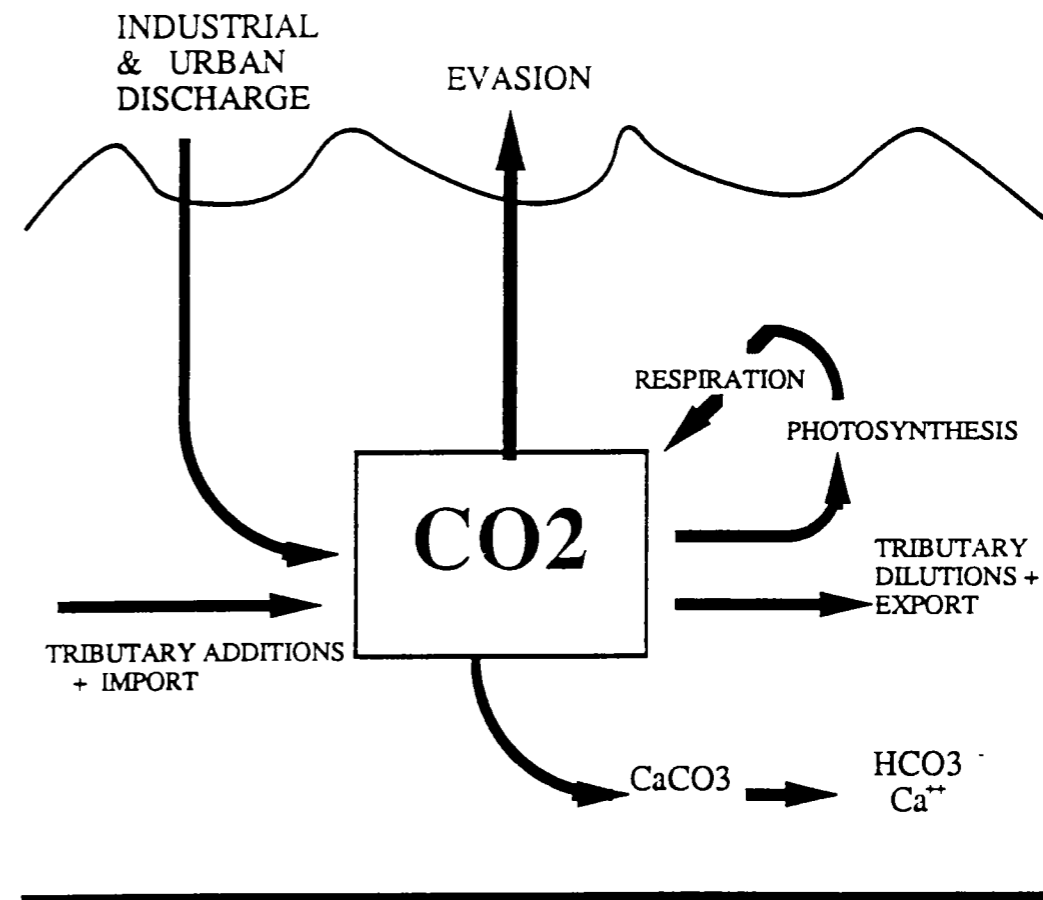
Sources and Sinks of CO₂

Figure 8 portrays a conceptual view for sources and sinks for CO₂ in the Hudson River. Respiration rates were calculated from diurnal curves.

The diurnal curves were used to make metabolic calculations, and Table 1 summarizes these results. These data show negative net production, indicating the Hudson River is a net heterotrophic system. Howarth et al. (1991) argued that this occurs mostly because of the input of allochthonous organic materials from forest ecosystems. So how does this effect the CO₂ concentrations in the Hudson River?

During July, the average net production was -0.67 grams of carbon/m²/day in the form of CO₂ (Table 1). This 0.67 grams was an input of CO₂ from respiration which does not continue in the loop for photosynthesis (Figure 8); instead this CO₂

**FIGURE 8
CO₂ BUDGET
IN THE HUDSON RIVER**



builds up in the water.

The Hudson River is a source for atmospheric CO₂ because of the exchange between the supersaturated waters and the immediate atmosphere. This indicates that in terms of the Hudson River's CO₂ concentrations, evasion to the atmosphere is a sink for CO₂. Because CO₂ was measured on different spatial and temporal scales, the calculation was approached in three different ways.

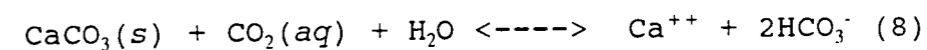
The diurnal measurements provided the most accurate estimate because of the frequency of sampling. From the three diurnal estimates I calculated a flux of between 0.18 and 0.27 grams of carbon to the atmosphere/m²/day. These estimates were used to check my flux calculation of the whole river, which can be made from the long river cruise data. The river was broken down into seven sections, each section bracketed on both sides by sites where CO₂ measurements were made. The two measurements from each side were averaged and used in the flux calculation. Once the surface area for each section was calculated, a net flux from each section was obtained. Next, the estimates from each of the seven sections were summed to furnish a whole river estimate. The section of the river including Rhinecliff shows a flux of 0.25 grams of carbon/m²/day. This estimate falls well within the range generated by the more detailed diurnal estimates and adds confidence in a whole river flux estimate calculated from the long river cruise data. Using the long river cruise data, the

flux of carbon from the river during your July through September time frame is between 39 and 58 billion grams of carbon a day.

Finally the section of the river bracketed by Poughkeepsie and Rhinecliff can be treated in the same manner as one of our seven sections from the long river cruises. This is beneficial because I have a complete annual data base for both Rhinecliff and Poughkeepsie and can therefore furnish an annual flux rate. An average flux of 59 grams of carbon/m²/year (0.16 grams of carbon/m²/day), with a high of 182 grams of carbon/m²/day in September and a low of 8.3 grams of carbon/m²/day in January is reported for the 1992-1993 year.

Calculations from U.S.G.S data showed that none of the tributaries can add or dilute enough water to change the river's CO₂ concentrations, except during periods of high flow. There are two reasons for this: a tributary does not have enough flow compared to the river's, and preliminary measurements and calculations show that the tributaries' CO₂ concentrations are too close to the river's concentration to make any addition of water a source or sink.

Another possibility for a source or sink of CO₂ is the following reaction:



The Hudson River is undersaturated in terms of CaCO_3 , and therefore Reaction 8 will only move in the forward direction. Furthermore, the rate of this reaction is so fast that CO_2 being consumed by this reaction will be consumed immediately, never showing up in the CO_2 pool. In other words; as soon as CO_2 is respired it reacts with CaCO_3 and will never build up in the Hudson River. For this reason the above reaction is a possible sink for CO_2 in the Hudson River, and a possible source for HCO_3^- and Ca^{++} .

From a combination of spatial and temporal sampling I estimated that 39 to 58 billion grams of carbon flux from the river to the atmosphere per day. So, how much carbon is this? An average coal burning power plant emits 889 grams of carbon/kilowatt hour (Brown 1992). Therefore during a summer day the Hudson River degasses the amount of carbon degassed by a power plant producing 44,000-68,000 kilowatt hours. An average house in Dutchess county uses 500 kilowatt hours/month, therefore on a single day the Hudson River degasses the amount of CO_2 equal to that of a coal power plant to meet the energy demands of 2600-4000 houses.

After subtracting primary production, Howarth (1992) reported a respiration rate of 566 grams of carbon/ m^2 /year. I calculated a respiration rate by adding up all sinks of CO_2 and to compare to this estimate. Subtracting my degassing (the only sink) estimate of 61 grams from Howarth's estimate left us with 505 grams unaccounted for. The most striking

possibility deals with Equation 8; a large amount of the CO_2 generated by respiration could be immediately reacting with CaCO_3 and generating HCO_3^- and Ca^{++} . Unfortunately the DIC method used by this study was not accurate enough to quantify this possibility. I recommend when using a free water CO_2 method to measure metabolism to also measure Ca^{++} .

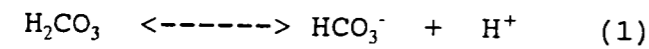
It should be noted that there was a large amount of field work involved with the project reported above, yet all the data could not be included. The most notable data which did not make it into this report was the derivation of an equation which indirectly calculates pH from DIC and CO_2 measurements, three vertical profiles, and DIC, O_2 , and chlorophyll measurements.

ACKNOWLEDGEMENTS

I would like to thank Jon Cole whose continued insights and supports were invaluable. I would also like to thank Joe Boyer and Nina Caraco who were very patient with helping me along with the whole writing process, Dave Fischer who was the most excellent companion on those long days on the river, and Betsy Blair and John Waldman for all the work they put into the editing process and set up of the Polgar program.

APPENDIX
CALCULATING pH

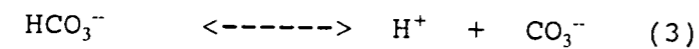
In order to calculate pH indirectly one must measure DIC, and CO₂. One must also have an understanding of the equilibria reactions of CO₂ in water. (Manahan, 1991) The first dissociation of CO₂ in water is:



its equilibration equation is:

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (2)$$

The second dissociation portrays the following equation:



and has the below equilibration equation:

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (4)$$

In order to find total dissolved carbon one adds up the constitutes:

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (5)$$

Since CO₂ is the only constitute actually measured, using equations 2 and 4, one must express all other constitutes in terms of CO₂, and then incorporate it into equation 5:

$$[\text{H}^+]^2(\text{DIC}-[\text{CO}_2]) - [\text{H}^+]([\text{CO}_2]k_{a1} - K_{a2}[\text{CO}_2]k_{a1}) = 0 \quad (6)$$

APPENDIX
POUGHKEEPSIE WEEKLY pH DATA
CALCULATED MEASURED

DATE	pH	pH	TEMP (C)
11-Sep-92	7.54	7.78	21.5
18-Sep-92	7.59	7.70	22
25-Sep-92	7.65	7.77	20
02-Oct-92	7.63	7.77	18
09-Oct-92	7.67	7.76	17
19-Oct-92	7.64	7.76	14
23-Oct-92	7.69	7.78	13
30-Oct-92	7.72	7.68	11
06-Nov-92	7.69	7.72	8.8
13-Nov-92	7.78	7.73	7.3
20-Nov-92	7.81	7.79	5.9
25-Nov-92	7.79	7.77	5.5
04-Dec-92	7.84	7.78	5
10-Dec-92	7.87	7.82	4
18-Dec-92	7.99	7.75	2.2
29-Dec-92	7.88	7.80	0.6
08-Jan-93	7.95	7.80	0.5
15-Jan-93	7.87	7.75	0.8
23-Jan-93	7.79	7.82	0.4
04-Feb-93	7.71	7.72	0.1
11-Feb-93	7.78	7.63	0.3
19-Feb-93	7.70	7.69	0.2
10-Mar-93	7.70	7.63	1
23-Mar-93	7.72	7.62	1.2
29-Mar-93	7.77	7.68	2
14-Apr-93	7.83	7.92	7.2
21-Apr-93	7.77	7.87	9.5
28-Apr-93	7.86	NA	7.9
11-May-93	7.49	7.60	7.6
26-May-93	NA	NA	7.6
02-Jun-93	7.53	7.63	7.63
15-Jun-93	7.58	7.66	19.3
22-Jun-93	7.71	7.74	19.8
29-Jun-93	7.61	7.70	23
06-Jul-93	7.68	7.54	22.8
14-Jul-93	7.82	NA	27.4
20-Jul-93	7.75	7.53	24.4
27-Jul-93	7.62	7.60	24.1
03-Aug-93	7.67	7.64	25
11-Aug-93	7.79	7.65	25.3
18-Aug-93	7.73	7.61	25
31-Aug-93	7.69	7.67	24.1

APPENDIX
POUGHKEEPSIE WEEKLY MEASUREMENTS

DATE	DIC (umol/L)	CO2 AIR (umol/L)	CO2 WATER (umol/L)	DO (mg/L)	TEMP (C)	CHLORO- PHYLL a (ug/L)
11-Sep-92	1261.0	13.4	79.9	9.4	21.5	2.05
18-Sep-92	1234.8	14.5	70.8	10.2	22	2.81
25-Sep-92	1173.2	14.7	60.8	8.9	20	NA
02-Oct-92	1108.0	16.6	61.5	6.4	18	NA
09-Oct-92	1075.5	16.5	55.7	8.0	17	2.81
19-Oct-92	1043.0	20.2	61.6	8.0	14	1.61
23-Oct-92	1106.3	22.3	59.5	7.8	13	0.94
30-Oct-92	931.9	14.4	48.9	9.5	11	1.23
06-Nov-92	903.2	21.6	52.3	9.5	8.8	0.87
13-Nov-92	1153.5	22.3	57.1	9.8	7.3	0.69
20-Nov-92	1109.7	24.3	52.6	11.8	5.9	1.00
25-Nov-92	1100.7	24.3	55.3	10.4	5.5	1.16
04-Dec-92	1123.8	24.8	50.9	11.0	5	1.03
10-Dec-92	980.6	22.8	42.9	10.7	4	0.56
18-Dec-92	1015.8	25.3	35.2	12.1	2.2	-0.45
29-Dec-92	1025.4	32.3	47.4	12.2	0.6	0.54
08-Jan-93	1150.2	36.0	45.7		0.5	0.81
15-Jan-93	953.7	31.6	45.4	12.4	0.8	0.76
23-Jan-93	821.3	30.4	46.3		0.4	0.81
04-Feb-93	817.6	28.9	55.7	13.3	0.1	0.48
11-Feb-93	1129.1	41.9	65.1	12.9	0.3	0.30
19-Feb-93	NA	37.8	74.3	13.5	0.2	NA
10-Mar-93	962.1	28.1	65.2	12.4	1	0.54
23-Mar-93	873.0	28.9	56.7	12.6	1.2	0.64
29-Mar-93	1003.3	25.7	56.6	12.0	2	1.81
14-Apr-93	838.1	26.6	37.4		7.2	0.28
21-Apr-93	799.8	23.4	38.4	11.1	9.5	0.68
28-Apr-93	734.4	22.9	30.1	11.9	7.9	3.31
11-May-93	808.8	24.7	73.1		7.6	1.50
26-May-93	NA	26.2	73.5		7.6	NA
02-Jun-93	959.5	23.4	79.6	8.0	7.63	NA
15-Jun-93	1034.9	18.0	62.0		19.3	1.90
22-Jun-93	1076.7	16.0	48.3	7.4	19.8	3.80
29-Jun-93	1077.4	13.0	58.2	6.8	23	3.03
06-Jul-93	1308.4	13.4	60.5	6.9	22.8	1.54
14-Jul-93	1301.1	11.8	41.8		27.4	4.62
20-Jul-93	1287.1	14.5	49.9		24.4	NA
27-Jul-93	1115.7	17.3	57.3		24.1	NA
03-Aug-93	1297.2	12.1	59.2		25	3.09
11-Aug-93	1409.0	13.6	49.7		25.3	3.95
18-Aug-93	1250.0	14.7	50.0		25	NA
31-Aug-93	1282.7	10.7	56.6		24.1	NA

APPENDIX
DIURNAL MEASUREMENTS

DATE	TIME (MILITARY)	DIC (umol/L)	CO2 (umol/L)	pH	CHLOROP -HYLLa (ug/L)
06-Jul-93	1100	1308.4	54.9	7.67	10.11
06-Jul-93	1400	1301.7	52.9	7.64	10.34
06-Jul-93	1700	1317.7	52.7	7.63	9.05
06-Jul-93	2000	1307.0	49.6	7.6	8.75
06-Jul-93	2300	1329.2	51.8	7.59	9.17
06-Jul-93	200	1325.6	57.0	7.56	8.56
06-Jul-93	500	1332.4	56.5	7.53	6.08
06-Jul-93	800	1346.1	59.5	7.53	10.60
20-Jul-93	1100	1265.4	51.0	7.6	4.76
20-Jul-93	1400	1262.2	NA	7.59	4.03
20-Jul-93	1700	1272.3	48.4	7.64	4.75
20-Jul-93	2000	1281.9	52.0	7.59	3.06
20-Jul-93	2300	1254.6	59.3	7.6	2.49
20-Jul-93	500	1262.8	62.6	7.57	1.91
20-Jul-93	800	1290.2	62.1	7.6	4.00
27-Jul-93	1100	1149.2	43.8	7.75	2.55
27-Jul-93	1400	1178.5	42.3	7.78	3.87
27-Jul-93	1700	1173.3	43.5	7.73	3.11
27-Jul-93	2000	1169.7	43.5	7.78	4.83
27-Jul-93	2300	1207.8	47.7	7.73	2.95
27-Jul-93	500	1192.8	50.4	7.72	3.9
27-Jul-93	800	1185.3	50.2	7.71	3.23

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