

## AN IFYGL CARBON BUDGET FOR LAKE ONTARIO<sup>1</sup>

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*Abstract.* A carbon budget was produced for each month of the International Field Year for the Great Lakes (IFYGL) year (April 1972 to March 1973) to determine the importance of the various sources and sinks of carbon. Major sources were found to be CO<sub>2</sub> which was fixed in organic matter during primary production and inorganic carbon in tributary streams, especially the Niagara River. The major sinks were found to be inorganic carbon outflow at the St. Lawrence River and net CO<sub>2</sub> gas exchange between the inorganic carbon pool and the atmosphere. Inflow and outflow of organic matter in rivers, sedimentation of organic and inorganic matter, ground water transport, and municipal and industrial perturbations accounted in total for less than 10% of the annual budget.

The lake had an inventory of approximately  $4.0 \times 10^{10}$  kg of inorganic carbon and approximately an order of magnitude less organic carbon. The riverborne flux of inorganic carbon of  $0.5 \times 10^{10}$  was 13% of the lake's inventory, assuming complete mixing; a minimum mean residence time of 8 years can be calculated from that inventory.

The seasonal cycle inherent in the fixation of carbon in primary production was primarily balanced by a complementary seasonal cycle in the air-lake CO<sub>2</sub> gas exchange system. The lake acts as a sink for CO<sub>2</sub> gas in the warm months when primary productivity is highest and as a source of CO<sub>2</sub> in the colder part of the year.

The IFYGL year had higher than normal rates of water flow, but this does not appear to have perturbed the inorganic carbon system. A comparison of IFYGL carbon budget results with corresponding estimates calculated for a typical year from historical data shows no major differences.

### INTRODUCTION

The field phase of the International Field Year for the Great Lakes (IFYGL), a large multi-disciplinary study of Lake Ontario,

was carried out from April 1972 to March 1973. A major product scheduled to come from our participation in this program is an overall ecological model describing in some detail the chemical-biological

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<sup>1</sup>This study was undertaken as part of the International Field Year for the Great Lakes, a joint United States-Canadian contribution to the International Hydrologic Decade.

interactions in Lake Ontario. Central to the theme of this model is an understanding of the lake's carbon system.

Toward this end, we presented an overview of this system, including estimates of the budget terms for a typical year based on composite data from a number of years (Robertson and Eadie 1975). However, as the results from IFYGL became available, it proved possible to combine aspects of several studies to calculate a detailed budget for the specific 12-month IFYGL period. This paper presents the results of these calculations and considers their significance in relation to the carbon cycle in the lake. The data available represent measurements generally well distributed in time and space so that a truly synoptic picture can be sought.

Investigations into the general chemistry of Lake Ontario were conducted previously by several groups and, although none specifically examined the carbon system, some components affecting this system were analyzed. The earliest lakewide survey data were reported in a publication of the Great Lakes Institute (1971); most earlier data were primarily from nearshore areas. Three cruises in 1965, analyzed by Casey et al. (1966), constituted the first interpretative report on some aspects of Lake Ontario's chemical distributions. The above two reports give the general ranges of pH and alkalinity to be expected in the warm part of the year. Kramer (1968) published the results of two Lake Ontario winter cruises during the 1965-66 season. He concluded that carbonate terrane lakes (Erie and Ontario) were saturated with respect to  $\text{CaCO}_3$  in summer and unsaturated in winter and that the partial pressure of

$\text{CO}_2$  was directly related to biomass. Dobson (1967) examined the rates of change of major ions in the lake on the time scale of decades and showed that alkalinity had not changed perceptibly within measurement accuracy since 1906. Sweers (1969), in an analysis of monitor cruises from 1966-67, found a mean pH in the hypolimnion during summer of 8.0 - 8.1 and a maximum pH in the surface of 8.6 in early summer with a second minor peak in late August. He also found minor minima in alkalinity roughly corresponding to the pH maxima.

In addition to the Great Lakes, carbon budgets were recently calculated for several other lakes. One of the first of these studies, produced for Green Lake in New York (Takahashi et al. 1968), included estimates of  $\text{CaCO}_3$  precipitation, photosynthetic production, and  $\text{CO}_2$  gas exchange with the atmosphere. The anaerobic nature of Green Lake made the results interesting, but quite inapplicable to a lake such as Ontario.

Schindler et al. (1973) outlined a general carbon budget for experimental lake 227 in western Ontario. This lake is small and has very low amounts of dissolved material and so differs greatly from Lake Ontario. Schindler and Fee (1973) even found primary production to be carbon limited at certain times of the day. The major carbon reservoir in this study was atmospheric  $\text{CO}_2$  with the lake acting as a sink in summer and as a source in the colder months.

O'Melia (1972) presented a carbon budget for the rather large Swiss Vierwaldstattersee. As the carbon system chemistry in this lake is similar to that in Lake Ontario, it is of special interest for our present purposes. In summer, O'Melia found an epilimnion loss of carbon of 7 moles/ $\text{m}^2$ /yr and a

sediment gain of 13 moles/m<sup>2</sup>/yr. In the winter, the lake gained 4 moles/m<sup>2</sup>/yr and the sediment lost 10 moles/m<sup>2</sup>/yr. The summer and winter gas exchange rates were +1 and -6 moles/m<sup>2</sup>/yr, respectively. The major changes in concentration of carbon in the lake were primarily related to CaCO<sub>3</sub> precipitation in summer and dissolution in winter. These general trends agree with the results of our study in showing an increase in the carbon inventory of the lake in summer due to photosynthetic fixation coupled with a decrease in winter through loss to the atmosphere.

### CARBON BUDGET EQUATION

The carbon budget can be expressed as the time rate of change in total carbon and be set equal to the sum of changes in the organic and inorganic components. The long-term trends in alkalinity analyzed by Dobson (1967) demonstrate that the lake is in a steady state with respect to inorganic carbon. Analogous long term data on organic carbon are lacking, and this represents the weakest element in our data set. However, we generally feel justified in assuming that the lake is in steady state with respect to total carbon over an annual cycle and that any imbalance detected by our calculations is a measure of accumulated system errors.

The basic equations concerning time variation of the carbon system can be presented as follows:

$$\frac{d(TC)}{dt} = \frac{d(IC)}{dt} + \frac{d(OC)}{dt} = 0$$

(assuming steady state)

$$\frac{d(IC)}{dt} = (IC)_I - (IC)_O +$$

$$\Delta E + \Delta(CP) + \Delta(IG) + \Delta(IW)$$

$$\frac{d(OC)}{dt} = (OC)_I - (OC)_O -$$

$$\Delta P + \Delta(OS) + \Delta(OG) + \Delta(OW),$$

where

TC = total carbon

IC = inorganic carbon

OC = organic carbon

$\Delta E$  = net flux of carbon between the atmosphere and the inorganic carbon pool in the lake

$\Delta(CP)$  = net precipitation of CaCO<sub>3</sub>

$\Delta(IG)$  = net addition of inorganic carbon by ground water

$\Delta(OG)$  = net addition of organic carbon by ground water

$\Delta(IW)$  = net addition of inorganic carbon in water used for industrial and municipal purposes

$\Delta(OW)$  = net addition of organic carbon in waters used for industrial and municipal purposes

$\Delta P$  = net carbon fixed in primary production

$\Delta(OS)$  = net sedimentary deposition of organic matter

Subscript I denotes river inflow terms.

Subscript O denotes river outflow terms.

The structure of these equations is similar to those of Schindler and Fee (1973) with the additional terms required to handle an open system. The budget assumes that the amounts of carbon added to the lake by dry dust fall and by precipitation are negligible.

The terms involving CO<sub>2</sub> gaseous exchange require some explanation. The total CO<sub>2</sub> gas crossing the air-water interface cannot be measured directly with the techniques employed during IFYGL. The change in the inorganic carbon content of the water ( $\Delta(IC)$ ) is equal to the net exchange of CO<sub>2</sub>

between this fraction and the air minus the net amount of CO<sub>2</sub> converted to organic carbon through photosynthesis ( $\Delta P$ ). Therefore, the total gas exchange for the lake is equal to net flux ( $\Delta E$ ) plus net primary production ( $\Delta P$ ).

of the inorganic carbon species were estimated by the use of the equations presented by Li et al. (1969). For these calculations pH was corrected to the in situ temperature, and the H<sub>2</sub>CO<sub>3</sub> dissociation constants were corrected to an ionic strength of 0.005.

#### CALCULATION OF THE BUDGET TERMS

An attempt was made to estimate each of the terms in the carbon budget for each month of the IFYGL period. The methods of calculation are presented separately for each term in the following subsections.

Very seldom were direct measurements of total inorganic carbon available for use in our calculations. However, values for pH, alkalinity, and temperature were commonly available. Thus, total carbon and the distribution

#### *Riverborne Inflows and Outflows of Inorganic Carbon*

Transport of inorganic carbon was calculated for the major inflows to and the outflow from Lake Ontario by multiplying monthly mean values of concentration of inorganic carbon by monthly mean streamflows. The data for calculating inorganic carbon concentrations for the inflows and outflow on the U.S. side of Lake Ontario were obtained primarily from the Environmental Protection Agency (EPA) STORET Archive System with supplemental information

TABLE 1. Streamflow (m<sup>3</sup>/s) for the IFYGL period.

Month	River					
	St. Lawrence	Niagara	Oswego	Genesee	Black	Small Rivers
Jan	7392	7238	431	114	212	1125
Feb	7373	6317	340	84	181	758
Mar	8851	7680	347	223	287	1677
Apr	7834	6662	537	214	300	1925
May	8563	7142	513	144	297	1350
Jun	8486	6893	414	207	211	627
Jul	9082	7162	557	241	149	781
Aug	9101	7027	184	44	70	393
Sep	8736	6682	83	25	44	174
Oct	8870	7008	107	46	65	416
Nov	8352	6931	369	130	177	802
Dec	7949	7411	468	229	174	1087
Average	8382	7013	363	142	181	926

from the U.S. Geological Survey (1972b, 1973b). Data from the Canadian side were made available by the Ontario Ministry of the Environment (MOE) and the Water Quality Branch of the Department of the Environment (DOE).

Table 1 presents the mean monthly values for river inflows to and outflow from the lake. The values for the Niagara and the St. Lawrence Rivers were adopted from DeCooke and Witherspoon (1974); those for the Oswego, Genesee, and Black Rivers were obtained from the U.S. Geological Survey (1972a, 1973a). Combined flow values for the smaller rivers and streams were estimated by subtracting the combined flows of these three large tributaries from monthly values for the combined flow of all tributaries (except the Niagara River) provided by DeCooke and Witherspoon.

As no chemical values were obtainable for these smaller rivers, their input of inorganic carbon had to be estimated indirectly. This was done by calculating the ratio of flow of the smaller rivers to that for the combined Genesee, Black, and Oswego Rivers and then multiplying the combined inorganic carbon input from the three larger rivers by the appropriate flow ratio.

#### *Riverborne Inflow and Outflow of Organic Carbon*

These terms were calculated in a manner similar to that described for the inorganic flow terms above. The same data sources were used and the flow values in Table 1 were employed.

#### *Net Exchange Between the Atmosphere and the Inorganic Pool in the Lake*

Several papers have been written on the theoretical and

empirical aspects of gas exchange across an air-water interface. We chose to adapt the empirical relationship developed by Kanwisher (1963) and Liss (1973) in which the exchange coefficients were shown to be a function of wind speed squared. Using their data, the following formula were obtained:

$$\text{Flux} = 10(0.3W^2 + 5) \cdot \Delta\text{PCO}_2 \cdot \alpha,$$

where

Flux = carbon flux (moles/m<sup>2</sup>/hr)

W = wind speed at 10 cm (m/s)

$\Delta\text{PCO}_2$  = partial pressure of CO<sub>2</sub> in surface water - 0.00033 (atm)

$\alpha$  = solubility of CO<sub>2</sub> in water (moles/l).

Wind speeds for land stations around the lake were taken from summaries of weather data for the IFYGL period which were produced by the Canadian Atmospheric Environment Service (1972-73). The means of these data were fitted to a 2nd order polynomial of Julian day and corrected for speed over water to speed over land by the monthly estimates of Richards et al. (1966) for the lower Great Lakes. A factor of one third was used to estimate the logarithmic decrease in speed from the 10 m measurement height to a 10 cm height. As noted above in the definition of  $\Delta P$ , a constant atmospheric CO<sub>2</sub> content was assumed.

In order to calculate  $\Delta P$ , the partial pressure of CO<sub>2</sub> in the surface waters must be estimated. This was done by using unpublished data gathered during IFYGL and made available by the Canada Centre for Inland Waters (CCIW) and the Lake Survey Center of the National Oceanic and Atmospheric Administration (NOAA). As the total inorganic carbon inventory of the lake was of some interest, estimates for the inorganic carbon species were made not only for the surface layers but also for three deeper levels.

The levels selected were 0-10 m (surface), 10-25 m, 25-50 m, and below 50 m. Lake wide means for pH, alkalinity, and temperature were calculated for each level and the total inorganic carbon values were calculated from these means. The percentage volume of the lake within each level was adapted from Hughes et al. (1972). A comparison of the gas exchange values obtained by the use of these means with values obtained by calculating the gas exchange separately for each station and then summing these to give a total for the lake indicated that the two methods provided estimates that agreed within 10% in all cases. For comparative purposes, calculations of the carbon inventory were also made for a typical year based on data gathered prior to IFYGL and available in reports published by CCIW (1966-69). The precision of the data used in our calculations is estimated to be  $\pm 0.5^\circ\text{C}$  for temperature, and  $\pm 0.5\%$  for alkalinity. These estimates are based on our own analyses as well as those for data gathered from the Great Lakes by CCIW and reported by Strachan (1973).

*Net Precipitation/Dissolution of  $\text{CaCO}_3$*

A report by Thomas et al. (1972) indicated a range of 366-1156  $\text{g/m}^2/\text{yr}$  for present-day total sedimentation rate in Lake Ontario and an average  $\text{CaCO}_3$  concentration of 0.43 weight percent of dry sediment with a standard deviation of 0.44%. If we assume a mean deposition rate of 500  $\text{g/m}^2/\text{yr}$  and a bottom area of  $1.9 \times 10^{10} \text{ m}^2$ , we can obtain a value of  $4.1 \times 10^7 \text{ kg}$  for the total carbon deposited as  $\text{CaCO}_3$  in a year.

Rough estimates of the monthly values of  $\text{CaCO}_3$  deposition were obtained by proportioning

this total according to the monthly variations in the ratio of the ion activity products (IP) to the saturation concentration ( $K_{\text{sp}}$ ). The ion activities for carbonate were obtained as explained in the preceding section and calcium concentration was assumed to be a constant 43 ppm (Dobson 1967). To obtain the monthly variations used in the budget, the carbonate concentrations in the bottom level were used; however, the relations to saturation were calculated for all levels.

*Inorganic and Organic Carbon Added by Ground Water*

The inorganic carbon introduced into the lake via ground water was calculated by using Haefeli's data (1970, 1972), i.e., a flow of approximately  $1.7 \text{ m}^3/\text{s}$  and an alkalinity of approximately 250 ppm. This term turned out to be negligibly small on a lakewide scale and was omitted from further consideration. As the organic carbon in the ground water was undoubtedly considerably less than the inorganic carbon, this term was also omitted.

*Net Exchange of Inorganic Carbon by Industrial and Municipal Sources*

Data on the chemical changes incurred by municipal and industrial usage of water proved very difficult to track down; thus, only flows were considered for this paper. Data were made available for the U.S. side by the New York State Department of Environmental Conservation and for the Canadian side by the Ontario Ministry of the Environment.

The flow capacity for municipal use in New York was  $5 \text{ m}^2/\text{s}$ , while the usage in Ontario was  $18 \text{ m}^2/\text{s}$ . In total these amounted to approximately 0.25% of the river inflow. Thus, since approximately

90% of the basin population is sewerred, the inputs of carbon from municipal sources can be assumed to be insignificant on a lakewide basis.

For industrial cooling, usage was much larger, 228 m<sup>3</sup>/s on the Canadian side and 8 m<sup>3</sup>/s on the U.S. side. However, this use probably had little effect on the carbon budget. For example, an examination of unpublished data from a fossil fuel plant on Lake Michigan showed that carbon content changed little in water used for cooling. In this plant the change in temperature was approximately 5-7°C, and small, variable changes occurred in alkalinity and pH. These effects were strongly localized and would have had minimal effects on a short-term, lakewide carbon budget.

#### *Net Fixation in Primary Production*

Net primary production is included in the budget as a complement to the net gas exchange as previously mentioned. Part of the CO<sub>2</sub> which crosses the air-lake interface is rapidly metabolized into the organic phase which later decomposes to reform CO<sub>2</sub>. It is this large pool of oxidizing organic matter which creates the large CO<sub>2</sub> partial pressures leading to CO<sub>2</sub> gas evasion in the winter.

Our estimate of the net primary productivity of Lake Ontario is based on a detailed study by Stadelmann et al. (1974) conducted during IFYGL. They concluded that primary production was approximately 270 g C/m<sup>2</sup>/yr in the inshore region and 170 g C/m<sup>2</sup>/yr in the offshore region. If we assume that 10% of the lake can be considered inshore, the total carbon fixed during the year can be calculated as approximately

$3.4 \times 10^9$  kg. As this value represents something between net and gross primary productivity, it is probably too high; at any rate, it is only a rough approximation.

#### *Net Sedimentary Deposition of Organic Matter*

Thomas et al. (1972) included a mean for sedimentary organic carbon of 1.98% with a standard deviation of 0.33%. By the use of the same sedimentation rate and area as in the CaCO<sub>3</sub> calculation, an organic carbon deposition rate of  $1.9 \times 10^8$  kg/yr was found. This rate also tended to be seasonal and lagged the productivity curve by the residence time. The mean particulate organic carbon (POC) residence time for Lake Ontario was calculated to be approximately 3 months. In the calculation of the monthly budget, the carbon sedimentation rate was assumed to lag the productivity curve by this length of time.

## RESULTS AND DISCUSSION

### *Overall Carbon Budget*

Our estimate of the carbon budget for Lake Ontario during IFYGL is presented in Table 2. It indicates that the major sources and sinks of carbon during this period were river-borne carbon, primary production and net gas exchange across the air-lake interface. The most important source was obviously the river systems which feed the lake, and the most important sink was the St. Lawrence River, which provides its only outlet. The stability from month to month in the inorganic carbon values from the rivers reflects the fact that the Niagara River, providing approximately 85% of the inflow, and the St. Lawrence River have relatively

TABLE 2. Carbon balance ( $\times 10^8$  g) for the IFYGL period.

Month	Inflow			Outflow					Net
	Inorganic	Organic	$\Delta P$	Inorganic	$\Delta E$	$\Delta(CP)$	Organic	$\Delta(OS)$	
	$(IC)_I$	$(OC)_I$		$(IC)_O$			$(OC)_O$		
Jan	5.0	0.5	0.4	4.4	9.1	0.13	0.3	0.03	-8.1
Feb	4.0	0.4	0.8	4.7	4.8	-0.13	0.3	0.02	-4.5
Mar	4.9	0.4	1.4	5.0	2.1	-0.11	0.3	0.04	-0.6
Apr	4.0	0.6	1.9	4.2	0.6	0.16	0.6	0.08	0.9
May	4.3	0.7	2.3	4.8	-0.1	0.17	0.6	0.11	1.7
Jun	4.4	0.7	2.7	4.0	-0.6	0.19	0.6	0.13	3.5
Jul	4.7	0.6	5.7	4.3	-0.8	0.17	0.6	0.15	6.6
Aug	4.8	0.3	7.7	4.4	-0.6	-0.13	0.7	0.32	8.1
Sep	4.9	0.5	7.1	4.0	-0.1	-0.14	0.7	0.43	7.6
Oct	5.5	0.7	2.6	3.8	0.9	-0.13	0.2	0.40	3.6
Nov	5.5	0.4	1.0	4.4	5.2	0.12	0.2	0.15	-3.2
Dec	5.3	0.6	0.5	4.7	8.7	0.12	0.3	0.06	-7.5
Sub-total	57.3	6.4	34.1	52.7	29.2	0.4	5.4	1.9	
Total		97.8					89.6		8.2

constant flows.

The monthly inflow and outflow of carbon is illustrated in Fig. 1. The bulge in inflow during late summer is a reflection of increased primary production and is balanced by the outflow of  $CO_2$  gas in the winter months. The midsummer difference of approximately  $7.5 \times 10^8$  kg carbon (inflow-outflow) represents roughly 2% of the total inorganic carbon inventory of the lake, which is approximately  $4 \times 10^{10}$  kg.

The time series of lake-wide means for pH and alkalinity at different levels are shown in Figs. 2 and 3 respectively. Average pH values show the same trends reported by Sweers (1969), with the maxima

in midsummer apparently related to biological activity. Our values show greater variability in the deep samples than Sweers reported, with trends following the seasonal pattern of the surface values. The means of alkalinity present a more scattered picture with a possible minimum occurring in September-October. The approximate mean value for the whole lake-year is 94 mg, which agrees well with Dobson's (1967) value, indicating no apparent increase in alkalinity in the past 6 years.

#### *Riverborne Inorganic Carbon*

River water carrying entrained inorganic carbon in the form of  $HCO_3^-$ ,  $CO_3^{2-}$ , and  $CO_2$  is the largest

FIG. 1. Monthly means of total carbon inflow and outflow.

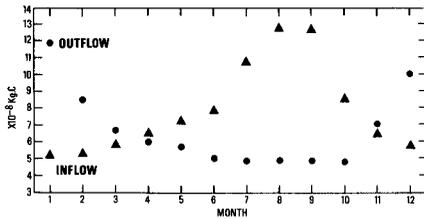


FIG. 2. Lakewide means of pH at 4 levels: 0(0-10 m), 10(10.1-25 m), 25(25.1-50 m), and 50(below 50 m).

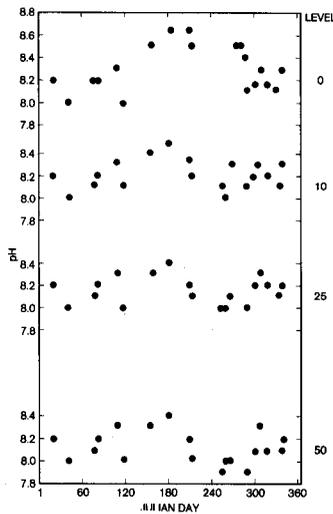
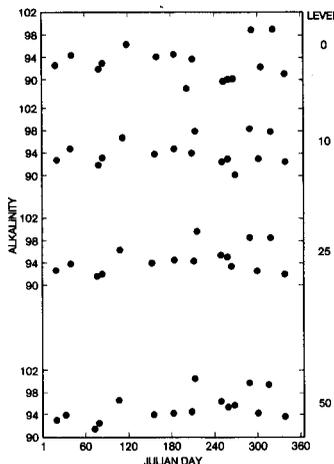


FIG. 3. Lakewide means of alkalinity (ppm) at 4 levels: 0(0-10 m), 10(10.1-25 m), 25(25.1-50 m), and 50(below 50 m).



source and the largest sink of this element for the lake. The values for these terms in our budget for the IFYGL period are substantially larger than the comparable values from the average year budget calculated by Robertson and Eadie (1975). This difference is related to the fact that the streamflows during IFYGL were considerably larger than normal (DeCooke and Witherspoon 1974).

A counteracting trend was observed in the U.S. EPA data on alkalinity from the Niagara River (Table 3). These values, on the average approximately 10% lower than comparable data averaged for the previous 7 years, were perhaps related to the dilution effect arising from the higher flows, although the St. Lawrence River during IFYGL showed means of alkalinity 10% higher than normal (Table 4).

A trend of lower values of alkalinity for the Niagara River can not be verified with the Canadian DOE data on the alkalinity during IFYGL, however. These latter data showed an average value that was higher than the U.S. value and about the same as the mean for the previous years. Without any direct intercomparisons of the analyses by the two sides, it was impossible to resolve the apparent discrepancies between the two data sets. However, it seems likely that one or both data sets contained a bias in measurement. Such biases have been demonstrated for other sets of IFYGL data (Robertson et al. 1974). For the purposes of this paper the sets were combined directly and the averages generated. These averages favor the U.S. data since there were more measurements on that side.

Monthly variations in flow and consequently in carbon flux were quite large in all rivers except the Niagara and the St. Lawrence. The mean total flow for the Oswego,

TABLE 3. Niagara River chemistry for the IFYGL period.

Month	U.S.				Canada		
	Number	pH	Alk	SD	Number	pH	Alk
Jan	3	8.7	1.73	0.08	1	7.7	1.80
Feb	6	8.3	1.73	0.04	1	7.7	1.94
Mar	5	6.8	1.60	0.03	1	7.9	1.84
Apr	3	7.3	1.26	0.01	1	7.5	1.86
May	7	7.7	1.40	0.08	1	7.6	1.62
Jun	7	7.8	1.63	0.02	1	7.8	1.78
Jul	10	7.9	1.60	0.02	1	7.6	1.72
Aug	8	7.7	1.77	0.10	1	8.2	1.78
Sep	14	7.0	1.77	0.03	1	8.1	1.78
Oct	5	6.7	1.72	0.06	1	7.3	1.96
Nov	9	7.3	1.73	0.06	1	7.4	1.98
Dec	6	8.0	1.63	0.11	1	7.6	2.02
Mean		7.6	1.63			7.7	1.86

Black, and Genesee Rivers averaged approximately 75% higher during IFYGL than in an average year. Table 5 shows the variability of these rivers in comparison with the Niagara and the St. Lawrence. By use of the approach outlined in the Methods Section, a carbon inflow of approximately  $0.45 \times 10^8$  kg/month was calculated for the small rivers and streams. Summing the monthly means of all river inputs and outputs, we get an excess inflow of approximately  $0.3 \times 10^8$  kg; but this estimate may be low due to the uncertainties in the alkalinity values from the Niagara River.

#### *CO<sub>2</sub> Gas Exchange*

When we first began our examination of the carbon system, we had very little idea of the

magnitude of the gas exchange factor or of its seasonal variation. When examined in the time frame of weeks, we found that it was the same order of magnitude as the river inorganic carbon flux and strongly seasonally dependent.

During spring and summer, the surface layers became undersaturated in CO<sub>2</sub> due to photosynthetic activity and the lake acts as a sink for atmospheric CO<sub>2</sub>. In the fall when photosynthetic activity subsides and stratification begins to break down, the waters of the hypolimnion, supersaturated with CO<sub>2</sub> from in situ oxidation of organic matter, begin to act as a source of CO<sub>2</sub>. Figure 4 shows the seasonal variability of the exchange; and, upon integration of the curves, we approximate 121 g C/m<sup>2</sup>/yr net outflux for the IFYGL year.

An interesting aspect of the

TABLE 4. River inorganic carbon for the IFYGL period (kg C/month).

Month	U.S.				Canada		
	Number	pH	Alk	SD	Number	pH	Alk
Jan	-	-	-	-	1	7.9	1.86
Feb	-	-	-	-	-	-	-
Mar	2	7.9	1.84	0.00	1	7.8	1.90
Apr	3	8.2	1.85	0.01	1	7.8	1.76
May	3	8.3	1.88	0.03	1	7.8	1.76
Jun	3	8.4	1.83	0.01	1	8.0	1.72
Jul	2	8.2	1.82	0.10	1	6.9	1.78
Aug	3	8.1	1.76	0.08	1	7.3	1.78
Sep	3	8.2	1.85	0.06	1	7.8	1.62
Oct	3	8.0	1.87	0.08	1	7.9	1.78
Nov	3	8.2	1.90	0.01	1	7.7	1.80
Dec	2	7.5	1.86	0.03	-	-	-
Mean		8.1	1.85			7.7	1.78

gas phenomenon appeared when the seasonal distribution of the in situ partial pressure of  $\text{CO}_2$  was examined. The partial pressures of  $\text{CO}_2$  at the four levels previously defined were calculated from whole lake means of pH, alkalinity, and temperature for each level. Figure 5 shows a plot of the results of these calculations for the upper (0-10 m) and lower (< 50 m) levels. The values for the two middle levels were intermediate and so were omitted from the figure for clarity. From these calculations it becomes apparent that the lake as a whole is always supersaturated with  $\text{CO}_2$ , although in late spring and summer the upper 10 m certainly become undersaturated due to  $\text{CO}_2$  fixation. To verify this conclusion, data collected from 1964-69 were analyzed in the same way (Fig. 6). When these two figures were compared

they showed the same general trends, although the winter decrease was much more gradual during IFYGL, possibly indicating some perturbation in the overturning process. Also the levels of  $\text{CO}_2$  never got as high during IFYGL as in previous years, possibly due to the disturbance of stratification by Hurricane Agnes in June of that year.

#### *Precipitation of $\text{CaCO}_3$*

As mentioned previously, estimates of the ion products for  $\text{CaCO}_3$  were made for each level during IFYGL. The results from the upper and lower levels, compared with saturation, are in Fig. 7. Such calculations were also made for an average year (Fig. 8). Strong seasonal trends were observed, with high levels of supersaturation occurring in the warmer months and undersaturation occurring at all

TABLE 5. River inorganic carbon for the IFYGL period (kg C/month).

Month	River				
	St. Lawrence ( $\times 10^8$ )	Niagara ( $\times 10^8$ )	Oswego* ( $\times 10^7$ )	Genesee ( $\times 10^7$ )	Black ( $\times 10^6$ )
Jan	4.38	4.01	3.52	1.10	-
Feb	-	3.22	2.54	0.72	2.69
Mar	4.99	3.88	2.88	1.89	7.84
Apr	4.24	3.07	2.98	0.84	7.34
May	4.80	3.42	2.95	0.59	4.96
Jun	4.02	3.60	2.75	0.44	1.73
Jul	4.25	3.78	4.06	0.31	-
Aug	4.38	4.19	1.46	0.18	-
Sep	4.04	4.38	0.56	0.15	1.27
Oct	3.84	4.72	-	0.61	2.66
Nov	4.42	4.24	3.76	4.06	5.25
Dec	4.67	4.01	4.38	3.90	4.18
Mean	4.37	3.88	2.89	1.23	4.21

\* Data from Lake Survey Center of NOAA, Detroit, Michigan  
Small river discharge on the order of  $0.45 \times 10^8$  kg/month

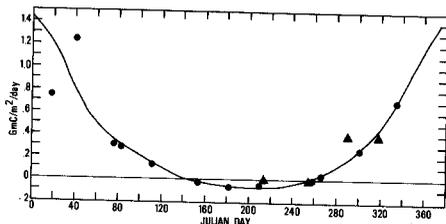
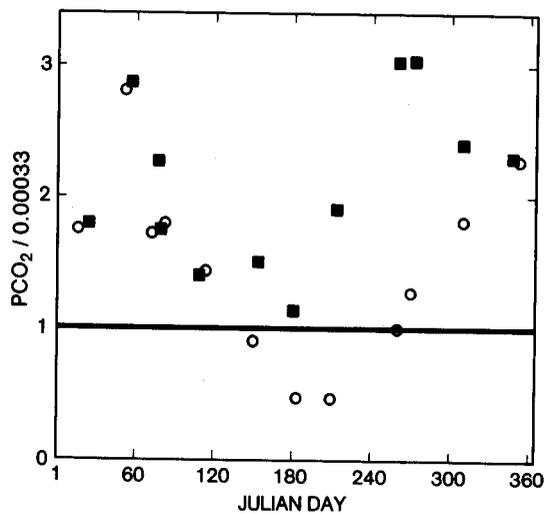


FIG. 4. Air-lake  $\text{CO}_2$  gas exchange, positive values for evasion. CCIW date ( $\circ$ ), Lake Survey Center data ( $\blacktriangle$ )

FIG. 5. Partial pressure of  $\text{CO}_2$  gas relative to 1 atmosphere (STP) during IFYGL. Level 1 (0-10 m -  $\circ$ ), level 4 (below 50 m -  $\blacksquare$ ).



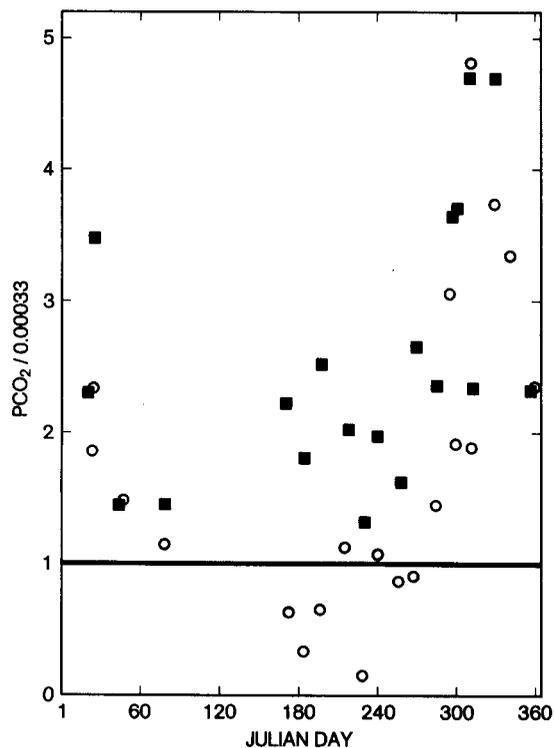


FIG. 6. Partial pressure of  $\text{CO}_2$  gas relative to 1 atmosphere (STP) during a "typical year." Level 1 (0-10 m -  $\circ$ ); level 4 (below 50 m -  $\blacksquare$ ).

levels in the colder portion of the year, probably causing redissolution of sedimentary  $\text{CaCO}_3$ . As in the  $\text{PCO}_2$  curves, there appeared to be some anomaly in the IFYGL results which occurred around Day 180, possibly because the hurricane destroyed stratification and induced deep mixing, thereby abnormally warming the deeper waters.

#### *River Organic Carbon*

The rivers carry a considerable amount of organic matter into and out of the lake. Table 6 shows the monthly means for the major rivers. The data for IFYGL indicate an excess inflow of nearly  $0.8 \times 10^7$  kg C/month. On a yearly basis this is equivalent to one

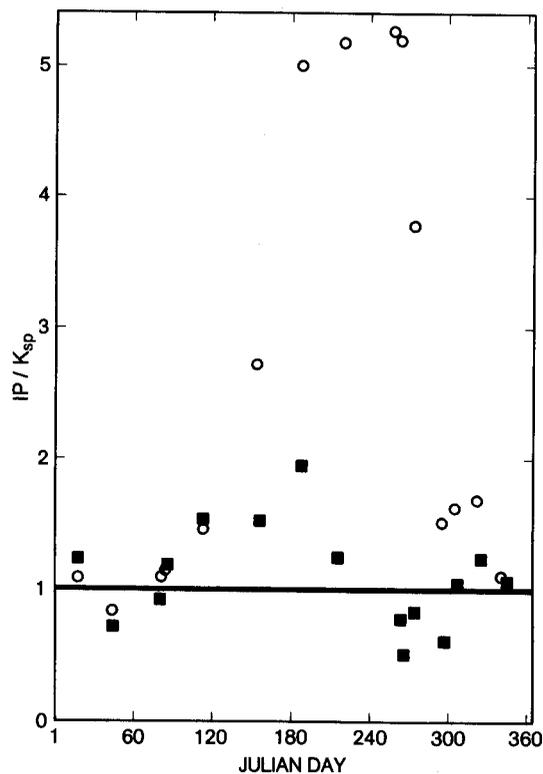


FIG. 7. Ratio of  $\text{CaCO}_3$  activity product (IP) to saturation ( $K_{sp}$ ) during IFYGL. Level 1 (0-10 m -  $\circ$ ); level 4 (below 50 m -  $\blacksquare$ ).

half of the total amount of sedimentary organic carbon accumulated in a year throughout the whole lake. This large monthly inflow is approximately 3% of the organic carbon fixed in situ by primary production.

#### *Exchange Between Epilimnion and Hypolimnion*

In an effort to determine the magnitude of Fickian diffusion of inorganic carbon upward from the hypolimnion, the mean gradient of total inorganic carbon across the thermocline was calculated to be approximately  $0.05 \times 10^{-3}$  moles/l for the period of epilimnion undersaturation (Julian days 140 - 265). The coefficient of vertical eddy diffusivity, from the work of

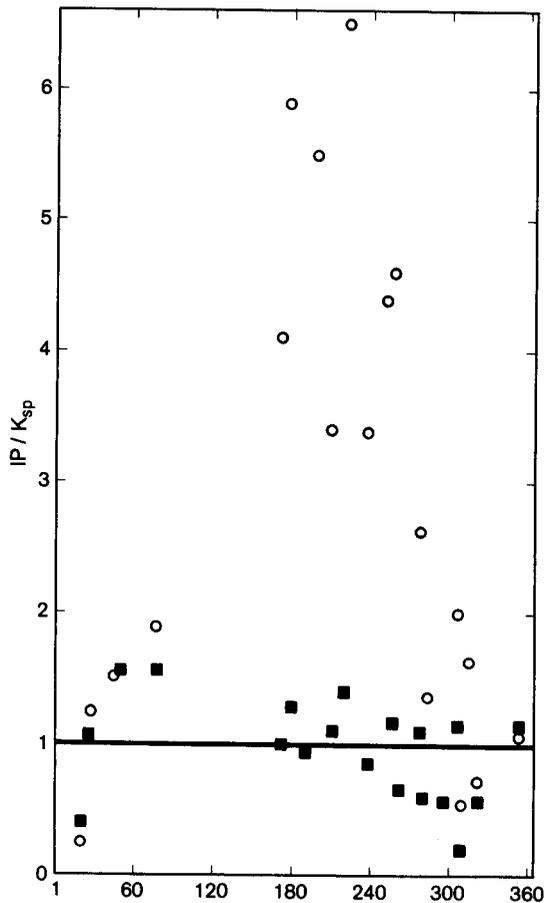


FIG. 8. Ratio of  $\text{CaCO}_3$  activity product (IP) to saturation ( $K_{sp}$ ) during a "typical year". Level 1 (0 - 10 m - ○); level 4 (below 50 m - ■).

Kullenberg et al. (1973) for Lake Ontario, ranged from 0.05 to approximately  $0.5 \text{ cm}^2/\text{s}$  for the thermocline during this period. This is, as expected, larger than the coefficients calculated for Lake 227 (Hesslein and Quay 1973) and the Vierwaldstattersee (O'Melia 1972). Assuming a thermocline of 10 m thickness, we calculated the upward diffusive flux as:

$$0.2 \frac{\text{cm}^2}{\text{s}} \times 0.05 \times 10^{-3} \frac{\text{moles}}{\text{l}} \times \frac{1}{10 \text{ m}} \\ \times \frac{8.64 \times 10^4 \text{ s}}{\text{day}} \times \frac{10^3 \text{ l}}{\text{m}^3} \times \frac{\text{m}^2}{10^4 \text{ cm}^2}$$

$$= 8.64 \times 10^{-3} \text{ moles C/m}^2/\text{day}$$

$$= 2 \times 10^6 \text{ kg C/day (whole lake)}$$

Thus, for the summer months the amount diffusing from the hypolimnion ( $0.6 \times 10^8 \text{ kg C/month}$ ) was of the same order of magnitude as the air lake exchange contribution. This internal recycling of carbon is an important factor in the dynamics of the lake's carbon system.

#### *Evaluation*

The fact that the carbon inflows balanced the outflows to within 10% is evidence of the accuracy of the measurements involved in our budget. The imbalance of  $8.2 \times 10^8 \text{ kg}$  carbon represents approximately 2% of the lake's total inorganic carbon inventory. Such an imbalance may be due to a real build-up of carbon in the lake during the IFYGL year, but the precision in our measurements, especially those for pH and alkalinity, does not allow verification of a difference of this magnitude.

Aside from the previously mentioned shortcomings in alkalinity and pH measurements, which are correctable with current technology, other weaknesses in the budget require examination. The largest approximation is in the measurement of primary productivity, which is inherently an extremely difficult parameter to measure on a lakewide basis. The measurements made by Stadelmann et al. (1974) yielded a number larger than net primary productivity. If we were to argue our logic backwards concerning the gas exchange - net primary production relationship, we could calculate net primary production from pH, alkalinity, temperature, wind speed, and sediment organic matter, (the organic matter not reoxidized). For the IFYGL year this comes out

TABLE 6. River organic carbon for the IFYGL period (kg C/month).

Month	River				
	St. Lawrence ( $\times 10^7$ )	Niagara ( $\times 10^7$ )	Oswego ( $\times 10^6$ )	Genesee ( $\times 10^6$ )	Black ( $\times 10^6$ )
Jan	2.7	4.9	4.5	0.9	-
Feb	-	2.6	3.4	0.7	0.9
Mar	2.9	3.3	2.8	1.0	-
Apr	5.6	4.4	8.1	0.9	3.6
May	6.2	5.9	3.0	0.9	4.8
Jun	6.0	5.4	6.0	3.2	-
Jul	5.9	4.6	7.8	0.7	-
Aug	7.2	1.7	-	0.6	0.9
Sep	6.6	-	3.5	0.4	0.6
Oct	1.9	6.6	-	0.9	-
Nov	1.8	3.5	6.8	2.1	2.5
Dec	2.8	5.0	6.5	3.4	2.4
Mean	4.5	4.4	5.2	1.4	2.2

to be  $2.4 \times 10^9$  kg C or approximately 70% of Stadelmann et al's figure. If we add to this the internal contribution of carbon due to vertical diffusion for the four stratified months during which a gradient exists, we obtain a value of  $2.6 \times 10^9$  kg C for total production.

A second weakness in our analysis is inherent in the calculation of  $\text{CO}_2$  gas exchange. The theoretical-empirical relationships involved in this process were recently the subject of several research efforts (Quinn and Otto 1971; Liss 1973), and it is hoped that further work in this area will improve our knowledge of the response of the exchange coefficient to environmental parameters. In our calculations we probably under-

estimated the gas exchange term due to our use of mean monthly wind speeds in the wind speed squared relationship.

The dynamics of sediment water interchanges is another area that is poorly understood. Our analysis of  $\text{CaCO}_3$  precipitation/dissolution is unsupported by any in situ measurements designed for that purpose and, while we have stated that oxidation of sediment organic matter is probably seasonal, we have no evidence to support this.

Finally, an analysis of the carbon budget on a monthly time scale masks the diurnal and possibly other high-frequency fluctuations. An understanding of the dynamics of the cycle on shorter scales is important from the standpoint of developing models of the system.

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