

FACTORS INFLUENCING PARTIAL PRESSURE CARBON DIOXIDE LEVELS IN  
FLORIDA LAKES: pH, AQUATIC MACROPHYTES, AND GEOLOGY

By

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## TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS .....	3
LIST OF TABLES .....	5
LIST OF FIGURES .....	6
ABSTRACT .....	7
CHAPTER	
1 INTRODUCTION .....	9
2 MATERIALS AND METHODS .....	14
3 RESULTS AND DISCUSSION .....	22
Partial Pressure CO <sub>2</sub> Values from Historical Lake Data .....	22
Limnological Variables .....	23
Effect of Macrophyte Presence on <i>p</i> CO <sub>2</sub> Levels in a Florida Lake .....	25
Lake Metabolism in Relationship to <i>p</i> CO <sub>2</sub> Levels in a Florida Lake .....	27
Heterotrophy in Lakes .....	28
4 CONCLUSIONS .....	46
WORKS CITED .....	49
BIOGRAPHICAL SKETCH .....	53

## LIST OF TABLES

<u>Table</u>		<u>page</u>
3-1	Comparison of various limnological and physical parameters measured in the 627-lake study to Cole's 1994 study.....	30
3-2	Mean, standard error and range of the variables measured in 627 lakes.....	31
3-3	Correlation coefficients for all variables in relation to $p\text{CO}_2$ , with N values.....	34
3-4	Average $p\text{CO}_2$ and pH levels for each Florida Region.....	40
3-5	Average of nutrient and chlorophyll concentrations by month and station in Orange Lake, Florida.....	44
3-6	Average carbon estimate variables and wind by month and station in Orange Lake, Florida.....	44
3-7	Average $p\text{CO}_2$ by month and station in Orange Lake, Florida.....	45
3-8	Aquatic plant data collected on July 7, 2005. Source: Florida LAKEWATCH 2005.....	45
3-9	Percent coverage of macrophytes in Orange Lake and the estimated $p\text{CO}_2$ for that plant coverage value.....	45
3-10	Net ecosystem production values for each station by month with an average for all samples at each station in Orange Lake, Florida.....	45

## LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1-1	The relationship of free carbon dioxide and pH taken from Juday et al. (1935). The dotted line horizontal line indicates atmospheric level of carbon dioxide. Free CO <sub>2</sub> is represented by the dashed line “Calculated CO <sub>2</sub> .” .....12
1-2	Relation between pH and the relative proportions of inorganic carbon species modified from Wetzel 2001. ....13
2-1	Satellite photo of Orange Lake, Florida with sampling sites indicated by diamonds.....21
3-1	Locations of 627 lakes sampled in the state of Florida.....32
3-2	Relationship of pH to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. Lake values are represented by open circles, with modeled pH changes shown in black. The black line indicates atmospheric <i>p</i> CO <sub>2</sub> level. ....33
3-3	Relationship of pH to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. ....34
3-4	Relationship of TP (μg/L) to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. ....35
3-5	Relationship of TN (μg/L) to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. ....36
3-6	Relationship of Chlorophyll (μg/L) to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. ....37
3-7	Relationship of color (Pt-Co Units) to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study. ....38
3-8	Relationship of specific conductance (μS/cm @ 25°C) to <i>p</i> CO <sub>2</sub> (μatm) values for the 627 lake study .....39
3-9	Average pH and <i>p</i> CO <sub>2</sub> values by region. Regions move from northwest of Florida to south Florida in a southeast direction. ....41
3-10	Monthly <i>p</i> CO <sub>2</sub> averages by station for Orange Lake.....42
3-11	Partial pressure carbon dioxide values in relationship to % oxygen saturation for 284 historical lakes. The vertical line represents 100% oxygen saturation. The horizontal line represents atmospheric level of <i>p</i> CO <sub>2</sub> .....43

Abstract of Thesis Presented to the Graduate School  
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Chair: Daniel E. Canfield Jr.

Major: Fisheries and Aquatic Sciences

Physical, chemical, and biological factors associated with the supersaturation of CO<sub>2</sub> in aquatic ecosystems are not clearly evident. The goal of our study was to evaluate partial pressure carbon dioxide (*p*CO<sub>2</sub>) levels in a set of Florida Lakes and to investigate if any limnological factors are correlated with levels of *p*CO<sub>2</sub>. The *p*CO<sub>2</sub> levels were calculated for 627 Florida Lakes using pH, specific conductance, alkalinity and water temperature. Eighty percent of lakes were found to be supersaturated with carbon dioxide. Trophic state indicators such as total phosphorus (TP), total nitrogen (TN) and chlorophyll (Chl) were all weakly correlated with *p*CO<sub>2</sub> concentrations (TP, *r* = -0.30 TN, *r* = -0.35 Chl *r* = -0.48). The limnological parameter pH had a highly significant positive correlation with *p*CO<sub>2</sub> concentration (*r* = 0.91). When modeling changes in *p*CO<sub>2</sub> concentrations, pH seems to be the regulating factor in *p*CO<sub>2</sub> levels in Florida lakes.

Plants remove carbon dioxide from the atmosphere by carbon assimilation, and produce carbon dioxide during cellular respiration processes. Photosynthesis and respiration directly influence the pH of the water. The effect of aquatic macrophyte presence on *p*CO<sub>2</sub> levels was examined using a summer study (June-August 2005) that examined *p*CO<sub>2</sub> levels in both the plant and open water areas in a hypereutrophic Florida lake. The presence of plants in a

hypereutrophic Florida Lake significantly increased  $p\text{CO}_2$  measurements. The pH was found to be lower in plant stations in comparison to open water stations. The same study was used to evaluate how the presence of plants affected lake metabolism using the diurnal curve method. Presence of plants significantly decreased the net ecosystem production estimates based on dissolved oxygen and wind data. All stations on the study lake (both plant and open water) were heterotrophic over the duration of the study.

Saturation of carbon dioxide in an aquatic ecosystem is often used as an indicator of heterotrophy at the ecosystem scale. To investigate this statement, dissolved oxygen data on a group of 284 Florida Lakes were used to examine the relationship between  $p\text{CO}_2$  and dissolved oxygen saturations. Several lakes exhibited both supersaturation of oxygen and carbon dioxide simultaneously. Therefore, dissolved oxygen was determined to be an inadequate predictor of lake heterotrophy in 25% of 284 Florida lakes.

The limnological parameter pH is often called the master variable in determining the aqueous geochemistry of an aquatic system. Many attempts have been made to quantify and rank variables of significance to predict mean values of lake pH. The pH value of a water body is directly influenced by geologic factors. When investigating the relationship between  $p\text{CO}_2$  levels and pH across the state of Florida, a geologically regulated trend was found. As pH values increased in a southeastern direction across the state,  $p\text{CO}_2$  levels decreased. Changes in pH values between regions were reflected in changes in  $p\text{CO}_2$  levels between the same regions. Changes in regional geology may explain variation between lakes in reference to  $p\text{CO}_2$  levels.

## CHAPTER 1 INTRODUCTION

The limnological parameter pH is often considered a master variable in determining the biological, chemical and physical processes of an aquatic system. Juday et al. (1935) examined relationships between pH levels and carbon dioxide levels in several lakes in Wisconsin. Juday et al. (1935) calculated pH values from free carbon dioxide values, and compared these calculated values to directly measured values. They found no significant difference (Figure 1-1). Juday et al. (1935) also found that lakes did not exhibit carbon dioxide levels exceeding the atmospheric level of carbon dioxide above a pH of 8. The relationship between pH and the relative proportions of inorganic carbon species (Figure 1-2) of  $\text{CO}_2$  (+ $\text{H}_2\text{CO}_3$ ),  $\text{HCO}_3^-$ , and  $\text{CO}_3^{=}$  in solution is clearly recognized (Wetzel 1983). At a pH of above 8, the proportion of carbon in the form of free carbon dioxide is very small (Figure 1-2).

In the past decade, many researchers have supported the idea that organic matter located within lake basins can either be mineralized or lost as  $\text{CO}_2$  to the atmosphere (Cole et al. 1994, 2000; Richey et al. 2002; Sobek et al. 2003; Striegl et al. 2001). When the level of carbon dioxide within a water body exceeds the amount of carbon dioxide present in the atmosphere (supersaturation), the water body becomes a carbon source (Kling et al. 1991; Hesslein et al. 1991; Cole et al. 1994, 1998).

Cole et al. (1994) conducted a study of carbon dioxide levels in 1835 globally distributed lakes. Cole used both direct and indirect measurements of  $\text{CO}_2$  and found that 87% of lakes were supersaturated with  $\text{CO}_2$ . Cole found a mean partial  $\text{CO}_2$  pressure for all lakes of 1036 micro atmospheres. The atmospheric level of carbon dioxide is about 370 micro atmospheres.

Physical and chemical and biological factors associated with the supersaturation of  $\text{CO}_2$  in aquatic ecosystems are not clearly evident (Cole 1994; Kling 1991). There has been much

investigation into the role of allochthonous carbon and its effect on lake metabolism (Prairie et al. 2002). The role of the lake as a CO<sub>2</sub> producer may vary with trophic state and other limnological factors affecting CO<sub>2</sub>, including chemical composition, lake morphometry, and surrounding terrestrial ecosystems (Hanson 2003). It also has not yet been investigated whether the presence of aquatic macrophytes would have an effect on *p*CO<sub>2</sub> levels in a freshwater lake.

Aquatic macrophytes are prevalent in many Florida lakes and play an important role in the structure and function of lakes (Brenner et al. 1991). Macrophytes are a major component of total biomass and primary productivity (Canfield et al. 1983). Aquatic macrophytes are an integral part of lake metabolism. In aquatic ecosystems, metabolism directly affects concentrations of dissolved inorganic carbon (DIC) and dissolved oxygen (DO) concentrations (Hanson 2006). Aquatic macrophytes produce carbon dioxide during cellular respiration processes ( $C_6H_{12}O_6 + 6 O_2 \rightarrow 6 CO_2 + 6 H_2O + \text{energy}$ ) and also excrete dissolved organic compounds which are acted on by microorganisms and are oxidized into carbon dioxide and returned to the atmosphere (Wetzel 1969).

Understanding the carbon balance of a lake helps us to understand both the biological activity occurring within a lake and how the surrounding watershed may be affecting the lake. Whole-ecosystem metabolism integrates the net effect of all primary producers and all consumers on the carbon cycle (Hanson 2006). Ecosystem production may be negative or positive (Howarth et al. 1996). When ecosystem production is positive, the system is considered autotrophic, and the water body can store organic carbon (Schindler et al. 1972). When ecosystem production is negative, the system is considered heterotrophic, and respire more carbon than what was produced within the system (Cole 2000). There is much debate regarding

the metabolic balance between heterotrophy and autotrophy in lakes in general (Carignan et al. 2000; del Giorgio and Peters 1994).

Given the complexities of dissolved carbon dioxide dynamics in freshwater lakes, an investigation of the physical, chemical and biological factors associated with changes in partial pressure carbon dioxide levels in Florida lakes is needed. My objectives for this study are:

- **Objective 1:** To evaluate partial pressure carbon dioxide ( $p\text{CO}_2$ ) levels in a set of Florida Lakes;
- **Objective 2:** To investigate if any limnological factors are correlated with levels of  $p\text{CO}_2$  in a set of Florida Lakes;
- **Objective 3:** To investigate the effect of aquatic macrophyte presence on  $p\text{CO}_2$  levels in a Florida Lake;
- **Objective 4:** Evaluate lake metabolism and its relationship to  $p\text{CO}_2$  levels in a Florida Lake;

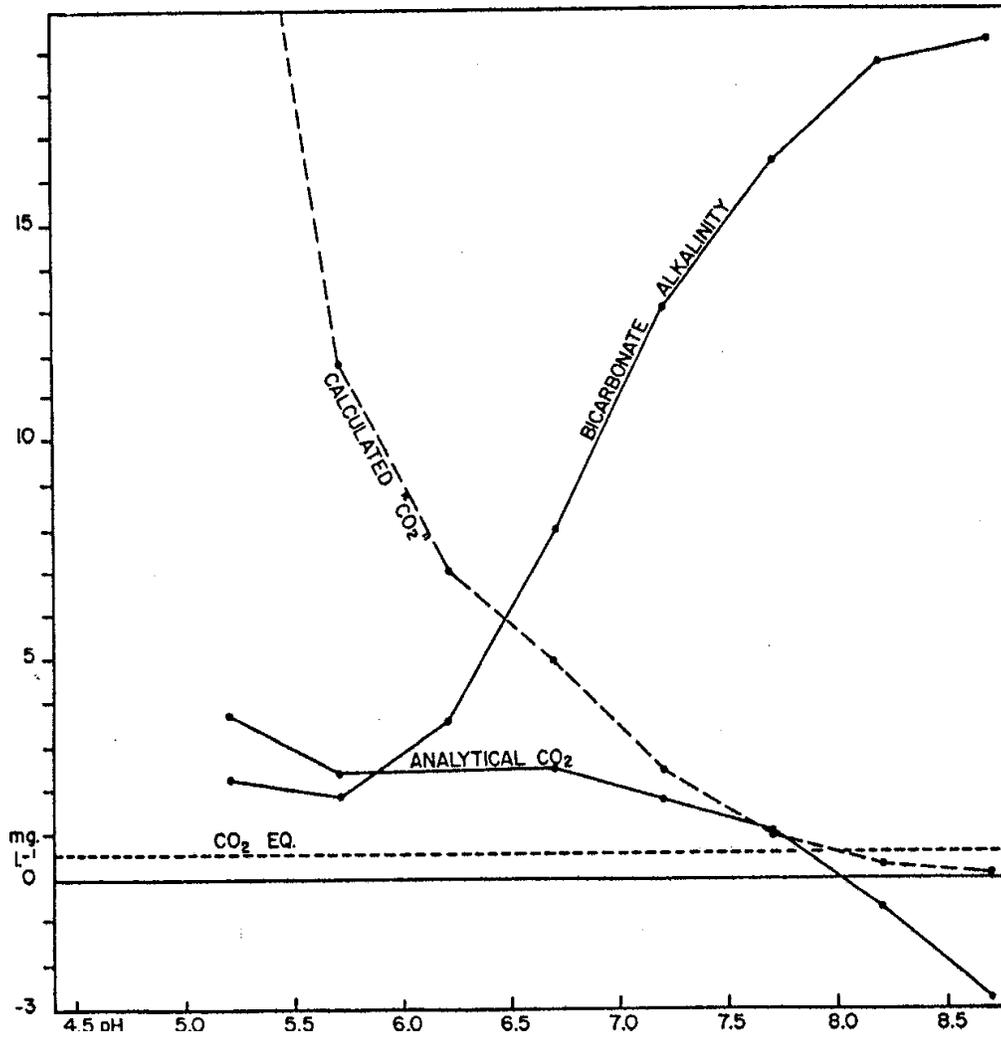


Figure 1-1. Relationship of free carbon dioxide and pH taken from Juday et al. (1935). Dotted horizontal line indicates atmospheric level of carbon dioxide. Dashed line represents "Calculated CO<sub>2</sub>."

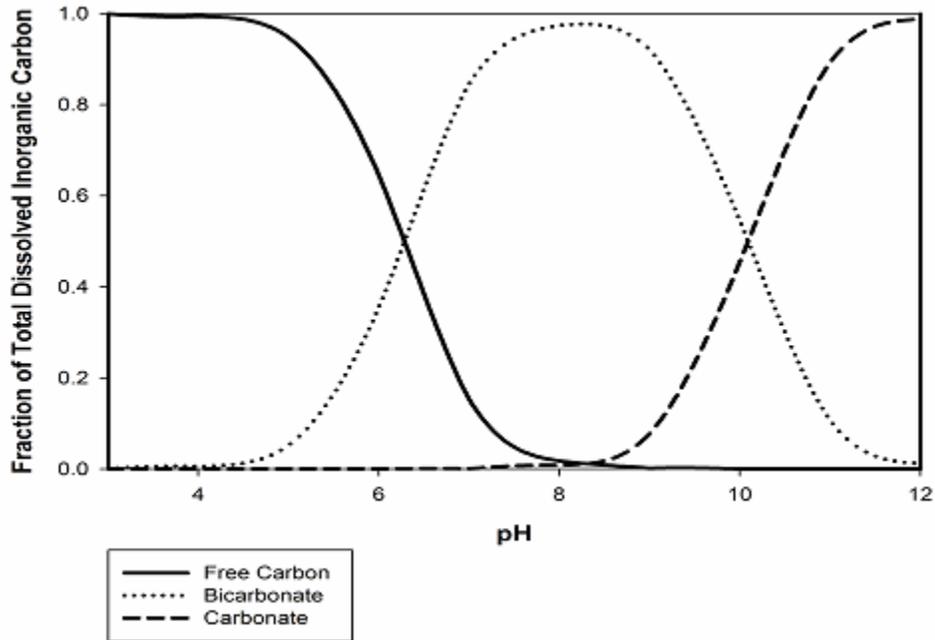


Figure 1-2. Relationship between pH and the relative proportions of inorganic carbon species. Adapted from Wetzel R.G. 2001. Limnology. Lake and River Ecosystems. Academic Press, San Diego.

## CHAPTER 2 MATERIALS AND METHODS

Published water chemistry information was obtained for 627 lakes that were sampled between one and 48 times over a 17-year period of record (Canfield 1981; Canfield and Hoyer 1992; Florida LAKEWATCH 1993, 1996; Greis 1995). Seventy-five percent of the lakes were sampled four or less times, with the remaining 25% being sampled between five and 48 times. One hundred and fifty-nine lakes were sampled 10 or more times.

Carbon dioxide concentrations were computed using averaged pH, total alkalinity, and specific conductance values from the data set for each lake using the approach of Cole et al. (1994) and Prairie et al. (2002). Lakes with multiple samples per lake (more than one station) were averaged, followed by an average of the months sampled. A yearly average was taken from the averaged months. Finally all years for each lake were averaged to attain a grand average for each lake. Ionic strength (I) was calculated (Equation 2-1) from specific conductivity ( $\mu\text{S}/\text{cm}$  @ 25 C) values represented by “SC” (Cole et al. 1994; Prairie et al. 2002) as follows:

$$I = 0.000025 * 7 * SC \quad (2-1)$$

This equation is based on a relation between ionic strength and total dissolved solids, taken from Sawyer and McCarty (1967), which accounts for the first constant (0.000025), and an empirical relation between total dissolved solids and specific conductance, taken from Hem (1992), which accounts for the second constant (7).

Equilibrium disassociation constants of carbonic acid to hydrogen atoms and bicarbonates, and the disassociations of carbonates to bicarbonates were calculated ( $K_1$  and  $K_2$ ) where concentrations are indicated by square brackets [ ], activities are denoted by braces { }. These calculations are shown below in Equations 2-2 and 2-3 (Stumm and Morgan 1995).

$$K_1 = \frac{\{H^+\} [HCO_3^-]}{[H_2CO_3^*]} \quad (2-2)$$

$$K_2 = \frac{\{H^+\} [CO_3^{2-}]}{[HCO_3^-]} \quad (2-3)$$

These values were then used to calculate the fraction of free CO<sub>2</sub> (a<sub>0</sub>), bicarbonate (a<sub>1</sub>), and carbonate (a<sub>2</sub>) (Equations 2-4, 2-5, 2-6 respectively).

$$a_0 = \frac{1}{1 + 10^{(K_1 + pH)} + 10^{-(K_1 + K_2) + 2 * pH}} \quad (2-4)$$

$$a_1 = \frac{1}{1 + 10^{(-pH + K_1)} + 10^{(-K_2 + pH)}} \quad (2-5)$$

$$a_2 = \frac{1}{10^{(-2 * pH + (K_1 + K_2))} + 10^{(-pH + K_2)} + 1} \quad (2-6)$$

These three values (a<sub>0</sub>, a<sub>1</sub>, and a<sub>2</sub>) together are the total amount of inorganic carbon compounds in the system (Stumm and Morgan 1995). Total carbon in the system (DIC, μM) is expressed as a concentration and is derived using the three carbon components (a<sub>0</sub>, a<sub>1</sub>, and a<sub>2</sub>) along with alkalinity (meq/L) in Equation 2-7 below.

$$DIC (\mu M) = \frac{10^5 * (\text{Alkalinity}(\text{meq/L}) * 0.000001 - 10^{(-14 + pH)} + 10^{(-pH)})}{(a_1 + 2 * a_2)} \quad (2-7)$$

Using Henry's Law, the solubility of carbon dioxide in water (KH) is determined which varies with temperature (Equation 2-8).

$$KH = 1.11 + 0.016 * \text{Temperature}(C) - 0.00007 * \text{Temperature}(C)^2 \quad (2-8)$$

The concentration of free CO<sub>2</sub> in the system is expressed in micromoles (Equation 2-9):

$$CO_2 (\mu M) = DIC(\mu M) * a_0 \quad (2-9)$$

Finally, CO<sub>2</sub> is expressed as a partial pressure in microatmospheres (Equation 2-10):

$$p\text{CO}_2 (\mu\text{atm}) = \frac{\text{CO}_2 \mu\text{M}}{10^{-(KH)}} \quad (2-10)$$

An average yearly temperature value of 21 C was used for solubility calculations for the 627 lake study due to lack of available water temperature data for the individual lakes.

All water samples were collected during daylight hours from the surface (0.5 m) at multiple (1-4) open-water sites within each lake. Water clarity was measured by use of a Secchi disc. Water samples were collected in acid-cleaned, triple rinsed Nalgene bottles, and placed on ice. In the early studies, unfrozen water samples were analyzed for total nitrogen (TN) and total phosphorus (TP). In later studies, portions of the collected water were subsequently frozen and used for later analysis of TN and TP. At the laboratory, a pH meter (an Orion Model 601A pH meter or an Accumet model 10 pH meter) calibrated with pH 4.0 and pH 7.0 buffers was used to measure pH. Total alkalinity (mg/L as CaCO<sub>3</sub>) was determined by titration with 0.02 N sulfuric acid (APHA 1085). Specific conductance (μS/cm @ 25 C) was measured using a Yellow Springs Instrument Model 21 conductivity bridge or a Yellow Spring Instrument Model 35 conductance meter. TP concentrations (μg/L) were determined using the procedures of Murphy and Riley (1962) with a persulfate digestion (Menzel and Corwin 1965). For some samples, total nitrogen was measured using USEPA methods involving sum of nitrate-nitrogen and Kjeldahenitrogen values (USEPA 1979). For other samples, TN concentrations (μg/L) were determined by oxidizing water samples with persulfate and determining nitrate-nitrogen with second derivative spectroscopy (D'Elia et al. 1977; Simal et al. 1985; Wollin 1987). Bachmann et al. (1996) found this method to be suitable for samples frozen for 90 days. Chlorophyll *a* concentrations (μg/L) were determined by filtering water through a Gelman type A-E glass fiber filter and using the method of Yentsch and Menzel (1963) with the equations of Parsons and Strickland (1963). Prior to 1994, chlorophyll concentrations (μg/L) were determined via

pigment extraction with aqueous acetone followed by measurement of optical density with a spectrophotometer (Method 10200 H; APHA 1989). After 1994, chlorophyll concentrations ( $\mu\text{g/L}$ ) were determined spectrophotometrically (Method 10200 H; APHA 1992) following pigment extraction with ethanol (Sartory and Grobbelaar 1984). Prior to 1993, color (Pt-Co units) was determined by using the platinum-cobalt method and matched Nessler tubes (APHA 1985). After 1993, color was determined by spectroscopy (Bowling et al. 1986). Calcium, magnesium and potassium concentrations ( $\text{mg/L}$ ) were determined by atomic absorption spectrophotometry (APHA 1985). For some samples (Canfield 1981; Canfield and Hoyer 1992; Florida LAKEWATCH 1993,1996; Greis 1995), calcium concentrations were determined from calcium hardness concentrations. Magnesium concentrations were then estimated from the difference between total hardness and calcium hardness concentrations (Hach Chemical Company 1992). Potassium, along with sodium, concentrations were determined by flame photometry (Methods 3500-Na D and 3500-K D, APHA 1989). Total iron concentrations were determined using the Ferrozine method (Method 8147, Hach Chemical Company 1992). Chloride concentrations ( $\text{mg/L}$ ) were measured by titration with 0.0141 N mercuric nitrate and using diphenylcarbazone for determining endpoints (Hach Chemical Company 1975). Sulfate concentrations were determined using a turbidimetric method with SulfaVer sulfate reagent (Method 4500-SO<sub>4</sub> E, APHA 1992).

Data on surface oxygen saturation were obtained from Florida Lakewatch for 284 lakes within the 627 lake data set (Florida LAKEWATCH unpublished data). Measured oxygen percent saturation values were compared to calculated  $p\text{CO}_2$  levels for 284 Florida lakes.

Orange Lake, an approximately 5,250-hectare lake located in southeastern Alachua County, Florida was the study site for the macrophyte and lake metabolism portion of this study.

Sampling of Orange Lake was conducted during the months of June, July and August 2005. One 24-hour sampling period was carried out each month. A total of four stations were chosen at Orange Lake (Figure 2-1). These stations included three stations established within aquatic macrophyte beds, and one open-water (no aquatic macrophytes) station. Each month, one water sample was taken at each station in 250-ml, acid-cleaned, triple-rinsed Nalgene bottles at a depth of 0.5 m for nutrient analysis. These samples were subsequently frozen and analyzed at the end of the summer season. This sample was used to determine total phosphorus ( $\mu\text{g/L}$ ) and total nitrogen ( $\mu\text{g/L}$ ) concentrations. Chlorophyll samples were filtered in the field and filters were subsequently frozen. At the end of the sampling term (Summer 2005) chlorophyll concentrations ( $\mu\text{g/L}$ ) were determined spectrophotometrically (Method 10200 H; APHA 1992) following pigment extraction with ethanol (Sartory and Grobbelaar 1984).

Measurements were taken at every station every three hours for a 24 hr period, yielding eight sampling “sets” per day. Specific conductance ( $\mu\text{S/cm}$ ), dissolved oxygen ( $\text{mg/L}$ ), pH, and water temperature ( $^{\circ}\text{C}$ ) were taken every 0.5 m from surface to bottom with a Yellow Springs Instrument Model 560 multi-probe handheld system. A Simeral model DIC anemometer was used to measure wind speed ( $\text{m/sec}$ ) at each sampling period. A 250-ml water sample was taken at 0.5 m depth in a 250 mL acid-washed dark Nalgene bottle at each station every three hrs for laboratory analysis of total alkalinity ( $\text{mg/L}$  as  $\text{CaCO}_3$ ). These samples were kept on ice and analyzed directly after the 24 hr sampling was completed. Total alkalinity ( $\text{mg/L}$  as  $\text{CaCO}_3$ ) was determined by titration with 0.02 N sulfuric acid (Method 2320 B; APHA 1992). All recorded values were converted to  $\text{meq/L}$ .

To assess lake metabolism, the diurnal curve method was used to estimate gross primary production and respiration within the lake (Odum and Hoskin 1958; Bachmann et al. 2000). At

each sampling site, the average water column amount of DO (mg/L) was calculated by multiplying the average oxygen concentration ( $\chi$ ) of the water column by the depth in meters (Z) of the water column (Equation 2-11).

$$\text{Average Water Column DO} = \chi (\text{water column DO}) * Z \quad (2-11)$$

The uncorrected rate of oxygen change (g/m<sup>2</sup>/hr) was the average water column amount of DO at the end of the sampling interval minus the average water column amount of DO at the beginning of the interval divided by the length of the interval in hours (Equation 2-12).

$$\text{Uncorrected O}_2 \text{ Change} = \frac{\text{Integral O}_2 \text{ End} - \text{Integral O}_2 \text{ Beginning}}{\text{Interval Length}} \quad (2-12)$$

The gas transfer coefficient (diffusion coefficient DC) across the water surface for station 4 (the open-water station) was calculated from the wind velocity (m/sec) represented by “W” and water temperature (C), represented by “T” using the equations of Hartman and Hammonds (1985) (Equation 2-13).

$$DC = 34.6 (1 + (T - 20) + 0.026 * (0.0000206^{0.5}) * W^{1.5}) \quad (2-13)$$

For the plant stations (Stations 1, 2, and 3), the equations of Hartman and Hammonds (1985) were used with an alteration made in wind speed to adjust for the fact that wind had limited interaction with the water surface due to plant cover. For plant stations 1, 2, and 3, wind speeds were reduced to 0.1 m/sec.

The oxygen saturation deficit (OSD) was found by subtracting the saturation concentration (mg/L) from the surface concentration (Equation 2-14) of dissolved oxygen (mg/L).

$$\text{OSD} = \text{Surface DO} - \text{Saturation O}_2 \quad (2-14)$$

This was multiplied by the gas transfer coefficient to find the rate that oxygen was entering or leaving the lake surface during each sampling interval (g/m<sup>2</sup>) (Equation 2-15).

$$\text{Diffusion} = \text{Average (OSD of Interval)} * DC / 24 \quad (2-15)$$

The corrected oxygen change was the sum of the uncorrected oxygen change and the oxygen flux due to diffusion (Equation 2-16).

$$\text{Corrected Oxygen Change} = \Sigma \text{Uncorrected Oxygen Change} + \text{Diffusion} \quad (2-16)$$

The sum of the oxygen changes over the 24 hr period was the net oxygen production for the day in units of  $\text{g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ . To convert to units of  $\text{g C m}^{-2} \text{ d}^{-1}$ , the  $\text{g O}_2 \text{ m}^{-2} \text{ d}^{-1}$  was multiplied by 0.375 and divided by the photosynthetic quotient (PQ) of 1.2 (Wetzel and Likens, 1991).

Respiration was estimated as the average of the corrected oxygen changes during intervals between sunset and sunrise. This was converted to  $\text{g C m}^{-2} \text{ d}^{-1}$  by multiplying by 0.375 and a respiratory quotient (RQ) of 1.0 (Wetzel and Likens, 1991). Gross production was the sum of net production and respiration.

Data were analyzed using JMP 4.0 statistical software (SAS Institute Inc.). All trophic state parameters and ions were logarithmically transformed to attain normal distribution. All variables were correlated with logarithmically transformed values for  $p\text{CO}_2$ . An  $\alpha$  value of 0.05 was used for all statistical tests.

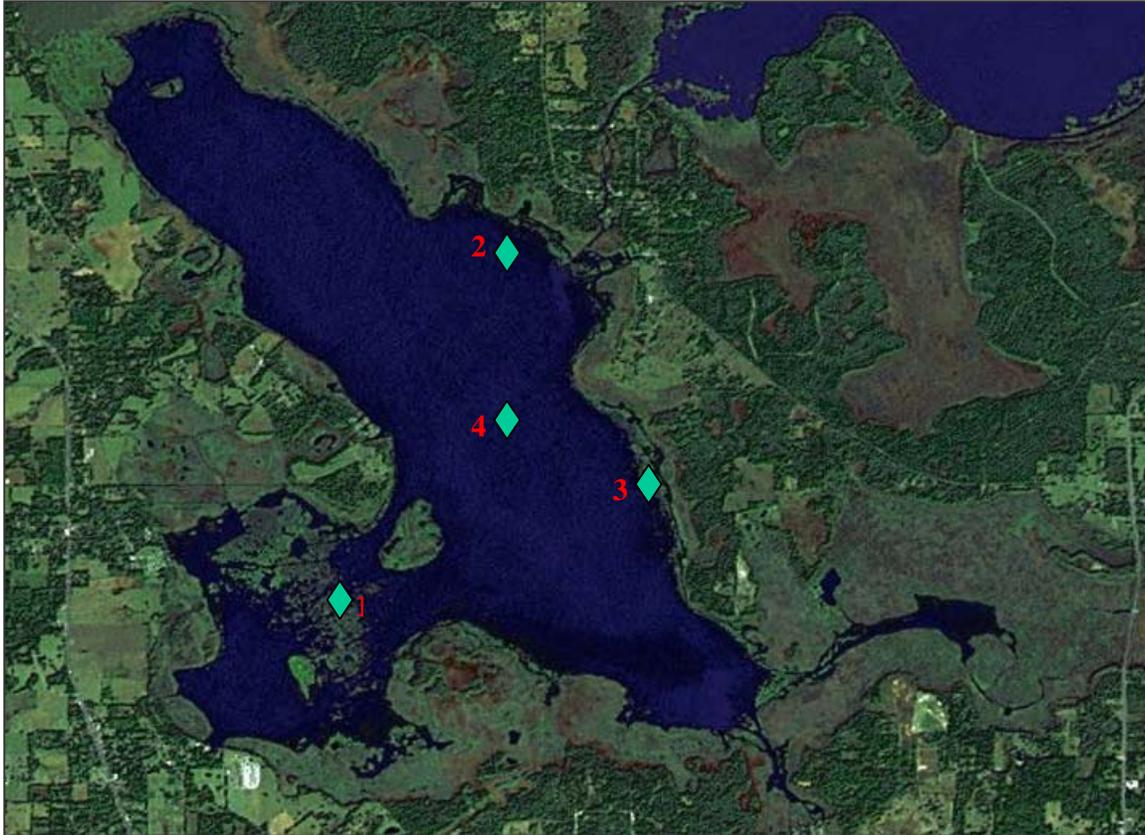


Figure 2-1. Satellite photo of Orange Lake, Florida with sampling sites indicated by diamonds.

## CHAPTER 3 RESULTS AND DISCUSSION

### **Partial Pressure CO<sub>2</sub> Values from Historical Lake Data**

A total of 4,730 water samples were collected from 627 lakes located throughout Florida (Figure 3-1). The calculated partial pressure carbon dioxide level ( $p\text{CO}_2$ ) values for the lakes exhibited a large range (below -0.0003 to 915,000  $\mu\text{atm}$ ). The average calculated  $p\text{CO}_2$  was 13,000  $\mu\text{atm}$ . Twenty-five percent of Florida lakes however, ranged from below zero (meaning they take in carbon dioxide from the atmosphere) to 800  $\mu\text{atm}$  with a median value of 400  $\mu\text{atm}$ . The next quartile of lakes ranged from 800  $\mu\text{atm}$  to 1500  $\mu\text{atm}$  with a median value of 1000  $\mu\text{atm}$ . Cole's mean  $p\text{CO}_2$  of 1036  $\mu\text{atm}$  was within this range. The third quartile ranged from 1500  $\mu\text{atm}$  to 3000  $\mu\text{atm}$  with a median value of 2000  $\mu\text{atm}$ . The fourth quartile of lakes ranged from 3000  $\mu\text{atm}$  to 916,000  $\mu\text{atm}$  with a median value of 460,000  $\mu\text{atm}$ .

When calculated  $p\text{CO}_2$  values are very high, some would suggest there may be an allochthonous carbon supply to the lake through surface water input (Jonosson 2001; Duarte 2005). The geometric mean for the Florida lakes is 2,000  $\mu\text{atm}$ , which is nearly identical (1036  $\mu\text{atm}$ ) as Cole's average  $p\text{CO}_2$  for 1835 lakes (Table 3-1). The geometric mean is a more appropriate comparison to Cole's findings because it better represents the central tendency of the Florida data set. Cole's values for  $p\text{CO}_2$  ranged from 1 to 20,249  $\mu\text{atm}$ . Florida lakes exhibited similar ranges in pH, temperature, specific conductance, and alkalinity to Cole's data set (Table 3-1), but only 11% of the Florida lakes fell above Cole's maximum of 20,249  $\mu\text{atm}$ .

To model the effect of changes in pH, all  $p\text{CO}_2$  calculation variables were held at a constant average (determined by mean values for the 627 lakes), while pH was changed in increments of one unit from 3 to 12 (Figure 3-2). Also, pH values for all 627 lakes were raised one unit of pH, and lowered one unit of pH, and  $p\text{CO}_2$  was calculated for all lakes with both

changes. When pH was changed by one unit, there were significant differences found between the calculated  $p\text{CO}_2$  values and the original  $p\text{CO}_2$  values. Partial pressure carbon dioxide values were significantly higher ( $p < 0.0001$ ) when pH was decreased by one unit ( $p < 0.0001$ ).

To model changes in temperature, the value of 21 C was raised to 31 C and lowered to 11 C and  $p\text{CO}_2$  values were subsequently recalculated. No significant difference was found between the three (11 C, 21 C, 31 C)  $p\text{CO}_2$  values calculated for the lakes using the alteration in average yearly temperature ( $p > 0.925$ ). To model changes in specific conductance, all  $p\text{CO}_2$  calculation variables were held at a constant average (determined by mean values for the 627 lakes), while specific conductance values were changed from 50  $\mu\text{S}/\text{cm}$  to 400  $\mu\text{S}/\text{cm}$ . Partial pressure carbon dioxide values were calculated over a range in pH values from 3 to 12. No significant difference was found between varying values for specific conductance ( $P > 0.925$ ).

My calculations indicate 80% of the Florida lakes are supersaturated with carbon dioxide. Supersaturation in this instance is defined as any value exceeding the atmospheric level of carbon dioxide (370  $\mu\text{atm}$ ) by more than 10%. This is similar to Cole's finding that 87% of his study lakes were supersaturated with carbon dioxide.

### **Limnological Variables**

The lakes, as a group (Table 3-2), had an average pH of 6.7, but individual average lake pH values ranged from 3.9 to 11.7. Total alkalinity (meq/L) ranged from 0 to 467,000 meq/L with an average alkalinity of 500 meq/L. Lakes ranged from oligotrophic (TP < 15  $\mu\text{g}/\text{L}$ , TN < 400  $\mu\text{g}/\text{L}$ , Chlorophyll a < 3  $\mu\text{g}/\text{L}$ ) to hypereutrophic (TP > 100  $\mu\text{g}/\text{L}$ , TN > 1500  $\mu\text{g}/\text{L}$ , chlorophyll a > 40  $\mu\text{g}/\text{L}$ ) (Forsberg et al. 1980) with an average TP of 46  $\mu\text{g}/\text{L}$ , an average TN of 860  $\mu\text{g}/\text{L}$ , and an average chlorophyll of 17  $\mu\text{g}/\text{L}$ . Water clarity (Secchi depth) ranged from < 0.1 m to 7.2 m with an average Secchi depth of 1.7 m. Color (Pt-Co units) ranged from 0 (very clear) to almost 700 (black water) with an average color value of the lakes being 52 Pt-Co units.

There exists a significant relationship ( $r = 0.91$  Figure 3-3) between pH and  $p\text{CO}_2$  as expected from the findings of Juday et al. (1935). If you examine Figure 3-3, and Figure 1-2 from Juday and others, both graphs do not show supersaturation carbon dioxide levels in lake waters when the pH of water was  $>8$ . Both the findings in Wisconsin lakes and Florida lakes follow the relationship between pH and the relative proportions of inorganic carbon species (Figure 1-2) of  $\text{CO}_2$  ( $+\text{H}_2\text{CO}_3$ ),  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  in solution (Wetzel 1983). The data suggests that the availability of free  $\text{CO}_2$  in an aquatic system is regulated by the pH of the system itself.

Using pairwise correlation analysis, significant correlations were found for each of the limnological variables in relation to  $p\text{CO}_2$  (Table 3-3). Trophic state indicators (i.e., TP, TN, Chlorophyll ) were negatively, but weakly (TP,  $r = -0.30$ ; TN,  $r = -0.35$ ; Chl,  $r = -0.48$ ) correlated to  $p\text{CO}_2$  ( Figures 3-4, 3-5, and 3-6 respectively). With dense populations of phytoplankton present, the surrounding natural water becomes depleted of carbon dioxide due to photosynthesis (Talling 1976). So one would expect a negative relationship between chlorophyll and  $p\text{CO}_2$ . Secchi disc measurements were positively, but very weakly correlated ( $r = -0.10$ ).

It was surprising that the correlation of  $p\text{CO}_2$  with color ( $r = 0.09$ ) was not stronger (Figure 3-7). Increases in color can often be attributed to the loading of humic compounds from terrestrial inputs (Duarte 2005). These compounds, rich in dissolved organic carbon (DOC) can convert from DOC to  $\text{CO}_2$  (Reche et al. 2002). When DOC undergoes bacterial degradation upon entry to the aquatic system, there is a potential to raise aquatic respiration beyond the limits imposed by aquatic photosynthesis (Cole 1999; Scully et al. 2003; Duarte et al. 2005). If DOC from the watershed was a large contributing factor to increases levels of  $p\text{CO}_2$  in Florida lakes, there should be a greater correlation between the two variables. Specific conductance was weakly correlated ( $r = -0.46$ ) with  $p\text{CO}_2$  levels (Figure 3-8).

Canfield et al. (1988), found based on a survey of 165 lakes within Florida that the mineral composition of the lakes was strongly related to Florida's geologic and physiographic development. The study (Canfield 1988) was a limnological survey of 165 lakes within Florida. They found, with the exception of iron and color, pH values and chemical concentrations generally increased as one moved from northwest to southeast. If this trend exists for pH values in Florida lakes, then partial pressure carbon dioxide levels should therefore decrease as one moves from northwest to southeast. This pattern does indeed exist. Using the lake regions established in Griffiths et al. (1997), Table 3-4 shows the average pH and  $p\text{CO}_2$  values by region. As the regions progress from the northwest to south Florida, the  $p\text{CO}_2$  levels show a general decrease as pH increases (Figure 3-9).

#### **Effect of Macrophyte Presence on $p\text{CO}_2$ levels in a Florida Lake**

Samples from Orange Lake were taken in the summer of 2005. Samples had an average total phosphorus of 230  $\mu\text{g/L}$  from all three sampling periods (3- 5). Sample TP concentrations ranged from 190  $\mu\text{g/L}$  to 650  $\mu\text{g/L}$ . Total nitrogen averaged 2306  $\mu\text{g/L}$  with a range of 1600  $\mu\text{g/L}$  to 6100  $\mu\text{g/L}$ . Chlorophyll averaged 60  $\mu\text{g/L}$ , with a range of 10  $\mu\text{g/L}$  to 100  $\mu\text{g/L}$ . Based on the Forsberg and Ryding trophic scale (1980), this lake is hypereutrophic.

Total alkalinity (meq/L) averaged 360, with a range of 300 meq/L to 420 meq/L. Measured water temperature averaged 29.6 C with a range of 27.8 C to 31.2 C. Specific conductance averaged 86  $\mu\text{S/cm}$  over the three sampling months. Specific conductance ranged from 81 to 92  $\mu\text{S/cm}$ . The pH of Orange Lake averaged 5.9 over the 3 monthly sampling periods, with a range of 4.9 to 6.8 (Table 3-6). The calculated partial pressure carbon dioxide ( $p\text{CO}_2$ ) averaged 21,000  $\mu\text{atm}$  over the 3 sampling periods, with a range of 10,000 to 48,000  $\mu\text{atm}$ . Based on these calculations, Orange Lake was a continual source ( $p\text{CO}_2 > 370 \mu\text{atm}$ ) of carbon dioxide to the atmosphere over every sampling period and at each station (Table 3-7).

In June,  $p\text{CO}_2$  values ranged from 11,000  $\mu\text{atm}$  to 17,000  $\mu\text{atm}$  (range includes stations 1,2,3 and 4). In July,  $p\text{CO}_2$  values ranged from 24,000  $\mu\text{atm}$  to 48,000  $\mu\text{atm}$  and in August,  $p\text{CO}_2$  values ranged from 10,000  $\mu\text{atm}$  to 18,000  $\mu\text{atm}$ . In the month of July, large areas of Orange Lake were subject to a mechanical aquatic plant maintenance technique known as “cookie cutting.” This process cuts large segments of floating and rooted vegetation. It causes water agitation and sediment resuspension. This process may be the reason July  $p\text{CO}_2$  values were greater than both June and August. The range for Orange lake  $p\text{CO}_2$  values (10,000  $\mu\text{atm}$  to 48,000  $\mu\text{atm}$ ) falls within the top 25<sup>th</sup> percentile of values exhibited in the 627 study. In the 627-lake study, Orange Lake had an average  $p\text{CO}_2$  value of 1449  $\mu\text{atm}$ . This difference can be explained by the difference in pH values from the historical data collection to the present.

In 1987, Orange Lake was sampled in 5 different months at 3 stations (Canfield and Hoyer, 1992). The average pH over that time period was 7.6. Referring to modeled pH and  $p\text{CO}_2$  changes in Figure 3-3, a  $p\text{CO}_2$  value of about 1000 would be expected for a pH of 7.6. In the data collected on Orange Lake in 2006, the average pH value was 5.9. A pH value of 5.9 corresponds to a  $p\text{CO}_2$  level of about 30,000 according to the modeled values in Figure 3-3. The change in pH might be the cause of the difference in  $p\text{CO}_2$  values from the historical data and present data.

In each month, Stations 1, 2, and 3 (the macrophyte stations) had significantly higher  $p\text{CO}_2$  levels than the open water station 4 (Table 3-7, Figure 3-10). This result was anticipated for three possible reasons:

(1) With the excessive growth of macrophytes on the shorelines in such shallow depths, I would expect a higher content of organic matter from the breakdown of decaying plant matter by bacteria. This process releases carbon into the water column.

(2) Another factor that may increase shoreline levels of  $p\text{CO}_2$  is terrestrial runoff entering the system. This runoff may contain large amounts of humic compounds. These compounds, rich in dissolved organic carbon (DOC) can photomineralize convert from dissolve organic carbon (DOC) to carbon dioxide ( $\text{CO}_2$ ) (Reche et al. 2002).

(3) The average pH of stations 1,2 and 3 (the plant stations) was lower than station 4 (open water station) over the 3 month period.

A plant survey was conducted by Florida LAKEWATCH in July 2005 on Orange Lake. The percent volume infested with aquatic macrophytes (PVI) and the percent area covered by macrophytes (PAC) were determined. Lakewatch found that 58% of the surface area of Orange Lake in July 2005 was covered with aquatic macrophytes (Table 3-8). They also found that 14% of the lake's volume was filled with aquatic vegetation. Finally, LAKEWATCH calculated a floating-leaved zone of 380 m. Floating and emergent plants extended from the shoreline 380 m into the open water area of the lake. The average  $p\text{CO}_2$  value for the plant stations (1, 2, and 3) was 24,000  $\mu\text{atm}$ , while the average  $p\text{CO}_2$  value for the open water station (4) was 17,000  $\mu\text{atm}$ . This represents more than half of the lake, having a significantly higher ( $p= 0.002$ )  $p\text{CO}_2$  level than the rest of the lake. When making estimations using data obtained on Orange Lake in Summer 2005, a change from 0% to 100% of macrophyte coverage in the lake increased average  $p\text{CO}_2$  levels 25% (see Table 3-9). With large changes in plant coverage a noticeable change in  $p\text{CO}_2$  may be apparent. However, small-scale changes would result in trivial changes in  $p\text{CO}_2$  levels. This suggests that aquatic macrophytes as a whole may not be as important as I had thought to  $p\text{CO}_2$  levels in the lake.

### **Lake Metabolism in Relationship to $p\text{CO}_2$ Levels in a Florida Lake**

The calculated net ecosystem production (NEP) for each station by month is shown in Table 3-10. Station 1 values ranged from -1.6 to -3.1  $\text{mg C/m}^2$  over the three months with an

average  $-2.4 \text{ mg C/m}^2$ . Station 2 values ranged from  $-2.1$  to  $-3.2 \text{ mg C/m}^2$  with an average value of  $-2.5 \text{ mg C/m}^2$ . Station 3 values ranged from  $-5.1$  to  $-6.2 \text{ mg C/m}^2$  with an average of  $-5.6 \text{ mg C/m}^2$ . Station 4 values ranged from  $-5.2$  to  $-10.7 \text{ mg C/m}^2$  with an average value  $-8.6 \text{ mg C/m}^2$ . There was no significant difference in net ecosystem production values between the 3 months ( $p= 0.666$  at  $\alpha = 0.05$ ). There is a significant difference between the 4 stations ( $p= 0.003$  at  $\alpha = 0.05$ ). The open-water had a significantly lower NEP than the macrophyte stations.

The data indicate that plants stations are significantly less heterotrophic than the open water stations in Orange Lake. This may be due to the different impact wind has the surface of the water at the various stations. The plant stations were located in the littoral areas where the sampling equipment was in a bed of plants. Lack of wind interaction and a greater potential for higher photosynthesis rates would make these stations less heterotrophic. The data indicate that this lake remains in a heterotrophic state for at least some periods during the summer months.

### **Heterotrophy in Lakes**

Some scientists contend that supersaturation of carbon dioxide indicates heterotrophy at the ecosystem level (Raymond et al 2000). In contrast, Bachmann et al. (2000) concluded on the basis of light and dark bottle oxygen measurements and diel oxygen measurements that Lake Apopka, a hypereutrophic lake in central Florida, was heterotrophic (Bachmann et al.2000). The data on Lake Apopka from the 627-lake study indicate that Lake Apopka is not supersaturated with respect to the atmosphere ( $p\text{CO}_2$  of  $78.3 \text{ } \mu\text{atm}$ ). This is a heterotrophic lake that does not exhibit supersaturation levels of carbon dioxide with respect to the atmosphere. The pH of Lake Apopka is approximately 8, which is in accord with the findings of Juday et al. (1935) and the 627-lake study. In this case, the relationship between pH and the relative proportions of inorganic carbon species is demonstrated in an aquatic system. At a pH of 8, the fraction of dissolved inorganic carbon expressed as free  $\text{CO}_2$  is very small (see Figure 1-2).

Out of the 627 historical lakes, oxygen data were available for 284 lakes (Florida LAKEWATCH, unpublished data). There was a negative relationship between  $p\text{CO}_2$  and percent oxygen saturation (Figure 3-11). This group of lakes can be put into 4 categories. In Figure 3-11, the 4 quadrants of the graph represent these categories. In quadrant 1, lakes are supersaturated with carbon dioxide ( $p\text{CO}_2 > 370 \mu\text{atm}$ ), and undersaturated with oxygen ( $< 100\%$ ). Quadrant 2 represents lakes that are supersaturated with carbon dioxide, and supersaturated with oxygen ( $> 100\%$ ). Quadrant 3 represents lakes that are below saturation with respect to carbon dioxide and oxygen. Quadrant 4 represents lakes that are below saturation with respect to carbon dioxide, and supersaturated with oxygen. If a determination of heterotrophy is made on a basis of carbon dioxide supersaturation alone, 25% of these lakes could be mistakenly identified as heterotrophic. Twenty-four percent of the 284 lakes fall into quadrant 2. These lakes are supersaturated in both carbon dioxide and oxygen. Heterotrophy is generally indicated by supersaturation of carbon dioxide. In this case, it is unclear if there is more respiration (indicated by  $\text{CO}_2$  concentrations) than photosynthesis (indicated by  $\text{O}_2$ ) because both variables are in a state of supersaturation.

Table 3-1. Comparison of various limnological and physical parameters measured in the 627-lake study to Cole's 1994 study.

Parameter	Direct $p\text{CO}_2$ Measurements	Lake in autumn	Full season cycles	Lakes in summer	African lakes	Florida Lakes
Lakes (n)	37	1612	69	60	59	627
Samples (n)	390	1612	2395	179	79	4,730
pH (range)	4.7-9.5	3.8-9.4	4.2-9.8	4.9-9.3	6.0-9.9	3.9-11.7
DIC ( $\mu\text{M}$ ) (range)	4.9-2,500	13.3-4,077	6.6-4,800	11-3,578	43-145,790	-2053.7-35,286.6
$p\text{CO}_2$ ( $\mu\text{atm}$ ) (mean)	801	1031	1064	680	2296	*2000
$p\text{CO}_2$ ( $\mu\text{atm}$ ) (range)	107-4,128	20-9,789	1-7,845	5-8,991	32-20,249	-0.0003-9,000
Basis of $p\text{CO}_2$ estimate	Direct measurement	pH, DIC	pH, DIC, pH, ANC	pH, DIC	pH, ANC	pH, ANC
Sampling intensity	Weekly to quarterly	Each once in Autumn	Varied but more than 10 samples per year	Summer only	One to three times	Monthly to quarterly
Source	Cole 1994	Cole 1994	Cole 1994	Cole 1994	Cole 1994	This Study

\*Geometric Mean

Table 3-2. Mean, standard error and range of the variables measured in 627 lakes.

Variable	Mean	SE	Min	Max
pH	6.7 ± 0.048		3.9	11.7
Total Alkalinity (meq/L)	500 ± 25.15		0	467000
Temp (C)	21 ± 0		21	21
Specific Conductance (μS/cm @ 25 C)	200 ± 19.3		11	7200
atmospheric pCO <sub>2</sub> (μatm)	370 ± 0		370	370
pCO <sub>2</sub> μatm	13000 ± 2300		-0.0003	916000
Total Phosphorus (μg/L)	46 ± 4.22		1	1221
Total Nitrogen (μg/L)	860 ± 26.1		23	5600
Chlorophyll a (μg/L)	17 ± 1.25		0.47	300
Color (Pt-Co units)	52 ± 3.08		0	690
Secchi (m)	1.7 ± 1.29		0	7.3
Chloride (mg/L)	33 ± 5.58		1.7	2200
Silicon (mg/L)	1.1 ± 0.07		0	12.1
Sulfate (mg/L)	15 ± 0.73		0	186
Calcium (mg/L)	11 ± 0.49		0.19	94
Magnesium (mg/L)	8 ± 1.25		0.16	600
Sodium (mg/L)	15 ± 2.7		1	1160
Potassium (mg/L)	3 ± 0.17		0	50
Iron (mg/L)	0.1 ± 0.01		0	2.3

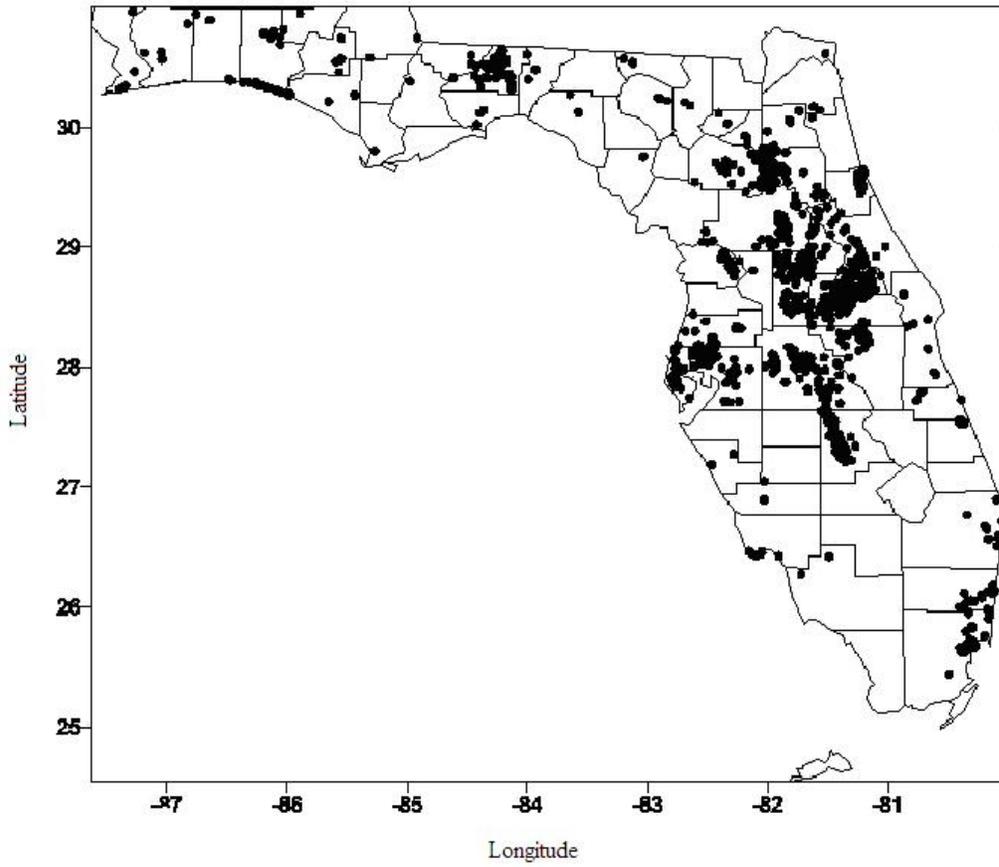


Figure 3-1. Locations of 627 lakes sampled in the state of Florida.

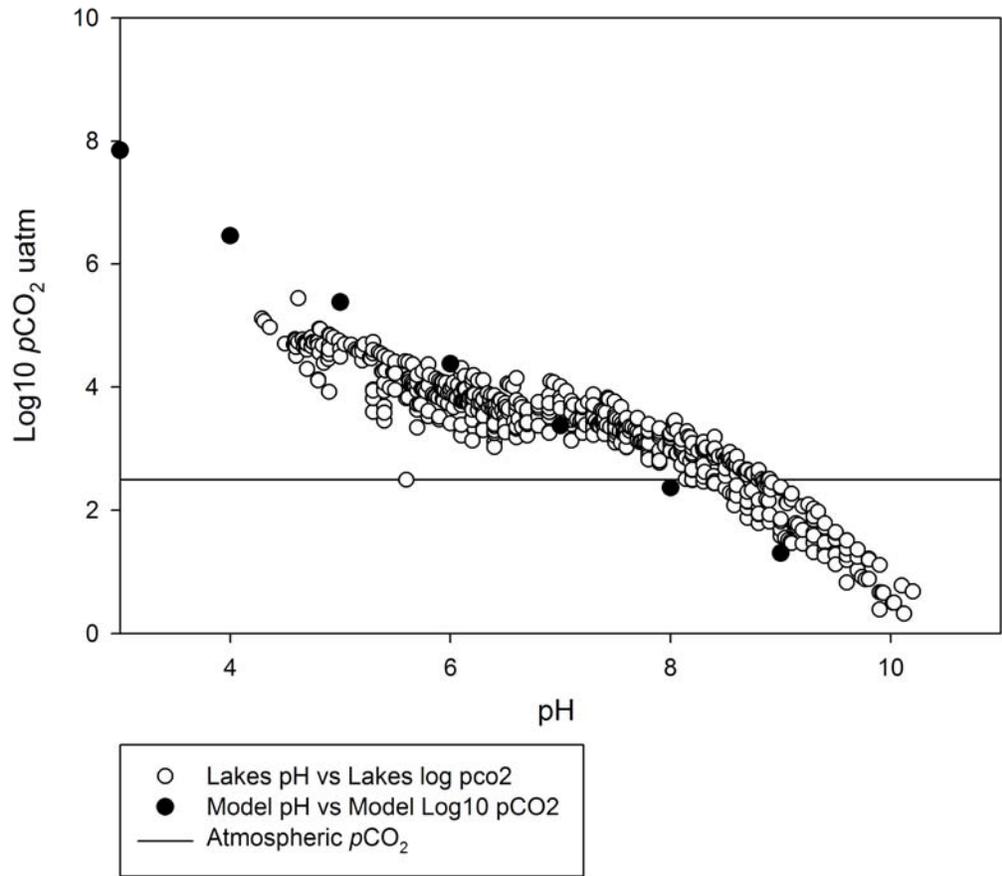


Figure 3-2. Relationship of pH to  $p\text{CO}_2$  ( $\mu\text{atm}$ ) values for the 627 lake study. Lake values are represented by open circles, with modeled pH changes shown in black. The black line indicates atmospheric  $p\text{CO}_2$  level.

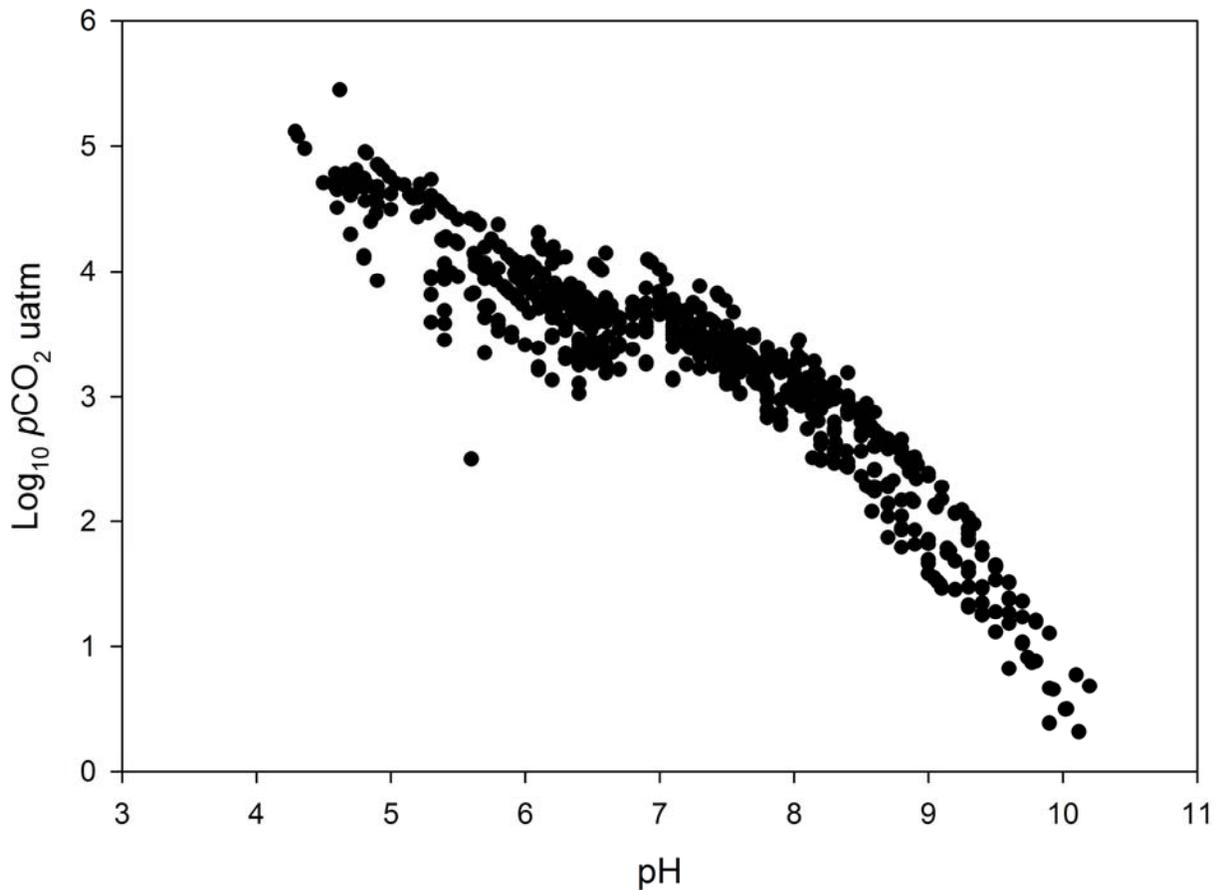


Figure 3-3. Relationship of pH to  $p\text{CO}_2$  ( $\mu\text{atm}$ ) values for the 627 lake study.

Table 3-3. Correlation coefficients for all variables in relation to  $p\text{CO}_2$ , with N values.

Variable	Correlation Coefficient	N	P Value
Total Phosphorus ( $\mu\text{g/L}$ )	-0.30	661	0
Total Nitrogen ( $\mu\text{g/L}$ )	-0.35	658	0
Chlorophyll a ( $\mu\text{g/L}$ )	-0.48	646	0.0184
Color (Pt-Co units)	0.09	636	0
Secchi (m)	0.19	479	0
Conductivity ( $\mu\text{S/cm @ 25C}$ )	-0.46	663	0.0001
Chloride (mg/L)	-0.35	659	0
Silicon (mg/L)	-0.11	510	0
Sulfate (mg/l)	-0.27	602	0
Calcium (mg/L)	-0.59	609	0
Magnesium (mg/L)	-0.44	609	0
Sodium (mg/L)	-0.36	612	0
Potassium (mg/L)	-0.50	610	0
Iron (mg/L)	0.29	469	0.0123

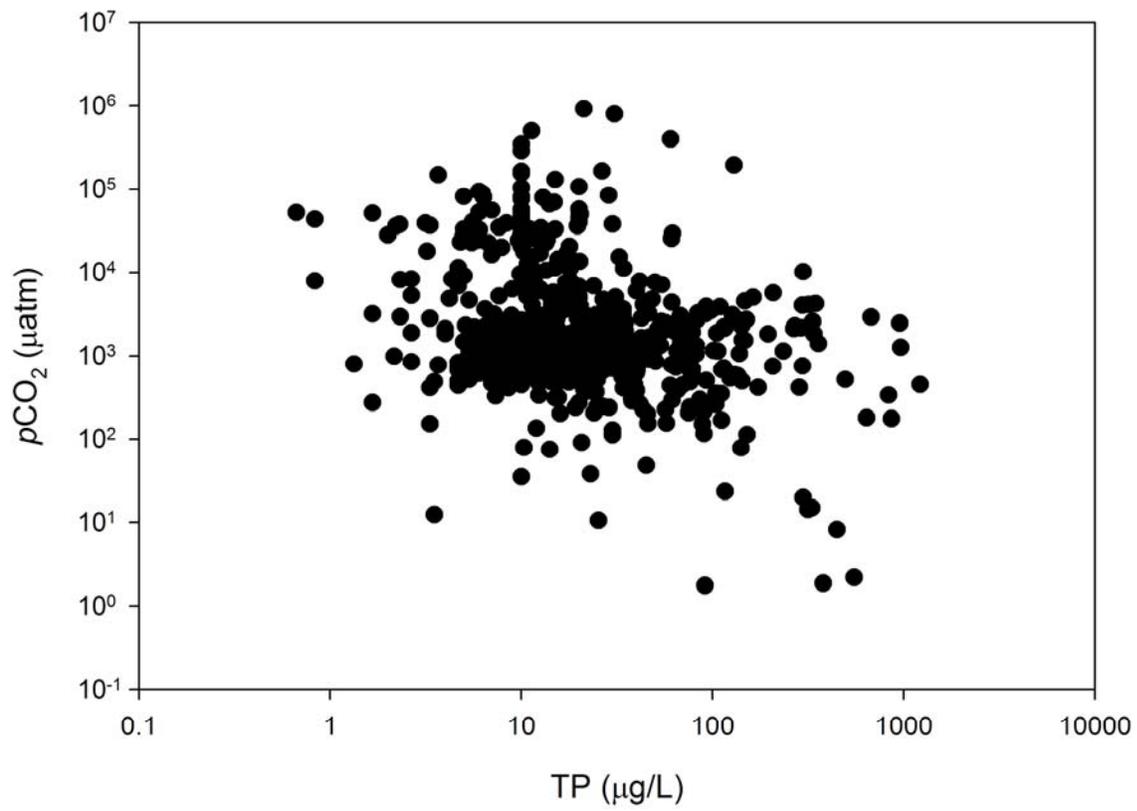


Figure 3-4. Relationship of TP (µg/L) to pCO<sub>2</sub> (µatm) values for the 627 lake study.

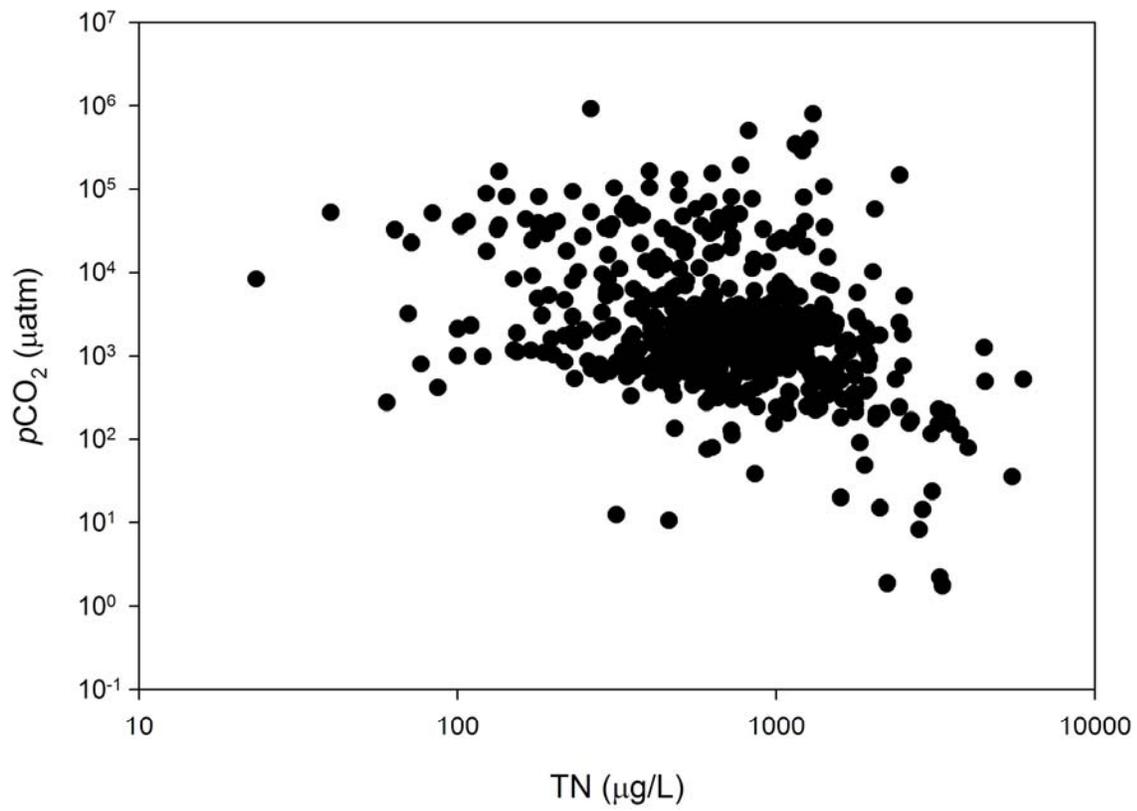


Figure 3-5. Relationship of TN (µg/L) to pCO<sub>2</sub> (µatm) values for the 627 lake study.

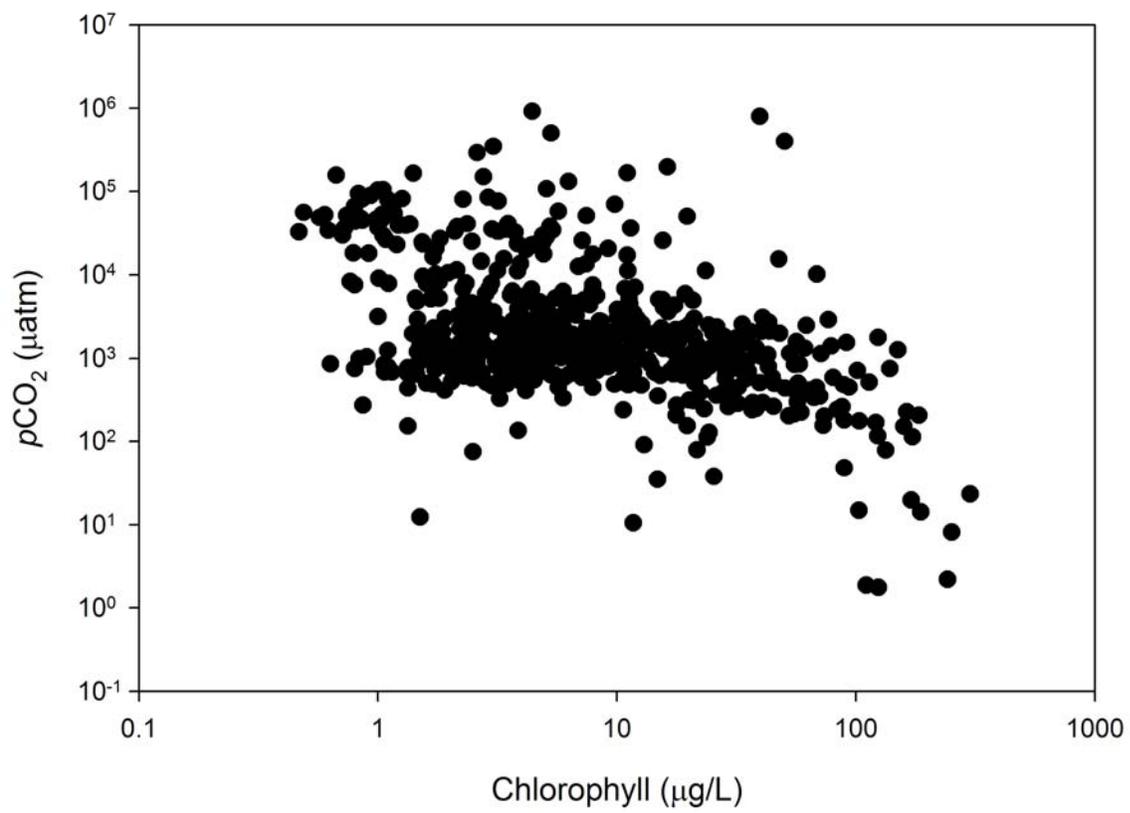


Figure 3-6. Relationship of Chlorophyll (µg/L) to pCO<sub>2</sub> (µatm) values for the 627 lake study.

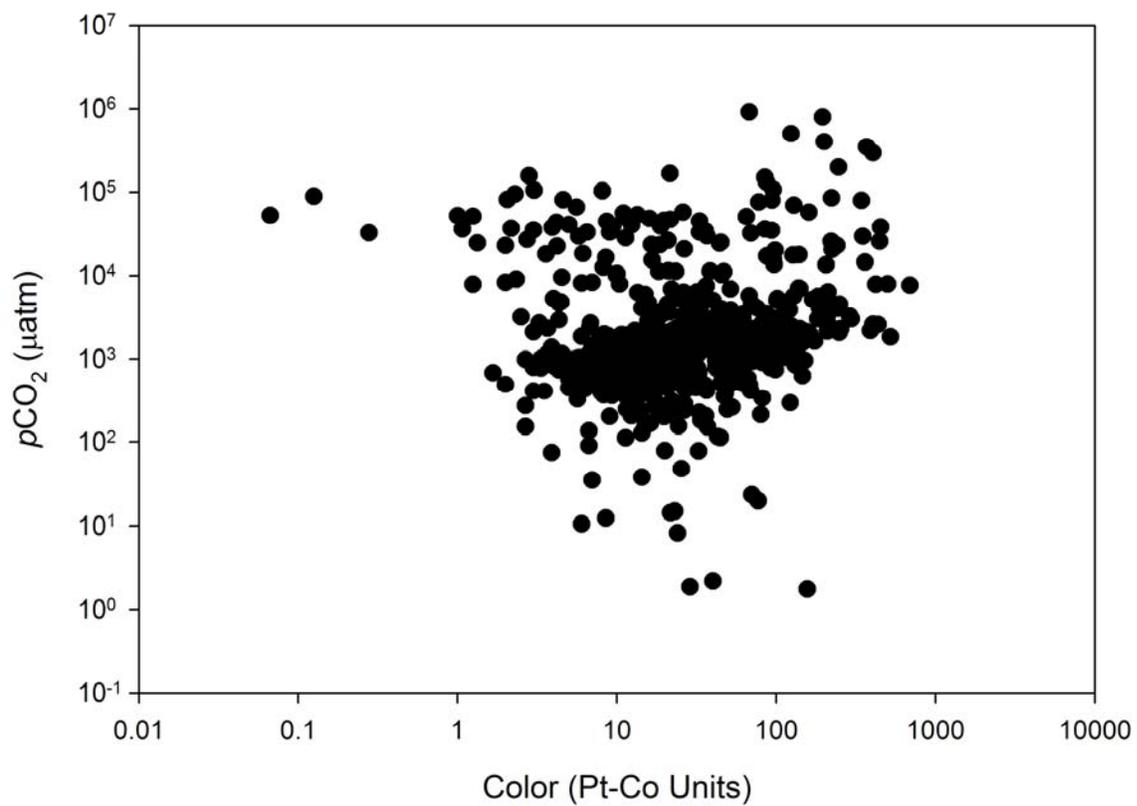


Figure 3-7. Relationship of color (Pt-Co Units) to  $p\text{CO}_2$  ( $\mu\text{atm}$ ) values for the 627 lake study.

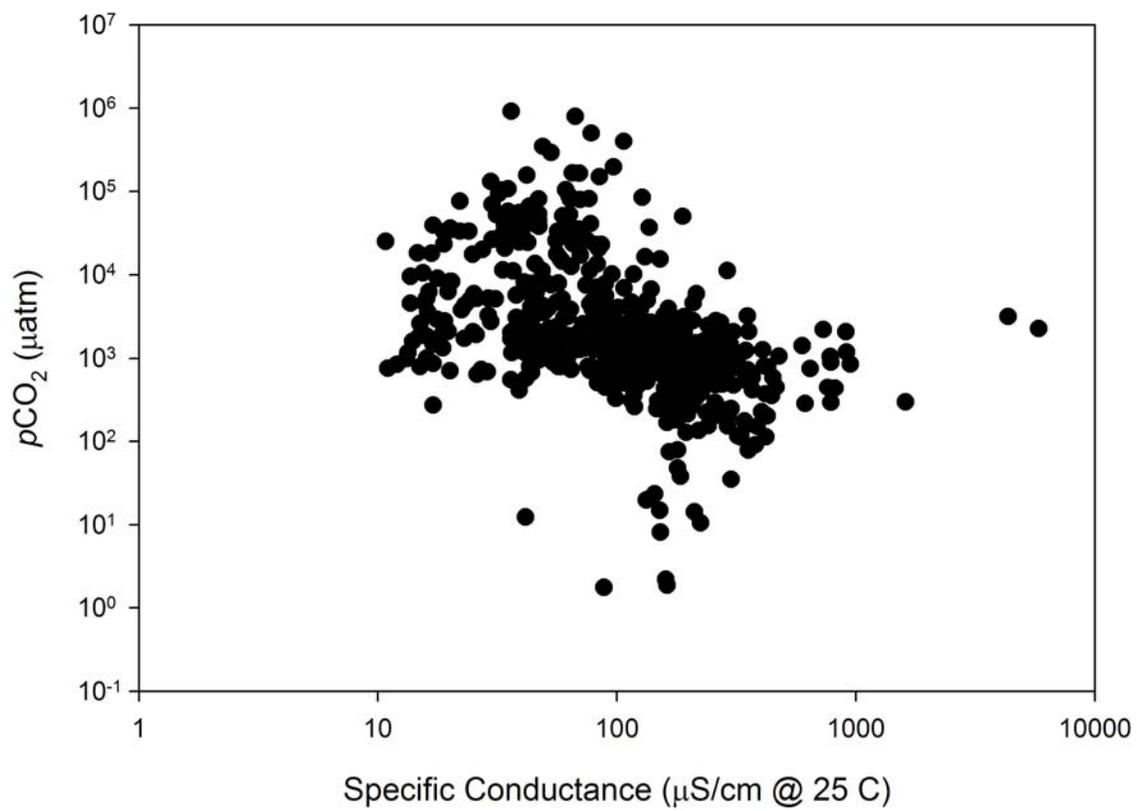


Figure 3-8. Relationship of specific conductance ( $\mu\text{S}/\text{cm}$  @  $25^\circ\text{C}$ ) to  $p\text{CO}_2$  ( $\mu\text{atm}$ ) values for the 627 lake study

Table 3-4. Average pCO<sub>2</sub> and pH levels for each Florida Region.

Region	pCO <sub>2</sub>	pH
65-01	47000	6.5
65-02	6000	6.2
65-03	11000	5.5
65-04	5000	6.7
65-05	10000	5.7
65-06	5000	6.8
75-01	52000	5.9
75-02	315000	4.8
75-03	4000	6.2
75-04	10000	5.9
75-05	6000	5.8
75-06	6100	7.6
75-07	1000	7.0
75-08	2000	7.7
75-09	30000	5.2
75-10	14000	6.7
75-11	5000	6.8
75-12	2000	7.4
75-13	22000	6.9
75-14	2000	6.6
75-15	3000	7.4
75-16	10000	7.1
75-17	1000	7.2
75-18	3000	7.2
75-19	4000	6.4
75-20	1000	7.0
75-21	3000	7.7
75-22	2000	7.7
75-23	8000	6.5
75-24	2000	7.3
75-25	300	8.1
75-27	5000	6.2
75-28	1000	7.9
75-30	1000	8.5
75-31	3000	7.7
75-32	3000	7.5
75-33	2000	7.0
75-34	4000	6.7
75-35	1000	7.6
75-36	17000	6.9
75-37	300	8.5
76-02	1000	8.2
76-03	8000	7.3

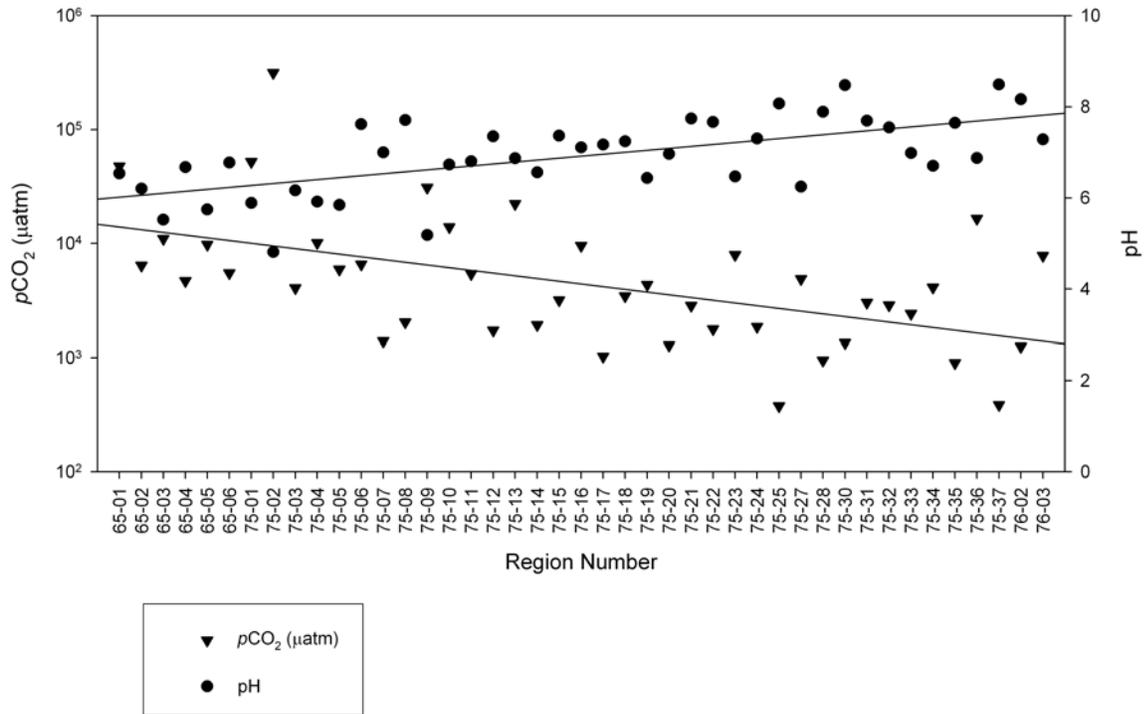


Figure 3-9. Average pH and  $p\text{CO}_2$  values by region. Regions move from northwest of Florida to south Florida in a southeast direction.

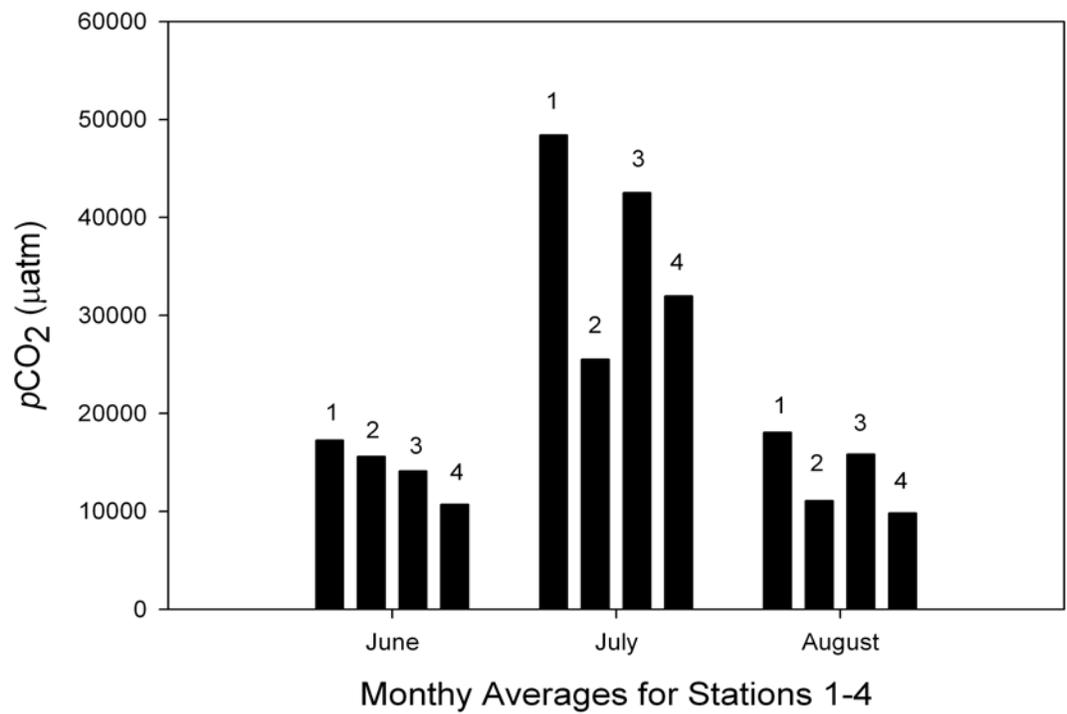


Figure 3-10. Monthly  $p\text{CO}_2$  averages by station for Orange Lake.

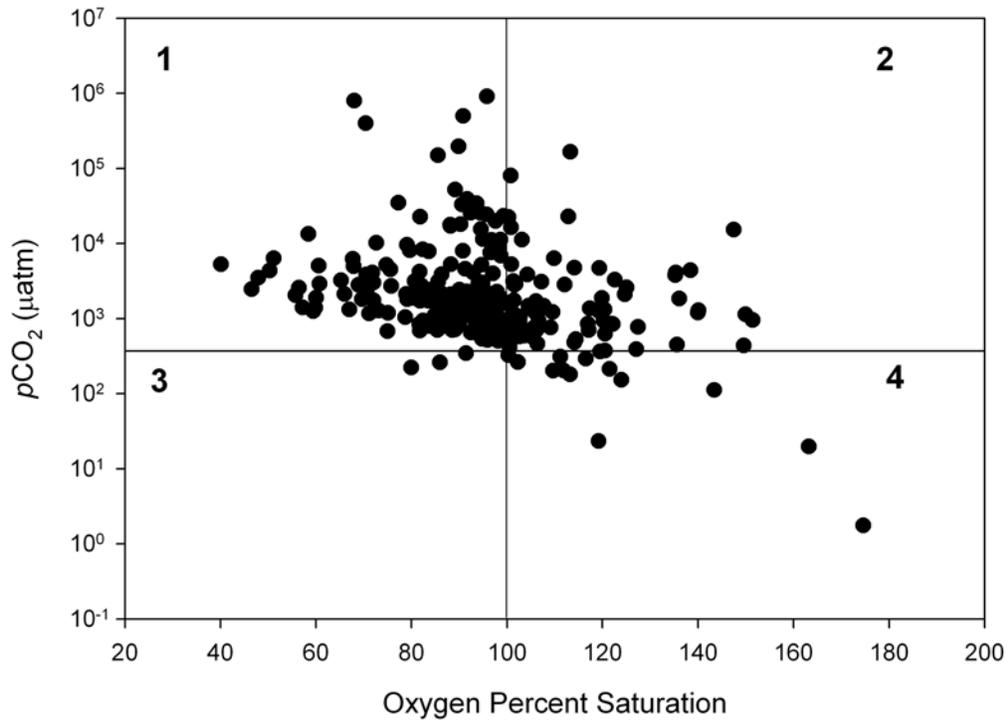


Figure 3-11. Partial pressure carbon dioxide values in relationship to % oxygen saturation for 284 historical lakes. The vertical line represents 100% oxygen saturation. The horizontal line represents atmospheric level of  $p\text{CO}_2$ .

Table 3-5. Average of nutrient and chlorophyll concentrations by month and station in Orange Lake, Florida.

Month	Station	Total Phosphorus (µg/L)	Total Nitrogen (µg/L)	Chlorophyll (µg/L)
6	1	240	2000	50
6	2	190	1800	30
6	3	290	2000	80
6	4	220	1800	20
7	1	230	1700	30
7	2	360	3300	100
7	3	300	2400	50
7	4	210	1600	10
8	1	260	1700	60
8	2	350	3000	90
8	3	220	1800	20
8	4	240	1700	30

Table 3-6. Average carbon estimate variables and wind by month and station in Orange Lake, Florida.

Month	Station	Total Alkalinity (meq/L)	Temp (C)	Specific Conductance (µS/cm @ 25 C)	pH	Wind (m/sec)
6	1	390	28.2	89	6.1	5
6	2	340	29.4	93	6.0	7
6	3	380	27.9	88	6.2	7
6	4	420	28.3	92	6.2	8
7	1	410	29.5	87	5.6	7
7	2	300	29.9	82	5.8	5
7	3	370	30.7	82	5.7	12
7	4	370	30.1	81	5.7	9
8	1	350	30.2	90	6.0	7
8	2	340	31.2	82	6.2	7
8	3	350	30.0	84	6.0	4
8	4	370	30.0	86	6.3	6

Table 3-7. Average  $p\text{CO}_2$  by month and station in Orange Lake, Florida.

Month	Station	$p\text{CO}_2$ ( $\mu\text{atm}$ )
6	1	17000
6	2	15000
6	3	13000
6	4	11000
7	1	48000
7	2	24000
7	3	42000
7	4	31000
8	1	18000
8	2	11000
8	3	15000
8	4	10000

Table 3-8. Aquatic plant data collected on July 7, 2005. Source: Florida LAKEWATCH 2005.

Variable	Value
% area covered with aquatic vegetation (PAC %)	58
% of lake's total volume filled with vegetation (PVI %)	13.5
Average emergent plant biomass (kg wet wt/m <sup>2</sup> )	3.2
Average floating-leaved biomass (kg wet wt/m <sup>2</sup> )	4.5
Average submersed plant biomass (kg wet wt/m <sup>2</sup> )	5.6
Average width of emergent and floating-leaved zone (m)	380
Average lake depth (m)	3

Table 3-9. Percent coverage of macrophytes in Orange Lake and the estimated  $p\text{CO}_2$  for that plant coverage value.

% Cover	Estimated $p\text{CO}_2$
0	18000
10	18000
20	19000
30	20000
40	20000
50	21000
60	21000
70	22000
80	23000
90	23000
100	24000

Table 3-10. Net ecosystem production values for each station by month with an average for all samples at each station in Orange Lake, Florida.

Station #	Net Ecosystem Production			
	June	July	August	Average
1	-1.6	-2.6	-3.1	-2.4
2	-2.1	-2.25	-3.2	-2.5
3	-5.6	-5.1	-6.2	-5.6
4	-5.2	-10.7	-9.8	-8.6

## CHAPTER 4 CONCLUSIONS

From a 627-lake study, a large numbers (80% of those sampled) of Florida lakes are potential sources of carbon to the atmosphere. Partial pressure carbon dioxide levels in Orange Lake even at their lowest calculated  $\mu\text{atm}$  were more than 26 times than that of the overlying atmosphere. It would be difficult to argue that this lake is not a carbon source to the atmosphere. The data set, however, is only representative of the summer months. Full seasonal data may not be necessary to accurately estimate  $p\text{CO}_2$  levels based on the temperature modeling in the 627 lake study. Certain meteorological events such as hurricanes may cause significant short term increases to  $p\text{CO}_2$  depending on runoff volume and its effect on alkalinity values, and also the amount of sediment resuspension.

Trophic state indicators, alkalinity, and specific conductance were all weakly correlated with  $p\text{CO}_2$  levels. The 627-lake study (Canfield 1981; Canfield and Hoyer 1992; Florida LAKEWATCH 1993, 1996; Greis 1995) supports the conclusion that levels of partial pressure carbon dioxide in lakes are controlled by pH levels in the lake. Much of the literature to date has focused on the effects of DOC from the watershed and its relationship to supersaturation (Dillon et al. 1997, Frankignoulle et al. 1998). The data from the 627-lake study (based on color data) did not support the higher correlations with dissolved organic carbon (DOC) found in the literature.

The role of aquatic macrophyte coverage and its potential effects on carbon dioxide concentrations in surface waters may need further investigation. When making estimations using data obtained on Orange Lake in Summer 2005, a change from 0% to 100% of macrophyte coverage in the lake increased average  $p\text{CO}_2$  levels 25% (see Table 3-9). These findings suggest that small-scale changes in aquatic macrophyte coverage would not produce significantly higher

changes in  $p\text{CO}_2$  levels in a Florida Lake. These findings may change if lakes of different trophic states are examined.

Data indicate that Orange Lake is supersaturated with carbon dioxide and seems to be a continual source of  $\text{CO}_2$  to the atmosphere. Partial pressure carbon dioxide levels were significantly higher in plant zones. However, net ecosystem production values were lower in plant areas than in the open water area. Both areas were heterotrophic (NEP was negative). This could be another indicator that plants themselves may not be a causal factor in increases  $p\text{CO}_2$  levels. The location of the plants in the littoral zone and their effect on pH, sediment resuspension and nutrient cycling may be more important factors.

Oxygen saturation data indicates that supersaturation of carbon dioxide alone should not be used as measure of heterotrophy at an ecosystem scale. There were several Florida lakes that were supersaturated with both oxygen and carbon dioxide.

The limnological parameter pH is a key parameter that influences many biological and chemical factors including species distribution, multiple equilibrium expressions, contaminant metal ion concentrations, naturally occurring organic and inorganic species and the dissociation of carbonic acid to name a few (Wetzel 2001). Many attempts have been made to quantify and rank variables of significance to predict mean values of lake pH. Several catchment and lake morphometric parameters have been investigated. The data from the 627 lake study followed a geologically regulated trend in pH as found by Canfield et al. 1988. The trend in pH corresponded with an expected trend in  $p\text{CO}_2$  values by lake region. This further supports that pH is the regulating factor in indirectly measured  $p\text{CO}_2$  values in Florida freshwater lakes. When looking for causal factors to explain variability in  $p\text{CO}_2$  levels between aquatic systems,

one should examine the possible influence of regional geology underlying the aquatic systems in question.

## WORKS CITED

- American Public Health Association (APHA). 1985,1989,1992. Standard Methods for the examination of water and wastewater, 16<sup>th</sup>, 17<sup>th</sup>, 18<sup>th</sup> Editions, Washington D.C.
- Bachmann, R., M. V. Hoyer, and D.E. Canfield, Jr. 2000. Internal heterotrophy following the switch from macrophytes to algae in Lake Apopka, Florida. *Hydrobiologia* 418:217-227.
- Bachmann, R. and D.E. Canfield Jr. 1996. Use of an alternative method for monitoring total nitrogen concentrations in Florida lakes. *Hydrobiologia* 323:1-8.
- Bowling, L, M. Steane, P.Tyler. 1986. Spectral Distribution and Attenuation of Underwater Irradiance in Tasmanian Inland Waters. *Freshwater Biology FWBLAB* 16:313-335.
- Brenner, M., M.W. Binford and E.S. Deevey. 1990. Lakes. Pages 363-391 in R.L. Myers and J.J. Ewel (eds.), *Ecosystems of Florida*. University of Central Florida Press, Orlando.
- Canfield, D.E. Jr., and R. Bachmann. 1981. Prediction of total phosphorus concentrations, chlorophyll a, and Secchi depths in natural and artificial lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 38:414-423.
- Canfield, D.E. Jr., K. Langeland, M.J. Maceina, W.T. Haller, J.V. Shireman, and J.R. Jones. 1983. Trophic state classification of lakes with aquatic macrophytes. *Canadian Journal of Fisheries and Aquatic Sciences* 40:1713-1718.
- Canfield, D.E. Jr., and M.V. Hoyer. 1988. Regional geology and the chemical and trophic state characteristics of Florida lakes. *Lake and Reservoir Management* 4:21-31.
- Canfield, D.E., Jr., and M.V. Hoyer. 1992. Aquatic macrophytes and their relation to the limnology of Florida lakes. Final Report submitted to the Bureau of Aquatic Plant Management, Florida Department of Natural Resources, Tallahassee, FL.
- Carignan R, D. Planas, C. Vis. 2000. Planktonic production and respiration in oligotrophic Shield lakes. *Limnology Oceanography* 45:189-99.
- Cole, J.J., M.L. Pace, S.R. Carpenter, and J.F. Kitchell. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnology Oceanography* 45, 1718-1730.
- Cole J.J. 1999. Aquatic microbiology for ecosystem scientists: new and recycled paradigms in ecological microbiology. *Ecosystems* 2:2152-25.
- Cole J.J., and N.F. Caraco. 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF<sub>6</sub>. *Limnology and Oceanography* 43:647-656.
- Cole, J. J., N. F. Caraco, G. W. Kling, and T. W. Kratz. 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265:1568-1570.

- del Giorgio PA, and R.H. Peters. 1994. Patterns in planktonic P:R ratios in lakes: Influence of lake trophity and dissolved organic carbon. *Limnology Oceanography* 39:772–87.
- D'Elia C.F., P.A. Steudler, and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. *Limnology Oceanography* 22:760-764.
- Duarte, C., and Y. Prairie. 2005. Prevalence of Heterotrophy and Atmospheric CO<sub>2</sub> Emissions from Aquatic Ecosystems. *Ecosystems* 8:862-870.
- Dillon P.J., and L.A. Molot. 1997. Dissolved organic and inorganic carbon mass balances in central Ontario lakes. *Biogeochemistry* 36:29–42.
- Florida LAKEWATCH. 2002. Florida LAKEWATCH Annual Data Summaries for 1986 through 2001. Department of Fisheries and Aquatic Sciences, University of Florida/Institute of Food and Agricultural Sciences. Library, University of Florida. Gainesville, Florida.
- Forsberg, C., S. Ryding. 1980. Eutrophication Parameters and Trophic State Indices in 30 Swedish Waste-Receiving Lakes. *Archiv fur Hydrobiologie* 89:189-207.
- Frankignoulle M., G. Abril, A. Borges, I. Bourge, C. Canon, B. Delille, E. Libert, and J.M. Théate. 1998. Carbon dioxide emission from European estuaries. *Science* 282:434–8.
- Greis, J. G. 1985. A characterization of 60 Ocala National Forest Lakes. Report by John G. Greis, Hydrologist. National Forests in Florida. Tallahassee, FL.
- Griffith, G.E., D.E. Canfield, Jr., C.A. Horsburgh, and J.M. Omernik. 1997. Lake Regions of Florida. EPA/R-97/127. U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Corvallis, OR. 89p.
- Hach Chemical Company. 1975, 1992. Procedures, chemical lists and glassware for water and wastewater analysis. HACH Chem. Co., Ames, Iowa.
- Hanson, P., R. Stephen, D. E. Carpenter, E. Armstrong, H. Stanley, and T. K. Kratz. 2006. Lake dissolved inorganic carbon and dissolved oxygen: changing drivers from days to decades. *Ecological Monographs* 76:343-363.
- Hanson, P.C., Bade, D. L., Carpenter, S. R., and T. K. Kratz. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnol. Oceanogr.* 48: 1112-1119.
- Harrison WG, J. Aristegui, E.J.H. Head, W.K.W. Li, A.R. Longhurst, and D.D. Sameoto. 2001. Basin-scale variability in plankton biomass and community metabolism in the subtropical North Atlantic Ocean. *Deep-Sea Res II* 48:2241–69.
- Hartman, B. and D. E. Hammond. 1985. Gas exchange in San Francisco Bay. *Hydrobiologia* 129:59-68.

- Hem, J.D. 1992. Study and interpretation of chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- 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. In: Wilhelms SC & Gulliver JS (Eds) Air-Water Mass Transfer, Second International Symposium on Gas Transfer at Water Surfaces (pp 413–431). Am. Soc. Civil Eng., New York, NY.
- Howarth, R. W., R. Schneider, and D. Swaney. 1996. Metabolism and organic carbon fluxes in the tidal, freshwater Hudson River. *Estuaries* 19: 848-865.
- Jonsson, A., M. Meili, A. Bergstram, and M. Jansson. 2001. Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake. *Limnology and Oceanography* 46: 1691-1700.
- Juday, C., E. Birge, and W. W. Meloche. 1935. The carbon dioxide and hydrogen ion content of the lake waters of northeastern Wisconsin. Wisconsin Academy of Sciences, Arts, and Letters.
- Kling G.W., G.W. Kipphut, and M.C. Miller. 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. *Science* 251:298–301.
- Menzel, D. W. and N. Corwin. 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. *Limnology and Oceanography* 10: 280-282.
- Odum, H. T. and C. M. Hoskin. 1958. Comparative studies on the metabolism of marine waters. *Institute of Marine Science, University of Texas* 5:16-46.
- Parsons, T.T. and J.D.H. Strickland. 1963. Discussion of spectrophotometric determination of marine-plant pigments, with revised equations for ascertaining chlorophylls and carotenoids. *Journal of Marine Research* 21: 155-163.
- Prairie Y.T., D.F. Bird, J.J. Cole. 2002. The summer metabolic balance in the epilimnion of southeastern Quebec lakes. *Limnology and Oceanography* 47:316–321.
- Raymond, P., J. Bauer, and J. Cole. 2000. Atmospheric CO<sub>2</sub> Evasion, Dissolved Inorganic Carbon Production, and Net Heterotrophy in the York River Estuary. *Limnology and Oceanography* 45:1707-1717.
- Reche, I., and M.L. Pace. 2002. Linking dynamics of dissolved organic carbon in a forested lake with environmental factors. *Biogeochemistry* 61:21-36.
- Sartory, D. P., and J. U. Grobbelaar. 1984. Extraction of chlorophyll a from freshwater phytoplankton for spectrophotometric analysis. *Hydrobiologia* 114: 177-187.
- Sawyer, C.N. and P.L. McCarty. 1967. *Chemistry for sanitary engineers*, 2nd ed.: McGraw-Hill, St. Louis, MO.

- Scully N.M., W.J. Cooper, and L.J. Tranvik. 2003. Photochemical effects on microbial activity in natural waters: the interaction of reactive oxygen species and dissolved organic matter. *FEMS Microbial Ecology* 46:353–7.
- Simal, J. 1985. Second derivative ultraviolet spectroscopy and sulfamic acid method for determination of nitrates in water. *Journal of Analytical Chemistry* 68:962-964.
- Sobek S, G. Algesten, A.K. Bergström, M. Jansson, and L.J. Tranvik. 2003. The catchment and climate regulation of pCO<sub>2</sub> in boreal lakes. *Global Change Biology* 9:630–641.
- StatView, Version 5. SAS Institute Inc., Cary, NC.
- Striegl R.G., P. Kortelainen, and J.P. Chanton. 2001. Carbon dioxide partial pressure and <sup>13</sup>C content of north temperate and boreal lakes at spring ice melt. *Limnology and Oceanography* 46:941–945.
- Stumm, W. and J.J. Morgan. 1981. *Aquatic chemistry*, 2nd ed.: New York, John Wiley & Sons, 780 p.
- Stumm, W., and J.J. Morgan. 1995. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley. NY.
- Talling J. F. 1976. The depletion of carbon dioxide from lake water by phytoplankton. *Journal of Ecology* 64:79-121.
- USEPA. 1979. *Methods for chemical analysis of waters and wastes*. U. S. Environmental Protection Agency. Washington D. C.
- Wetzel R.G. 2001. *Limnology. Lake and River Ecosystems*. Academic Press, San Diego.
- Wetzel, R.G. and G. E. Likens. 1991. *Limnological analyses*. Springer-Verlag, New York: 391 pp.
- Wollin, K. M. 1987. Nitrate determination in surface waters as an example of the application of UV derivative spectrometry to environmental analysis. *Acta Hydrochemica Hydrobiologia* 15:459-469 (Ger.).
- Yentsch, C. S. and D. W. Menzel. 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep Sea Res.* 10: 221–231.

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