Plankton Metabolic Balance and its Controlling Factors in the Coastal Zone of the Laurentian Great Lakes

by

Serghei A. Bocaniov

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Doctor of Philosophy
in
Biology

Waterloo, Ontario, Canada, 2007

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Plankton metabolic balance (PMB_m) of the surface mixed layer was calculated as the ratio of areal rates of gross photosynthesis (AGP) to community respiration (AR), and estimated for four Laurentian Great Lakes coastal sites of contrasting physical, optical and nutrient regime: western Lake Ontario, Hamilton Harbour, Georgian Bay and Woods Bay. The applied methods were the oxygen light-and-dark bottle and ^{14}C bottle methods as well as the oxygen stable isotope method (^{18}O method). PMB_m was net autotrophic in most of the cases (73% of the observations). Within- and inter-system variations in PMB_m were heavily dependent on both a ratio of light-saturated photosynthesis to community respiration (P_{max}/R) and a ratio of euphotic to mixing depths (Z_{eu}/Z_m). While short-term within-system variations in PMB_m were driven by the interplay of chlorophyll *a* (Chl *a*), total phosphorus (TP) and Z_{eu}/Z_m ratio, its inter-lake long-term variability had a different behaviour. Average ratios of AGP/AR were dependent only on DOC or single physical parameters such as Z_{eu} or Z_m, while PMB_m determined as the ratio between average AGP and AR was controlled by the joint effect of DOC, TP and Chl *a*. DOC affected average AGP/AR ratios primarily via its control over fluctuations of the physical environment and had a depressing effect on AGP rates but did not control rates of AR. Independent measurements of volumetric rates of photosynthesis (P) and community respiration (R) were made by ^{18}O method adjusted for wind-driven gas exchange and compared against estimates from bottle estimates. The ^{18}O method in Lake Ontario gave internally inconsistent results (e.g. negative absolute rates of P and R) and poor agreement with independent estimates of P, R and P/R despite superficially plausible estimates for P/R. The low productivity of Lake Ontario and frequent disturbances of water column masked the biological signal in both DO abundance and its isotopic signature, and

thus invalidated the assumptions of steady state conditions. However, in Hamilton Harbour and some other relatively sheltered sites that were sampled occasionally, ^{18}O method predicted absolute rates of P that were well correlated well with bottle estimates. Isotope model estimates for R and P/R in the harbour were not well correlated with bottle estimates but were of comparable magnitude on average, and differences were explicable in terms of physical forces and the different time scales of response for the two methods. The Hamilton Harbour hypolimnion presented an anomalous behavior in oxygen stable isotopes (^{18}O depletion) where seasonal development of DO depletion was not accompanied by the progressive isotope enrichment expected from respiratory fractionation. The Lake Ontario and harbour hypolimnion results both appear to show that simple steady state models that assume literature values for fractionation processes and ignore physical dynamics are of limited applicability to lakes.

Acknowledgements

First of all, my sincere thanks to my supervisor, Dr. Ralph E. H. Smith, for all his support, motivation, guidance and boundless ideas during my research work. I appreciate all his valuable suggestions and critical insights into the earlier drafts of this thesis. I also appreciate all his support and patience when I had to go through the difficult time with my family issues in 2006.

I would like to thank my PhD committee members, Dr. Robert E. Hecky, Dr. William Taylor and Dr. Sherry Schiff for their valuable feedbacks, suggestions and assistance that helped me to shape my research work.

I am also thankful to Murray N. Charlton for his help to conduct my field work in Hamilton Harbour and Lake Ontario.

I would like to acknowledge the help of Richard Elgood and the following students from his Environmental Isotope lab who helped me in my fieldwork work: Paul Malone, Kevin Maurice, Michelle Sabourin, Dave Snider and Simon Thuss.

Dedication

I dedicate this work in loving memory to my mother, Luidmila Bocaniova. Thank you for all your love as well as for your support of my PhD studies. I know you would be proud.

Table of Contents

List of Figures

List of Tables

Chapter 1: General Introduction

1.1 Introduction

Over the past decades, the knowledge of metabolic balance of aquatic ecosystems has been recognized as a central issue in understanding carbon flow and food web structure in marine and freshwater ecosystems (Carignan et al. 2000). This knowledge is crucial for understanding material and energy cycling within food webs (Polis et al. 1996), and helps to identify the source of carbon incorporated into all trophic levels of aquatic ecosystems, and thus to determine whether a given water-body has a classical predominantly phytoplankton-based food web or it has a food web significantly dependent on the inputs of the allochthonous organic matter from the watershed.

The metabolic balance of the lake surface mixed layer can be defined as a balance between lake gross primary production or gross photosynthesis (P) and community respiration (R). It is usually measured as the ratio of P to R (P/R). Gross primary production can be defined as the rate of production of new organic matter by photosynthesis (Cole et al. 2000), while respiration is the rate of dissipation of organic matter and can be defined as the sum of all metabolic processes that contribute to the oxidation of organic carbon to CO_2 (Falkowski and Raven 1997). The respiration of both autotrophs and heterotrophs is called community respiration. The difference between P and respiration by photosynthetic organisms is the potential rate of accumulation of new autotroph biomass, termed net photosynthesis or net primary production (NPP), while the difference between P and community respiration (R) is net ecosystem production (NEP).

All aquatic ecosystems are open systems and they may not be necessarily in metabolic balance at any time or over a long period of time. Therefore, P may or may not exceed R. When P exceeds R (P/R >1), ecosystems are net autotrophic, and they act as net sinks for CO_2 and net producers of O_2 and organic matter (Carignan et al. 2000). In contrast, when R exceeds P (P/R <1), ecosystems are net heterotrophic, and they act as net sources of CO_2 and net consumers of organic

carbon (Carignan et al. 2000). When P is equal to R (P/R = 1), then an aquatic ecosystem is in metabolic balance.

Despite the variety of methods for measurement of metabolic balance (P/R), there are basically four different approaches widely used in recent publications. Two of them are bottle methods: (i) use of ^{14}C assimilation technique for P calculations and oxygen dark bottle incubations to derive R measurements (e.g. del Giorgio and Peters 1994), and (ii) use of oxygen light-and-dark bottle incubations to calculate both P and R (e.g. Carignan et al. 2000). Two other, *in situ,* approaches are: (i) diel observations of dissolved oxygen or carbon dioxide concentrations in the surface waters of lakes (e.g Cole et al. 2000, Hanson et al. 2003), e.g. measuring dissolved oxygen concentrations of the surface water by the deployment of a recording dissolved oxygen sensor; and (ii) use of natural abundance of dissolved oxygen and its isotopic composition, the so-called ^{18}O method (Quay et al. 1995; Wang and Veizer 2000). To date, not much has been done to compare the results of those four methods and validate the meanings of the new methods (e.g. ^{18}O method) by the results from other well-established methods (e.g. oxygen bottle method). It is often assumed that bottle methods provide reasonable estimates of P and R for aquatic ecosystems although some studies have shown that *in situ* methods can give different, and often higher, values than bottle methods (e.g. Fahnenstiel and Carrick 1988). Bottle methods provide a direct but potentially artificial measure of plankton production and respiration, while *in situ* methods (e.g. diel methods) measure the ecosystem metabolism, including sediment and littoral zone metabolisms, and may be biased by mixing and advection of water masses with different DO concentrations. The two classes of method may not be expected to agree on day-to-day scale but may agree better on a larger and longer scale. Thus the question still remains if the currently applied bottle methods can give reasonable estimates of metabolic balance close to those determined by *in situ* methods (e.g. ^{18}O method).

Despite a number of studies, our understanding of plankton metabolism is still limited. The emergent view is leaning towards the idea that the heterotrophic metabolic balance (P/R <1) is very

common in lakes, implying an important role for allochthonous carbon, especially in lower productivity lakes. This is opposite to the classical view of plankton metabolism in which phytoplankton and other autochthonous producers have been viewed as the basis for all aquatic life. For example, del Giorgio et al. (1994) using bottle estimates to derive P (^{14}C method) and R (oxygen consumption in the dark) found that low productivity lakes were net heterotrophic with R being several times greater than P. However, the idea of prevalent heterotrophy in lakes has been challenged by Carignan et al. (2000) who used a single method (oxygen bottle incubation method) to measure both P and R, and found that even the most oligotrophic lakes were net autotrophic, with P nearly always exceeding R. The contradictory results of these two studies were explained by the uncertainty of the results of the ^{14}C method (Carignan et al. 2000) and by the effect of DOC on plankton metabolism (Prairie et al. 2002).

Recent studies of production and respiration are changing our understanding of plankton metabolism, but a disagreement on what controls PMB_m in lakes and on the prevalence of heterotrophy still exists. Some studies have suggested an important role of allochthonous subsidy (Cole et al. 2000; Prairie et al. 2002; Hanson et al. 2003) while others have pointed to the importance of the trophic status (del Giorgio and Peters 1994; Carignan et al. 2000; Roberts and Howarth 2006) or even to the physical environment, and in particularly to the ratio of optical to mixing depths (Harris 1978; Cushing 1989). Other studies have indicated an important role for the size structure of primary producers in estuarine (e.g. Smith and Kemp 2001) and marine systems (Tremblay and Legendre 1994). The existing disagreement on what primarily controls PMB_m may have been influenced by the way plankton metabolic balance was calculated. Some studies treated PMB_m as the ratio between average gross photosynthesis and community respiration (so-called ratio between averages, e.g. del Giorgio and Peters 1994; Hanson et al. 2003) and found important roles for both DOC and trophic status. Others calculated PMB_m as the average of ratios of gross photosynthesis and community respiration (e.g. Carignan et al. 2000) and found weak but statistically significant relationships with

physical factors such as mixing and optical depths, and no effect of DOC. Another possible source of disagreement is that some studies deal with the PMB_m of the SML only (e.g. Carignan et al. 2000) while others measure more of a system PMB (e.g. Hanson et al. 2003).

Most of the present knowledge of PMB_m and its controlling factors has come from smaller lakes, and often with a very short sampling durations on individual lakes (e.g. del Giorgio and Peters 1994; Hanson et al. 2003). Even assuming the sampling is representative, such studies can only provide information on between-system controls operating over very long time periods. These studies did not attempt to have insights into the seasonal dynamics of plankton metabolism for any given lake and do not resolve the factors responsible for within-system seasonal variability in PMB_m.

Moreover, small lakes are different from the large ones, and especially from the Laurentian Great Lakes (LGL). They are different not only in terms of the importance of physical forcing but also in a spatial differentiation between nearshore and offshore zones. Large and clear, oligo-mesotrophic LGL might be expected to tend towards autotrophy because of the low DOC, long water renewal times, and therefore, weaker coupling to their terrestrial catchments. However, there are some recent metabolic studies indicating frequent heterotrophic conditions in Lake Superior (Russ et al. 2004), and with a lesser degree Lake Michigan (Biddanda and Cotner 2002; Urban et al. 2005) and Lake Erie (Ostrom et al. 2005; but see Depew et al. 2006*b*). Previous studies on PMB_m in the LGL have been relatively localized in time and location, and limited mostly to offshore waters. Measurements have been infrequent and/or dependent on interpretations of geo-chemical variables such as natural abundance in oxygen stable isotopes (e.g. Russ et al. 2004; Ostrom et al. 2005). The interpretation of the latter requires care as it depends on various assumptions including those of steady-state in the oxygen budget. It is a truism that no ecosystem is truly at steady state, but the Great Lakes are so heavily forced by physical mechanisms that they may be even further from this idealization than most other lakes. As the oxygen stable isotope method has provided some of the

more extensive evidence for heterotrophy in the LGL it would be desireable to know how its results compare to alternative methods, but direct comparisons have not yet been published.

Cell size is an important parameter determining the pathways of material and energy flow in aquatic systems (Kalff 2002). It has been well documented that R is a function of the size of an organism (Falkowski and Raven 1997). In turn, P is also determined to some extent by the cell size as a result of the size-dependent physiological properties of the phytoplankton, such as photosynthetic efficiency and nutrient uptake (Malone 1980; Chisholm 1992). These all would suggest that the mean size of phytoplankton communities would reflect the P/R ratio with larger cells associated with the high values of P/R ratios and smaller cells associated with low values of P/R (Smith and Kemp 2001). Despite the enormous work on size fractionated plankton production, systematic studies of metabolic balance variations with respect to phytoplankton size distribution are only few (e.g. Smith and Kemp 2001) and have been done in estuaries and marine systems but not in lakes. Therefore, the contribution of different size fractions of freshwater phytoplankton to plankton metabolic balance deserves more attention and needs to be investigated.

1.2 Thesis Overview

The overall objectives of this thesis were: 1) To determine the environmental controls on the ratio of light saturated gross photosynthesis to community respiration (P_{max}/R) both within and between systems. The P_{max}/R ratio is essentially the PMB_m without the confounding influences of physical structure, specifically the ratio of euphotic to mixing depths (Z_{eu}/Z_m), as explained further in Chapter 2. In determining its behaviour, we determine the controls on the biological processes that contribute to the PMB_m of the system. 2) To test the idea that allochthonous organic inputs, as indexed by the dissolved organic carbon (DOC) concentration, control PMB_m through their effect on P_{max}/R. It is often assumed, implicitly or explicitly, that higher DOC and allocthonous organic matter levels stimulate R relative to P and thus drive PMB to a heterotrophic condition. If so, this should be evident

in the P_{max}/R ratio. 3) To test the expectation that epilimnetic PMB_m will be dependent on both P_{max}/R and Z_{eu}/Z_m. While P_{max}/R expresses the biological processes that determine the potential for heterotrophic or autotrophic balance, the PMB_m itself should additionally depend on the proportion of the system that is within the photic zone, and the Z_{eu}/Z_m ratio captures this influence. I hypothesize that these two ratios, one biological and the other essentially physical, should capture most of the variation in PMB_m. 4) To determine the environmental controls on PMB_m, and particularly to resolve the relative importance of allochthonous influence (DOC), trophic status (Chl *a*, TP), and plankton size structure. 5) To determine whether PMB_ms determined as the ratio of average P and R show different controls from those determined as the average ratio of P and R. The latter can be thought of as the most frequent, or typical, PMB_m while the former is closer to a seasonal, mass-weighted, PMB_m. They will not necessarily follow the same patterns. 6) To ascertain the predominant mechanism through which DOC affects plankton metabolic balance, particularly effects on P_{max}/R and Z_{eu}/Z_m. 7) To test if ^{14}C method with short 1-hour incubations is able to give estimates of gross photosynthesis. And, 8) to validate the results and meanings of the ^{18}O method by direct comparison with the traditional bottle incubations. This thesis is divided into three independent data chapters (Chapters 2-4), and each chapter deals with a specific aspect of my overall research objectives: objectives 1-2 (Chapter 2), objectives 3-7 (Chapter 3), and objective 8 (Chapter 4). These chapters were written in the journal paper format.

Chapter 2 sets the framework for the analysis of PMB_m, arguing that it is essentially a product of two ratios, P_{max}/R and Z_{eu}/Z_m, which can be analyzed separately. It deals mostly with the potential for autotrophic vs heterotrophic metabolism in lake plankton (P_{max}/R), and how the DOC, trophic status, physical structure and size structure of primary producers may affect it. In this chapter, not only current study data are used but also those reported by Carignan et al. (2000), Depew et al. (2006*b*) and Silsbe (2004). Carignan et al. dataset (2000) dealt with the small oligotrophic Shield lakes while the Depew et al. (2006*b*) dataset came from from their plankton metabolism study of

Lake Erie, and Silsbe (2004) reports data on P and R in three eutrophic bays of Lake Victoria. Combined, these datasets covered both small and large lakes, with a wide range in productivity. Methodology was similar in all studies, so the combined dataset provides excellent insights into the driving forces of within and between system variations in P_{max}/R.

Chapter 3 is a logical continuation of Chapter 2 but deals with integral PMB_m, determined as the ratio of areal rates of photosynthesis and community respiration in the surface mixed layer, and the effects of environmental variables such as DOC, total phosphorous (TP), chlorophyll-a (Chl *a*), P_{max}/R and Z_{eu}/Z_m on its within and between system variations. It introduces the differences between PMB determined as the average ratio and ratio between averages. It also discusses the relationship between light saturated rates of photosynthesis derived from two methods, ^{14}C and oxygen bottle methods. The pooled data set used in this Chapter includes data reported by del Giorgio and Peters (1994), Carignan et al. (2000), Hansson et al. (2003) and Depew et al. (2006*b*).

Chapter 4 attempts to interpret the results and the meanings of the novel *in situ* ^{18}O method by the direct comparison of its results with the bottle incubation methods. It also discusses the behaviour of the oxygen stable isotopes in the Hamilton Harbour hypolimnion. This leads to insight not only into the applicability of the steady state model that has to date been used to interpret stable oxygen isotope distributions but also to insights into how methods with intrinsically different time and space response scales may differ.

It is worth mentioning that not all data collected during my Ph.D. research work have been used in this thesis. More methodological work was done for the Lake Ontario and Hamilton Harbour sites. For example, on three occasions, ^{14}C incubations were run on the day of water sampling and in the morning of the following day, with simultaneous measurements of Chl *a*, TP and dissolved inorganic carbon (DIC) to see how storage may affect the primary production estimates. Also, the ^{14}C incubations were run simultaneously for the same water but with different ^{14}C stock solutions to see if

there is a difference in primary production. The Photosynthesis-Irradiance curves (P-I curves) were derived from ^{14}C and oxygen method to compare the photosynthetic characteristics (Appendix 4A). Extensive work has been done in Georgian Bay – Moon Bay – Moon River system (results are not presented here) to estimate the tributary impact on coastal ecology. These data will form the foundation for a separate paper. Moreover, diel fluctuations in dissolved oxygen, conductivity and temperature (as well as turbidity, pH and chlorophyll at times) were measured in the surface mixed layer of Hamilton Harbour (5 bi-weekly deployments), Lake Ontario (3 bi-weekly deployments) and of Georgian Bay (1 three-day deployment) by the long-term deployments (14 days each) of water quality data-loggers (YSI 6600 and Hydrolab Datasonde 4). These data will be used in another paper comparing metabolic rate measurements derived from three methods, diel oxygen method, bottle incubations and ^{18}O method.

Chapter 2

Dissolved organic carbon, trophic status and the potential for autotrophic vs heterotrophic metabolism in lake plankton.

2.1 Abstract

The ratio of light-saturated gross photosynthesis to community respiration in the dark (P_{max}/R) is an index of potential autotrophic activity relative to heterotrophic activity in plankton communities. Allochthonous organic matter, light and mixing regimes, and plankton community structure have all been suggested as controlling factors. We measured P_{max} and R at four Laurentian Great Lakes (LGL) sites of contrasting trophic status and DOC concentrations and used principal components analysis to show that P_{max}/R increased as the proportion of microplankton chlorophyll *a* (Chl *a*) increased. However, trophic level effects were stronger than cell size effects. With additional data from the literature, we found that total variation (including within-system and between system variations) was best explained by a regression model that increased with Chl *a* concentration but decreased with total phosphorus (TP) concentration and the ratio of euphotic to mixing depths (Z_{eu}/Z_m). Z_{eu}/Z_m was the only significant predictor of between-system (season average) variations of P_{max}/R. The pattern of total variation observed here implies some uncoupling of photosynthesis and respiration on the within-season time scale, while the between-system comparisons imply a longer-term balance subject to effects of the physical environment (Z_{eu}/Z_m) rather than trophic status. Over the low to moderate range of DOC in this data set (2.1 to 6.6 mgC L^{-1}) the results did not support the idea that higher allochthonous carbon inputs (i.e. higher DOC concentrations) yields lower P_{max}/R.

2.2 Introduction

The planktonic metabolic balance (PMB_m) of aquatic ecosystems can be defined as the ratio of areal rates of gross photosynthesis relative to community respiration (AGP/AR) calculated for the mixed layer. This ratio is an important characteristic of ecosystem function, classically argued to represent a quantitive index of trophic status (Odum 1956). It determines, in theory, whether the ecosystem is a net producer or consumer of organic matter, oxygen (O_2) and carbon dioxide (CO_2). The importance of allochthonous organic matter inputs into oligotrophic lakes, and the consequent likelihood of $PMB_m<1$ on the whole-lake and whole-year scale, have long been recognized (Wetzel 2001). More strikingly, characteristic values of $PMB_m<1$ in many lakes have been reported even for the summer time epilimnion (e.g. del Giorgio and Peters 1994; Prairie et al. 2002; Hanson et al. 2003; Pace et al. 2004), a time and place where a closer balance or even $PMB_m>1$ might be expected. However, some studies have found a primarily autotrophic ($PMB_m>1$) balance (e.g. Carignan et al. 2000) and there are disagreements about the controls on PMB_m. Some lake studies have pointed to the importance of trophic status (del Giorgio and Peters 1994; Carignan et al. 2000; Roberts and Howarth 2006) while others pointed to DOC concentration (Prairie et al. 2002; Hanson et al. 2003) or variations in the physical environment such as Z_{eu}/Z_m (Harris 1978; Cushing 1989). One estuarine study has indicated an important role for phytoplankton community size structure (Smith and Kemp 2001), consistent with ideas about the importance of cell size, sedimentation, and export production as controls on PMB in marine systems (Tremblay and Legendre 1994).

In order to better understand PMB_m for the mixing layer of a lake it is helpful to consider how it is calculated, what its main components are, and which of them are affected by the controlling factors in question. Various published formulas for the numerator, AGP, demonstrate that it is directly proportional to the ratio of the maximum rate of volumetric photosynthesis at light saturation (P_{max}) to the light attenuation coefficient (k_{PAR}) (Talling 1957*a*, *b*; Bannister 1974; Platt 1986). For example, Talling (1957*a*, *b*) showed that AGP is the product of P_{max}/k_{PAR} and $\ln(2I_o/I_k)$ where I_o and I_k are the

irradiance at the surface and at the onset of light saturation respectively. If the photic zone (Z_{eu}) is defined as a zone extending to 1% of the incident irradiance, then k_{PAR} is equivalent to $4.6/Z_{eu}$ and:

(2.1) $$AGP = [P_{max} \times Z_{eu}] \times [\ln(2I_o/I_k)/4.6] = [P_{max} \times Z_{eu}] \times f1$$

where $f1$ is a substitute for $\ln(2I_o/I_k)/4.6$ and is only moderately variable, depending partly on the relationship between P_{max} and α^B (the initial slope of the Photosynthesis -Irradiance curve at low PAR). There are other formulations for AGP (e.g. Falkowski and Raven 1997; Fee 1990) but all of them lead to the same conclusion regarding its dependence on P_{max} and Z_{eu}. Several studies have shown that variations of biomass, and thus P_{max}, and water transparency, and thus Z_{eu}, drive most of the variation of AGP in lakes as it is usually calculated (e.g. Hecky and Guildford 1984; Fahnenstiel et al. 1995; Smith et al. 2005) with the factors in $f1$ of only secondary importance.

Areal respiration is usually calculated as the volumetric rate of community respiration (R) multiplied by mixing depth (Z_m):

(2.2) $$AR = R \times Z_m$$

From eq. 2.1 and 2.2 it follows that:

(2.3) $$AGP/AR = [P_{max}/R] \times [Z_{eu}/Z_m] \times f1$$

Thus the value of PMB_m can be understood to reflect primarily the product of a biological variable (the autotrophic to heterotrophic metabolic potential ratio, P_{max}/R) and a physical one (the euphotic to mixing depths ratio, Z_{eu}/Z_m).

P_{max}/R is often taken as a key parameter determining phytoplankton survival in the mixed layer (Strickland 1960; Yentsch 1962) and reported patterns of PMB_m and P_{max}/R itself suggest some of its controlling factors. If DOC, as a proxy for allochthonous organic matter inputs, drives PMB_m this could be due to its effects on light penetration and mixing depths (Jones 1992; Kirk 1994; Fee et

al. 1996, Carpenter et al. 1998; Houser 2006), but could also be due to a depression of P_{max}/R by allochthonous subsidy of respiration (Bidanda et al. 2001; Pace et al. 2004; Hanson et al. 2003; Kritzberg et al. 2004). A tendency of PMB_m to increase with trophic status (Cole and Caraco 1993; Carignan et al. 2000) would suggest higher P_{max}/R in more eutrophic systems. Alternatively, Smith and Kemp's (2001) results imply that P_{max}/R in their estuarine system was inversely correlated with the proportion of smaller phytoplankton (picoplankton). Harris (1978) suggested that P_{max}/R should be negatively correlated with Z_{eu}/Z_m because phytoplankton communities with more efficient (high P_{max}/R ratio) metabolism are favoured where light availability is poor (low Z_{eu}/Z_m). These various possibilities have not yet been resolved.

The seasonal progression of events in temperate lake plankton communities often includes periods of looser or tighter coupling between production and consumption and a corresponding temporal variation of PMB_m and P_{max}/R (e.g. Scavia and Fahnenstiel 1987, Lampert and Sommer 1997). Especially in larger lakes, additional variability is likely to result from physical forcing events such as upwelling and downwelling (e.g. Boyce 1974, Rao and Murthy 2001*a*, *b*) and resuspension (e.g. Schelske et al. 2003). We currently know little about how such forcing influences P_{max}/R or PMB_m, or how the controls on within-system variations over time may compare to between-system controls operating over longer time periods.

In this paper, we focus on P_{max}/R as a parameter that can express a great deal about the structure and function of the plankton community without the confounding influences of physical structure (Z_{eu}/Z_m) that affect PMB_m. Using original measurements in Great Lakes coastal zones and additional data from the literature, we seek to determine the environmental correlates of P_{max}/R both within and between systems. A particular goal was to test the idea that allochthonous organic inputs, as indexed by DOC concentration, control PMB_m through P_{max}/R as opposed to the competing idea that among-lake variations in PMB_m reflect a fundamental relationship between P_{max}/R and trophic status. By including coastal sites with relatively strong physical forcing, we were also able to test

whether controls on shorter time scales, within systems, are likely to be the same as those applying among systems on longer time scales.

2.3 Methods

2.3.1 Design and study sites

The main sites for this study were Hamilton Harbour and western Lake Ontario (Fig. 2.1), providing contrasting physical, optical and nutrient regimes. More limited, additional sampling was done at Woods Bay and Georgian Bay (Fig. 2.1), Lake Huron to provide a broader range of trophic status and DOC conditions. These four sites represent a range of conditions encountered in the nearshore sites of the LGL (Neilson et al. 2003). The Lake Ontario station is a clear-water, high-energy coastal site that has TP in the oligo- or meso-trophic range and relatively low DOC concentration (Table 2.1), while the Hamilton Harbour station is more turbid and sheltered and has higher TP and DOC concentrations. The Georgian Bay site has even lower TP and DOC concentrations than Lake Ontario (Table 2.1), while the Woods Bay station has DOC concentrations even higher than Hamilton Harbour but is lower in TP. Lake Ontario and Hamilton Harbour were deeper than Woods Bay and Georgian Bay stations (Table 2.2).

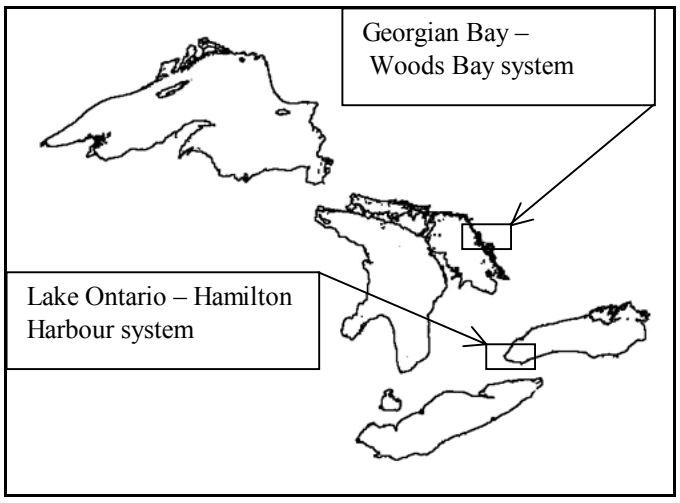

Fig. 2.1 Map of the Laurentian Great Lakes indicating locations of sampling systems

Table 2.1 Location of sampling sites and summary of studies reporting average TP and DOC concentrations for the chosen study systems.

Study site	Location	Latitude and longitude	TP (mmol m^{-3})	DOC (mg L^{-1})
Hamilton Harbour	W. Lake Ontario	43°17.3'N, 79°50.4'W	1.129[4]	4.22[1]; 3.9[3]
Lake Ontario	W. Lake Ontario	43°17.3'N, 79°43.9'W	0.314[5]	2.6[1,2]; 2.8[3]
Woods Bay	E. Georgian Bay	45°08.5'N, 80°00.1'W	0.203-0.223[6]	5.5[1], 4.93[8]
Georgian Bay	E. Georgian Bay	45°07.8'N, 80°05.4'W	0.142[7]	2.68[1]

[1] Smith et al. 2004; [2] Scully and Lean 1994; [3] Scully et al. 1996; [4] Murphy et al. 2003; [5] Gouvêa et al. 2006; [6] Carter et al. 1995; [7] Carter et al. 1995 (taken as the furthest offshore station in Twelve Mile Bay, station 5); [8] Smith and Bocaniov (unpub. data).

2.3.2 Field methods

Lake Ontario and Hamilton Harbour sites were sampled from early May to early September at intervals of approximately 2 weeks with one extra visit in October in 2004. Water chemistry was sampled several times in Woods Bay and Georgian Bay and metabolic rates were measured twice (June and August 2004). Water was collected with an integrated water sampler from the surface to the top of thermocline or from 0 to 10 m (Lake Ontario) and from 0 to 5 m (Hamilton Harbour, Woods Bay and Georgian Bay) if the water column was isothermal. The depth of the mixed layer was defined as the depth at which the temperature gradient exceeded 0.01 °C cm^{-1} and overall temperature change over 1 m depth was more than 1 °C (e.g. Carignan et al. 2000). Temperature profiles were measured using YSI 6600 or YSI 600XLM multiparameter sondes (YSI inc., USA). The water from each site was screened with the 200-µm nylon mesh (Nytex®) to remove large zooplankton and subsequently incubated at temperatures with 1-2°C of *in situ* values.

Photosynthetically active radiation (PAR) was measured at 1 m intervals using an underwater quantum sensor (Li-COR Inc.). The light extinction coefficient (k_{PAR}) was estimated by linear regression of the natural logarithm of irradiance vs depth (Kirk 1994), and Z_{eu} then calculated as the depth of 1% of the incident irradiance.

2.3.3 Analytical methods

Duplicate water samples for determination of total and size-fractionated Chl *a* as well as TP were taken at the beginning of each incubation experiment. For Chl *a* size fractionation, the pre-screened samples were additionally fractionated using 20-µm and 2-µm pore-size polycarbonate membrane filters (Poretics). Chl *a* samples were filtered under low vacuum through 0.7-µm pore-size GF/F glass fiber filters (AMD inc., Mississuga) then stored at –20°C for later analysis by fluorometry after 20-h extraction in 90% acetone in the dark at –20°C (Hiriart et al. 2002). Samples for TP were stored at -20°C pending analysis by the ascorbate method, following persulfate digestion (Wetzel and Likens 2000). In Georgian Bay and Woods Bay stations, DOC samples were collected as the filtrate through precombusted Whatman GF/F filters (0.6-µm pore size) and measured with a Dohrmann-Rosemount DC-190 High Temperature Total Carbon Analyzer, while those in Hamilton Harbour and Lake Ontario were analyzed similarly (Smith et al. 2004).

2.3.4 Metabolic measurements

Oxygen production and consumption measurements were made in acid-washed 300-mL BOD glass bottles following the general procedures of Carignan et al. (1998), including careful calibration of bottle volumes and control of temperature, and using five replicates for initial, light, and dark bottles. Illumination was by cool white fluorescent lamps providing approximately 330 µmol photons m^{-2} s^{-1}. Parallel measurements of photosynthesis vs irradiance responses using ^{14}C (S. Bocaniov, unpub. data) confirmed that the irradiance was saturating but not inhibiting. Light bottles were incubated for 6 hours and dark bottles for 6 hours (Hamilton Harbour and Woods Bay) or 18 hours (Lake Ontario and Georgian Bay). Dark bottle time-series experiments run twice with Hamilton Harbour water showed a linear relationship between oxygen concentration and incubation time up to 24 hours, with the regression equation explaining 89% or more of total variation in dissolved oxygen (DO) concentrations. Titrations were done usually within 24 hours after fixation and followed the procedures described in Carignan et al. (1998) using an automated titrator (Mettler Toledo DL 50).

The thiosulfate was standardized before titrations for each sampling date. Rates of P_{max} and R ($mmolO_2\ m^{-3}\ h^{-1}$) were calculated as the difference in DO between light and dark bottles (P_{max}), and as the difference in DO between initial and dark bottles respectively (R) (Wetzel and Likens 2000).

2.3.5 Data manipulations

In our data analysis, apart from the analysis of our own data, we analyzed pooled data consisting of three datasets: our own and those obtained from Depew et al. (2006*a*, *b*) and Carignan et al. (2000). Thus, the term "pooled" dataset data used in our Results or Discussion sections will refer to the combination of those three datasets (see Appendix A1). For the inter-site comparisons, the mean value for each of our sites was calculated, with separate means for each year of observation in Hamilton Harbour and Lake Ontario. For literature data (Carignan et al. 2000; Depew et al. 2006*a*, *b*), all the values reported for each specific lake were averaged and considered as one independent data-point. For the data of Depew et al. (2006*b*), only those data that were obtained within a period similar to our sampling season (30 April to 25 September 2002) were taken into consideration.

2.3.6 Statistical methods

All data were $\log_{10}$-transformed before the statistical analyses to comply with the assumptions of normality and homoscedasticity. The ordinary least-squared regressions (Model I) were used for predictive purposes, and reduced major axis regressions (Model II) for the analysis of two dependent variables, with a significance level of 5% ($p \leq 0.05$). The linear regression analysis was performed using SYSTAT statistical software for Windows (Version 10.2). In our correlation analysis we used either partial (PL) or semi-partial (SPL) correlations. The PL correlation is a correlation between dependent variable (DV) and independent variable (IV) after the correlation of other IV(s) are removed from each of the two. The SPL correlation is a correlation between a DV and an IV after removing from the latter what it shares with other IV(s). We used the PL correlation when we wanted to show how much of the DV variance which is not explained by other IV(s) in the model is estimated

by the IV in question. We also used the SPL correlations to indicate the "unique" contribution of the IV and show that it adds an incremental variance in DV above and beyond other IV(s) entered earlier in the equation formula. We also used a Principal Components Analysis (PCA) to visualize the differences between our sampling sites and identify the relationships between metabolic and environmental variables. Principal components were extracted from a correlation matrix based on the untransformed data.

2.4 Results

2.4.1 Physical-chemical variations

In Lake Ontario, the formation of a distinct thermocline was evident by mid June and after that it was maintained at variable depths in 2003 (Fig. 2.2B). The variations in Z_m in 2004 were quite similar to those in 2003 but were slightly more variable with near isothermal conditions in late July-early August 2004. In Hamilton Harbour, a thermal stratification was already observed in mid May but stable stratification with a well-defined permanent thermocline was not established until early June (2003; Fig. 2.3B) or even July (2004). The stratification was stable during the summer with a relatively shallow epilimnion of a few meters, and the pattern in Z_m observed in 2003 (Fig. 2.3B) was similar to that in 2004. The Woods Bay and Georgian Bay sites were always isothermal or nearly so.

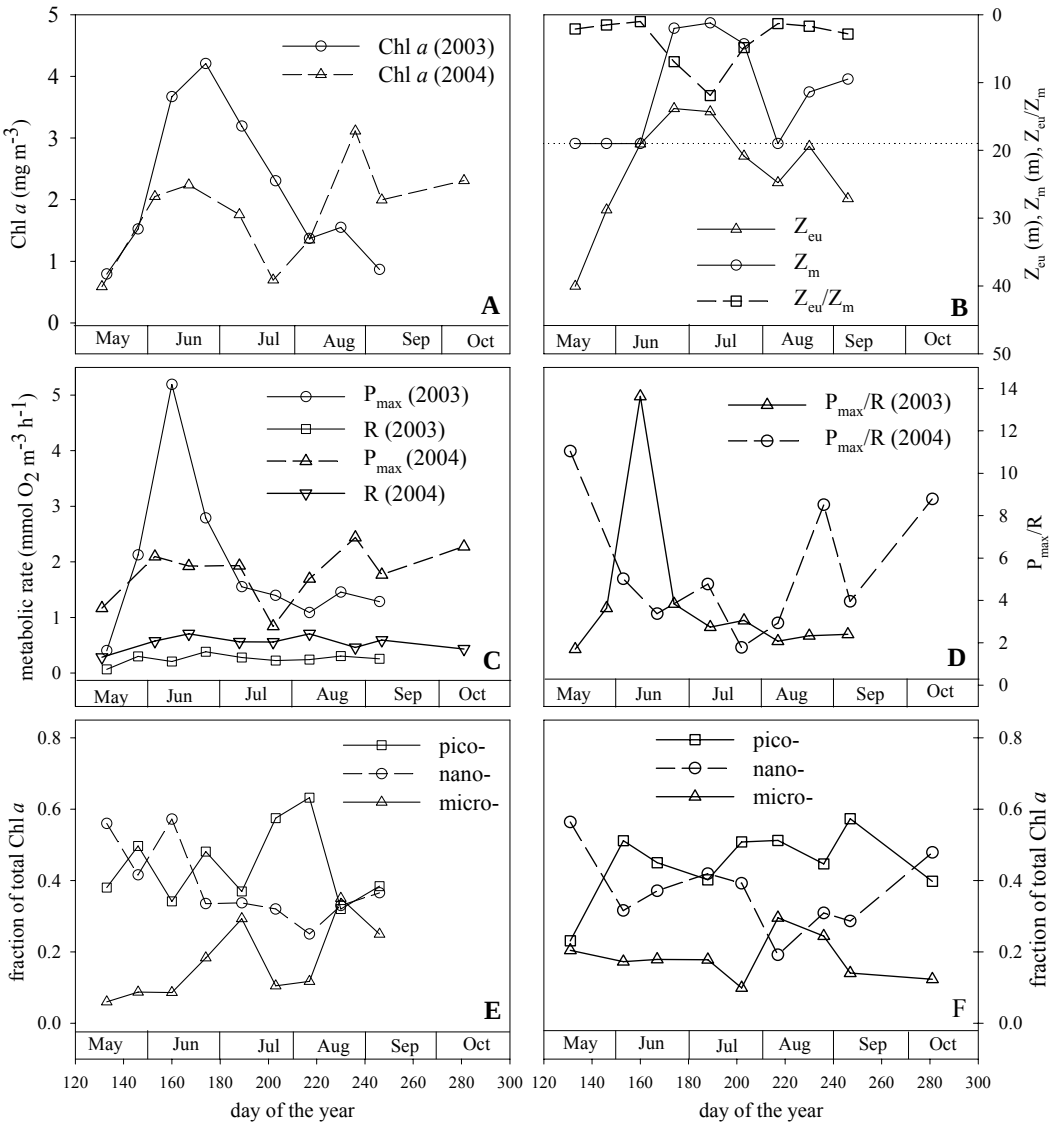

Fig. 2.2 (A) Chl *a* concentrations (mg m^{-3}) in Lake Ontario (LO) in 2003 (circles) and 2004 (triangles); (B) seasonal variations in euphotic depth (Z_{eu}, m) (triangles), mixing depth (Z_m, m) (circles) and Z_{eu}/Z_m ratio (squares) in LO in 2003; dotted line indicates station physical depth; (C) shows rates of light-saturated gross photosynthesis ($P_{max,}$ $mmolO_2$ m^{-3} h^{-1}) in LO in 2003 (circles) and 2004 (triangles up), and community respiration (R, $mmolO_2$ m^{-3} h^{-1}) in 2003 (squares) and 2004 (triangles down); (D) P_{max}/R ratios in LO in 2003 (triangles) and 2004 (circles); (E) and (F) proportions of picoplankton (squares), nanoplankton (circles) and microplankton (triangles) as a ratio of total Chl *a* in LO in 2003 (E) and 2004 (F).

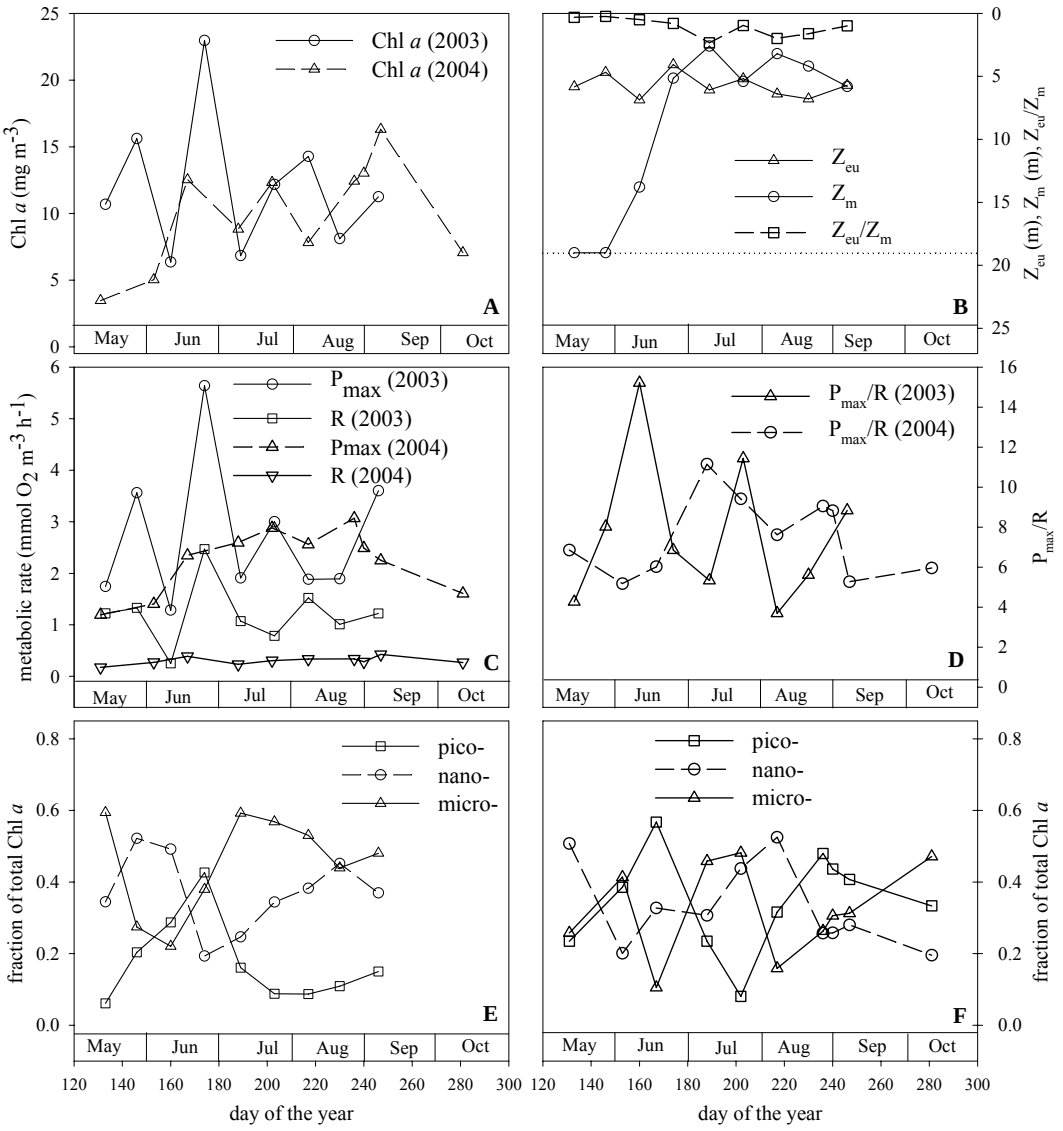

Fig. 2.3 (A) Chl *a* concentrations (mg m^{-3}) in Hamilton Harbour (HH) in 2003 (circles) and 2004 (triangles); (B) seasonal variations in euphotic depth (Z_{eu}, m) (triangles), mixing depth (Z_m, m) (circles) and Z_{eu}/Z_m ratio (squares) in HH in 2003; dotted line indicates station physical depth; (C) rates of light-saturated gross photosynthesis ($P_{max,}$ $mmolO_2$ m^{-3} h^{-1}) in HH in 2003 (circles) and 2004 (triangles up), and community respiration (R, $mmolO_2$ m^{-3} h^{-1}) in 2003 (squares) and 2004 (triangles down); (D) shows P_{max}/R ratios in HH in 2003 (triangles) and 2004 (circles); (E) and (F) proportions of picoplankton (squares), nanoplankton (circles) and microplankton (triangles) as a ratio of total Chl *a* in HH in 2003 (E) and 2004 (F).

The Lake Ontario station had a large Z_{eu} exceeding Z_m and station physical depth (Table 2.2) except at times of peak chlorophyll concentration, and varied similarly in 2003 (Fig. 2.2B) and 2004. Z_{eu} in Hamilton Harbour was only a few meters (Table 2.2) and was only slightly greater than Z_m during much of the summer stratification period in 2003 (Fig. 2.3B) and 2004. Z_{eu} was larger than Z_m (and physical depth) at the Georgian Bay site but was slightly lower than Z_m and physical depth in Woods Bay (Table 2.2). Ratio of Z_{eu} to Z_m in Lake Ontario and Georgian Bay were almost threefold and twofold larger than those in Hamilton Harbour and Woods Bay (Table 2.2).

Mean Chl *a* concentration (mg m^{-3}) measured in Hamilton Harbour was fivefold higher than in Lake Ontario (Table 2.2). Mean Chl *a* at the Hamilton Harbour and Lake Ontario sites did not differ significantly between 2003 and 2004, and patterns of seasonal variation were also similar between years (Fig. 2.2A, 2.3A). In Lake Ontario, Chl *a* showed a distinct peak at the beginning (late June) and the end (late August) of the sampling period with a midsummer minimum (Fig. 2.2A). The seasonal cycle of Chl *a* in Hamilton Harbour was more irregular, with concentrations increasing and decreasing by several mg m^{-3} or more at intervals of about one month (Fig. 2.3A). Compared to those in Lake Ontario, Chl *a* in Georgain Bay was lower while those in Woods Bay was somewhat higher (Table 2.2).

Total phosphorus concentrations (mmol m^{-3}) measured in Hamilton Harbour were in the meso-eutrophic range (Table 2.2) and in Lake Ontario in the oligo-mesotrophic range (Table 2.2), while those in Woods Bay and Georgian Bay were in the oligotrophic range (Table 2.2). DOC concentrations were highest in Woods Bay, followed by Hamilton Harbour, Lake Ontario, and Georgian Bay (Table 2.2).

Table 2.2 Mean chemical and physical properties of sampled water, and mean metabolic rates observed at four study sites in 2003 and 2004. See text for the explanation of the terms used. For each variable we show the range of values and mean value ± standard deviation (shown in brackets). The letter "*n*" stands for the observation number.

	Hamilton Harb. (n = 19)	Lake Ontario (n = 18)	Woods Bay (n = 2)	Georgian Bay (n = 2)
station depth, m	19	19	6	6
Z_{eu}, m	4.1 – 8.2 (6.1 ± 1.0)	13.9 – 40.0 (21.4 ± 6.4)	4.8 – 5.9 (5.4 ± 0.8)	9.6 – 13.0 (11.3 ± 2.4)
Z_m, m	2.6 – 19.0 (8.7 ± 5.6)	1.2 – 19.0 (12.4 ± 6.6)	6 (6)	6 (6)
Z_{eu}/Z_m	0.25 – 2.34 (1.01 ± 0.59)	0.84 – 11.93 (2.81 ± 2.76)	0.80 – 0.98 (0.89 ± 0.13)	1.61 – 2.17 (1.88 ± 0.40)
TP, mmol m^{-3}	0.47- 1.66 (0.949 ± 0.326)	0.16 – 0.50 (0.306 ± 0.085)	0.234 – 0.245 (0.240 ± 0.008)	0.126 – 0.129 (0.127 ± 0.002)
Chl *a*, mg m^{-3}	3.47 – 22.97 (10.901 ± 4.622)	0.59 – 4.21 (1.976 ± 1.038)	1.6 – 5.0 (3.31 ± 2.43)	0.87 – 0.94 (0.90 ± 0.05)
DOC, mg L^{-1}	3.15 – 5.21[1] (4.22 ± 0.35)[1]	2.05 – 2.9[1] (2.60 ± 0.13)[1]	4.1 – 6.4[3] (4.9 ± 1.0)[3]	2.3 – 4.2[3] (2.93 ± 0.87)[3]
picoplankton[2], %	6.14 – 56.75 (26.6 ± 15.4)	23.14 – 63.22 (44.5 ± 10.15)	26.76 – 33.98 (30.4 ± 5.1)	40.31 – 40.93 (40.6 ± 0.4)
nanoplankton[2], %	19.32 – 52.51 (35.0 ± 11.3)	19.16 – 57.20 (37.9 ± 10.8)	41.39 – 60.08 (50.7 ± 13.2)	35.21 – 37.84 (36.5 ± 1.9)
microplankton[2], %	10.53 – 59.40 (38.4 ± 14.6)	6.00 – 35.02 (17.6 ± 8.3)	13.17 – 24.63 (18.9 ± 8.1)	21.23 – 24.48 (22.9 ± 2.3)
P_{max}, mmolO_2 m^{-3} h^{-1}	3.58 ± 16.92 (7.408 ± 3.150)	0.116 – 2.826 (0.939 ± 0.577)	0.917 – 2.077 (1.497 ± 0.820)	0.447 – 0.620 (0.533 ± 0.123)
R, mmolO_2 m^{-3} h^{-1}	0.25 – 2.47 (1.051 ± 0.455)	0.050 – 0.383 (0.224 ± 0.084)	0.242 – 0.366 (0.304 ± 0.088)	0.094 – 0.165 (0.129 ± 0.05)
P_{max}/R	3.71 – 15.21 (7.614 ± 2.855)	1.70 – 13.63 (4.755 ± 3.435)	3.80 – 5.67 (4.73 ± 1.32)	3.76 – 4.76 (4.26 ± 0.70)

[1] accepted from Smith et al. (2004), in brackets: mean ± standard error; [2] as a percent of total Chl *a*; [3] based on four measurements.

2.4.2 Chlorophyll a size distribution

On average, Hamilton Harbour had the largest proportion of large phytoplankton as judged from Chl *a* with almost 40% of total Chl *a* in the microplankton size range (Table 2.2). Pico- and nanoplankton dominated the Chl *a* at all the other sites, with picoplankton forming the largest fraction in Lake Ontario and Georgian Bay, while nanoplankton dominated at Woods Bay (Table 2.2). Size distributions varied across the systems and observational seasons. In Lake Ontario (Fig. 2.2E, F), Chl *a* was mostly dominated by either nano- or picoplankton; while in Hamilton Harbour (Fig. 2.3E, F) all three main size fractions were dominant at times. Overall (n = 41), the proportion of microplankton in the total phytoplankton increased with Chl *a* (p = 0.000) and TP (p = 0.000) while the proportion of picoplankton fell (p = 0.02 and p = 0.006, respectively). The proportion of microplankton was negatively related to both Z_m (p = 0.027) and Z_{eu} (p = 0.000).

2.4.3 Metabolic variations

Principal components analysis helped to visualize the relationships among the key variables such as k_{PAR}, TP, Chl *a*, plankton-size structure, rates of R and net community production (NCP, NCP = P_{max} – R, mmolO_2 m^{-3} h^{-1}) (Fig. 2.4 and 2.5). The loadings on the first principal component (PC1; Table 2.3 and Fig. 2.4) reflected mainly the trophic status variables such as TP and Chl *a*, absolute rates of NCP and R, as well as phytoplankton size distribution (pico- vs. microplankton), while the second principal component (PC2) mainly reflected the size distribution of smaller phytoplankton (pico- vs. nanoplankton). There were basically two sets of data with different domains along PC1 (Fig. 2.5). Hamilton Harbour comprised one set, with generally larger ratios of microplankton to total phytoplankton, higher concentrations of TP and Chl *a*, rates of R and NCP, and larger values of k_{PAR}. The second group comprised Lake Ontario, Georgian Bay and Woods Bay sites, with generally better light penetration and lower values of TP, Chl *a* and metabolic rates, as well as larger proportions of picoplankton. Component loadings in PCA express the rate of change in one variable relative to the others (Table 2.3). This means that for each unit of change in PC1 score changes in Chl *a* and TP

concentrations and rates of R and NCP were similar, although TP changes were slightly smaller. Changes in the microplankton fraction were faster than those of pico- and nanoplankton fractions along the gradient of increasing TP and Chl *a* concentrations, with the microplankton fraction increasing and the fraction of picoplankton decreasing. As for PC2, for each unit in change in PC2 score, the changes in P_{max}/R and the proportion of picoplankton were almost identical but opposite in the direction.

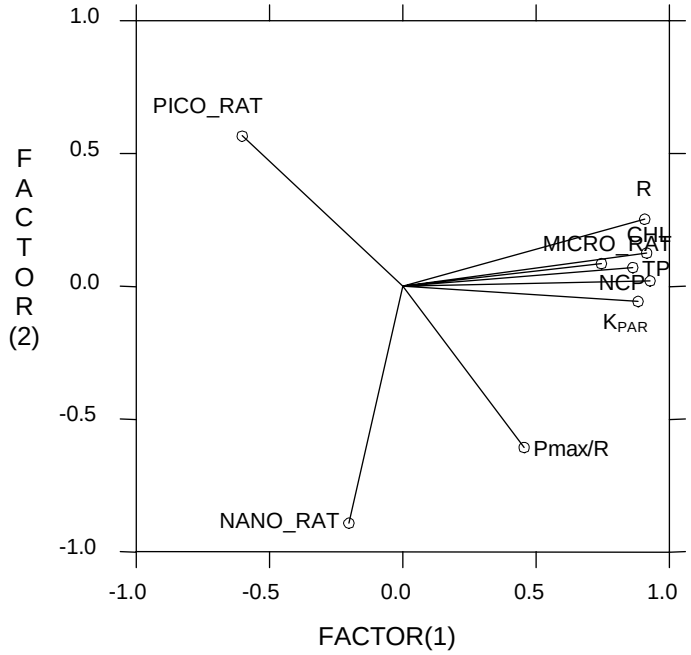

Fig. 2.4 Factors loadings plot for the PCA that includes the following variables: net community production (NCP, NCP = P_{max} - R), community respiration (R), P_{max}/R ratio, Chl *a*, TP, light attenuation coefficient (k_{PAR}), and proportions of picoplankton (PICO_RAT), nanoplankton (NANO_RAT) and microplankton (MICRO_RAT).

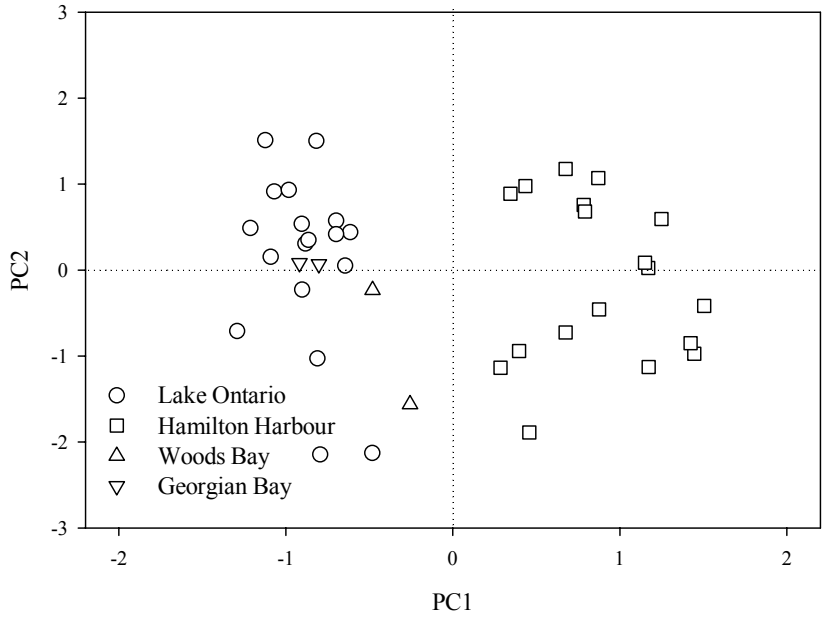

Fig. 2.5 Principal component ordination (scatter plot of principal component scores) of sampling stations: Lake Ontario (open circles), Hamilton Harbour (squares), Woods Bay (triangles up) and Georgian Bay (triangles down).

Table 2.3 Components loadings derived from the principal components analysis. Components were extracted from a correlation matrix based on the raw data. Results are shown for non-rotated loading matrix.

Variable	PC 1	PC 2
Chl *a*	0.914	0.125
TP	0.862	0.071
k_{PAR}	0.881	-0.057
picoplankton (fraction of total Chl *a*)	-0.604	0.567
nanoplankton (fraction of total Chl *a*)	-0.202	-0.892
microplankton (fraction of total Chl *a*)	0.745	0.087
R	0.906	0.253
NCP	0.927	0.020
P_{max}/R	0.454	-0.607
eigenvalue	5.203	1.581
% variance	57.81	17.57

Table 2.4 Linear regression models using $\log_{10}$-transformed data and relating rates of respiration, gross photosynthesis and their ratio to different water property characteristics. For the multiple regressions, the independent variables are listed in a decreasing order of explained variance. The ± symbol stands for the standard errors of the regression parameters. The following abbreviations are used: the coefficient of determination (r^2), the standard error of estimate (*SEE*), the p-value (p), and a number of observations (n). The following data were used: our own individual data (Models 1-6); pooled data using individual measurements (Models 7-8); pooled data using site-averaged measurements (Models 9-17).

Model	Dependent variable	Regression	r^2	*SEE*	p	n
1	P_{max}	-0.309±0.044 + 1.103±0.059[Chl *a*]	0.898	0.170	0.000	41
2	P_{max}	-0.25±0.05 + 1.04±0.06[Chl *a*] – 0.21±0.08[Z_{eu}/Z_m]	0.915	0.158	0.000	41
3	R	-0.852±0.046 + 0.803±0.062[Chl *a*]	0.810	0.178	0.000	41
4	R	-1.36±0.22 + 0.53±0.10[Chl *a*] + 0.64±0.18[T] + 0.34±0.14[TP]	0.870	0.151	0.000	41
5	R	-0.61±0.03 + 0.6±0.05[P_{max}]	0.804	0.181	0.000	41
5**	R	-0.64±0.04 + 0.77±0.06[P_{max}]				
6	P_{max}/R	0.543±0.05 + 0.30±0.07[Chl *a*]	0.312	0.204	0.000	41
7	P_{max}/R	0.75±0.02 – 0.45±0.07[Z_{eu}/Z_m]	0.236	0.229	0.000	126
8	P_{max}/R	0.43±0.08 + 0.37±0.07[Chl *a*] – 0.35±0.08[Z_{eu}/Z_m] – 0.30±0.10[TP]	0.361	0.210	0.000	126
9	P_{max}	-0.395±0.047 + 1.040±0.091[Chl *a*]	0.884	0.124	0.000	19
10	P_{max}	0.731±0.071 + 1.166±0.106[TP]	0.876	0.128	0.000	19
11	R	-0.969±0.041 + 0.857±0.081[Chl *a*]	0.869	0.110	0.000	19
12	R	-0.035±0.059 + 0.969±0.088 [TP]	0.877	0.106	0.000	19
13	P_{max}	0.149±0.193* + 0.570±0.180[Chl a] + 0.584±0.203[TP]	0.924	0.104	0.000	19
14	R	-0.475±0.169 + 0.531±0.177[TP] + 0.430±0.158[Chl *a*]	0.916	0.091	0.000	19
15	P_{max}/R	0.82±0.04 – 0.37±0.12[Z_{eu}/Z_m]	0.375	0.08	0.005	19
16	R/DOC	-0.73±0.08 + 0.75 ± 0.12[TP]	0.708	0.141	0.000	19
17	R	-0.64±0.02 + 0.81±0.05[P_{max}]	0.951	0.067	0.000	19

* not significant at the $p \leq 0.05$ level; ** reduced major axis model regression (Model II)

Rates of P_{max} ($mmolO_2\ m^{-3}\ h^{-1}$) in Hamilton Harbour were significantly different and much higher than those measured in Lake Ontario (Table 2.2). In these two systems, P_{max} appeared to be related to the dynamics of Chl *a*, with maxima observed during the peaks in Chl *a* biomass or during the last sampling time immediately before the major increase in biomass (Fig. 2.2A and 2.2C; 2.3A and 2.3C). Mean P_{max} in Woods Bay was significantly higher than in Georgian Bay and somewhat higher than in Lake Ontario (Table 2.2). Overall (n = 41), P_{max} had strong positive correlations with either Chl *a* (model 1, Table 2.4; Fig. 2.6A) or TP ($p < 0.000$, $R^2 = 0.693$; Fig 2.6B). However, a multiple regression containing Chl *a*, TP, Z_{eu}/Z_m as the independent variables showed that only Chl *a*, and Z_{eu}/Z_m were significant, and they could explain almost 92% of the variation (model 2, Table 2.4). Rates of P_{max} were also positively correlated with the proportion of microplankton ($p = 0.000$, $R^2 = 0.375$, n = 41) and negatively to the proportion of picoplankton ($p = 0.001$, n = 41). However, partial correlation analysis between P_{max} and phytoplankton size-distribution when controlling for Chl *a* showed that only the proportion of microplankton was weakly but significantly correlated with P_{max} ($p = 0.041$, n = 41). The proportion of microplankton explained significant additional variation when added as a predictor variable to the multiple regression model containing Chl *a* and Z_{eu}/Z_m. Semi-partial correlation showed that its share of the explained variance (less than 2%) was small compared to Chl *a* (42%) but was comparable to Z_{eu}/Z_m.

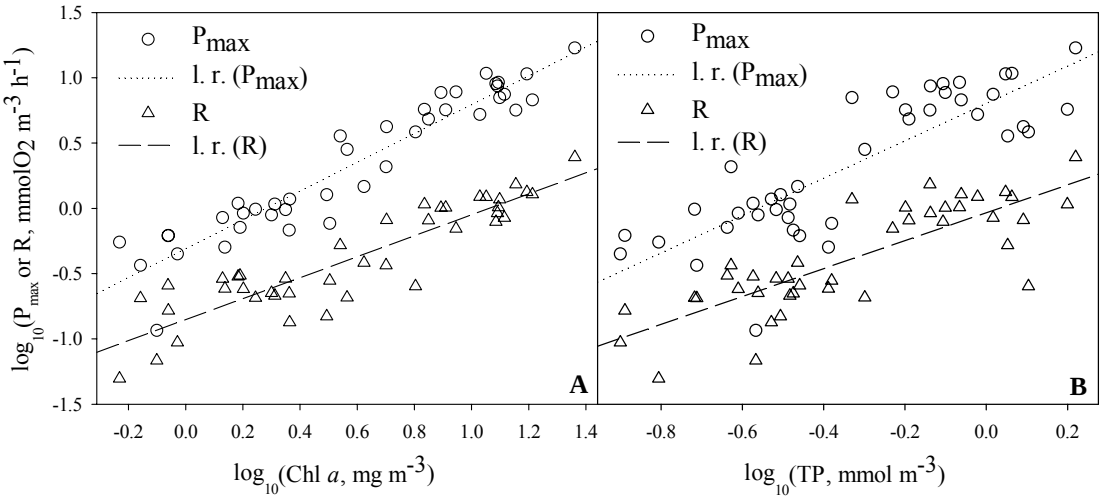

Fig. 2.6 The gross photosynthesis at light saturation (P_{max}, $mmolO_2$ m^{-3} h^{-1}) and community respiration (R, $mmolO_2$ m^{-3} h^{-1}) as functions of Chl *a* concentration (mg m^{-3}) (A) and TP concentrations (mmol m^{-3}) (B). A dotted line is a linear regression line of P_{max} [l.r. (P_{max})], and a dashed line is a linear regression line of R [l.r. (R)] on either Chl *a* or TP.

Average community respiration (R, $mmolO_2$ m^{-3} h^{-1}) as a percent of P_{max} was least in Hamilton Harbour (17%), most in Lake Ontario and Georgian Bay (24%) and intermediate in Woods Bay (20%). The average volumetric R ranged nearly one order of magnitude from its observed maximum in Hamilton Harbour to the minimum in Georgian Bay (Table 2.2). Overall, R had significant positive bivariate correlations with Chl *a* (model 3, Table 2.4; see also Fig. 2.6A), TP (p = 0.000, R^2 = 0.664; Fig 2.6B), T and the proportion of microplankton (p = 0.000, R^2 = 0.384). A multiple regression containing Chl *a*, TP and T as the independent variables (model 4, Table 2.4) explained almost 87% of the variability in R. Respiration was strongly and positively related to P_{max} (models 5 and 5**, Table 2.4; Fig 2.7A).

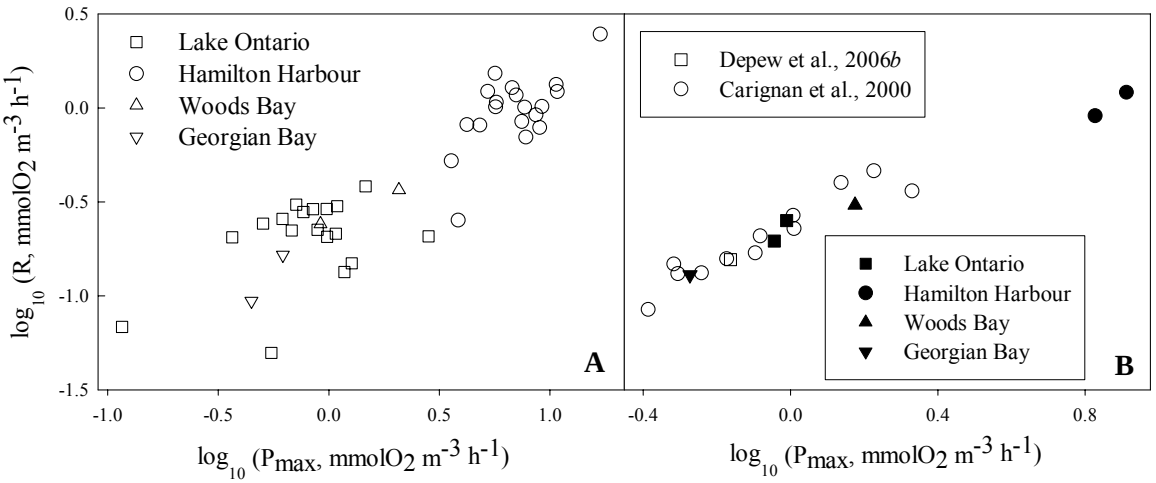

Fig. 2.7 The relationship between P_{max} and R. (A) shows individual data: Hamilton Harbour (circles), Lake Ontario (squares), Woods Bay (triangles up) and Georgian Bay (triangles down); (B) shows site-averaged data: Hamilton Harbour (solid circles), Lake Ontario (solid squares), Woods Bay (solid triangles up), Georgian Bay (solid triangles down), Carignan et al. (2000) data (open circles), Depew et al. (2006*b*) data (open square).

The linear regressions of P_{max} and R on Chl *a* (models 1 and 3, Table 2.4) had significantly different slopes, and the re-analysis of those models showed that P_{max} and R equal respectively to $10^{-0.309}$[Chl *a*]$^{1.103}$ and $10^{-0.852}$[Chl *a*]$^{0.803}$. These two functions give an expected functional dependence of P_{max}/R on Chl *a*: 3.49[Chl *a*]$^{0.3}$.

2.4.4 Variations in metabolic rates ratios (individual observations)

PCA showed that ratios of P_{max}/R were related almost equally to both principal components (Table 2.3) with a near 45° vector (Fig. 2.4) and therefore reflecting the importance of both trophic status and phytoplankton size distribution. Although loadings of P_{max}/R were similar on each component, PC1 explained 58% of the variance and PC2 only 18%, pointing to a larger influence from trophic status variables and cell-size structure than from phytoplankton size distribution alone.

Ratios of P_{max}/R in Hamilton Harbour were approximately 60% higher than in other three systems (Table 2.2). Dynamics of P_{max}/R in Lake Ontario and Hamilton Harbour were quite variable (Fig. 2.2D, 2.3D) with the maximum values usually observed during an algal bloom or the last

sampling time immediately before a major observed increase of Chl *a*. Overall (n = 41), ratios of P_{max}/R were positively correlated (bivariate linear regressions) with Chl *a* (model 6, Table 2.4; Fig. 2.8A, 2.9A), TP (p = 0.002), proportion of large cells (sum of nano- and microplankton) in the total phytoplankton (p = 0.005), and negatively correlated with the ratios of Z_{eu}/Z_m (p = 0.008; Fig. 2.9B) and the proportion of picoplankton (p = 0.033). Re-analysis of model 6 (Table 2.4), that is an actual regression of P_{max}/R ratio on Chl *a*, gives an equation $3.49[\text{Chl } a]^{0.3}$, exactly the same formula as a functional dependence of P_{max}/R on Chl *a* calculated earlier by dividing P_{max} by R. Multiple regression analysis of our own data showed that amongst Chl *a*, TP and Z_{eu}/Z_m only Chl *a* was a significant predictor. Of the Chl *a* size fractions, only the proportion of nanoplankton added significantly to the prediction of P_{max}/R achieved by Chl *a* but the unique contribution of nanoplankton towards predicting P_{max}/R was much smaller than that of Chl *a* (9% and 37% respectively).

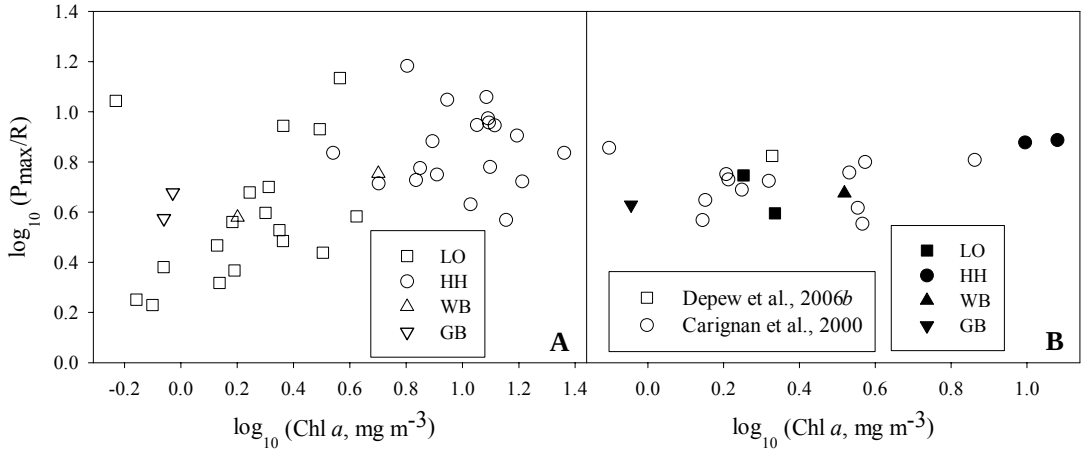

Fig. 2.8 The relationship between P_{max}/R and Chl *a*: (A) shows individual data: Hamilton Harbour (circles), Lake Ontario (squares), Woods Bay (triangles up) and Georgian Bay (triangles down); (B) shows site-averaged data: Hamilton Harbour (solid circles), Lake Ontario (solid squares), Woods Bay (solid triangles up), Georgian bay (solid triangles down), Carignan et al. (2000) data (open circles), Depew et al. (2006*b*) data (open square).

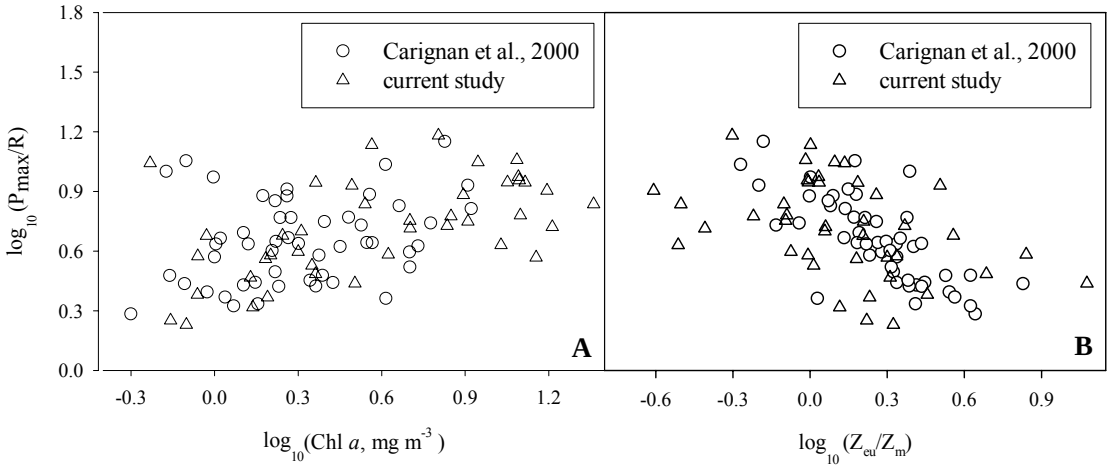

Fig. 2.9 The relationship between individual P_{max}/R and Chl *a* (A) and Z_{eu}/Z_m (B) in two studies: Carignan et al. (2000) (triangles) and the present study (circles).

Statistically significant correlations between P_{max}/R and either Chl *a*, TP or Z_{eu}/Z_m of similar directions have been found in some previous studies (Carignan et al. 2000; Depew et al. 2006*b*) and the literature data were added to ours to broaden the range of comparison (e.g. Fig. 2.9A, B). In this new dataset, Chl *a* concentrations (mg m^{-3}) ranged from 0.5 to 23.0 with a mean value of 3.6 ± 4 (± st. dev.), TP (mmol m^{-3}) ranged from 0.07 to 1.66 with the mean of 0.37 ± 0.3, and Z_{eu}/Z_m ranged from 0.25 to 11.93 with the mean value of 1.85 ± 1.44. The pooled dataset (n = 126) confirmed that P_{max}/R was positively related to either Chl *a* or TP (p = 0.000 and p = 0.009, respectively) and negatively to Z_{eu}/Z_m (model 7; Table 2.4). In this larger dataset, multiple regression showed that Chl *a*, TP and Z_{eu}/Z_m (model 8, Table 2.4) all exerted significant effects in the presence of others. P_{max}/R correlated positively with Chl *a* and negatively with TP and Z_{eu}/Z_m, and Fig. 2.10A illustrates how well these three variables can predict P_{max}/R using the multiple regression of model 8 (Table 2.4). Semi-partial correlation analysis showed that the unique contribution towards predicting P_{max}/R were 13.9% (Chl *a*), 11.2% (Z_{eu}/Z_m) and 5% (TP) for the three predictor variables.

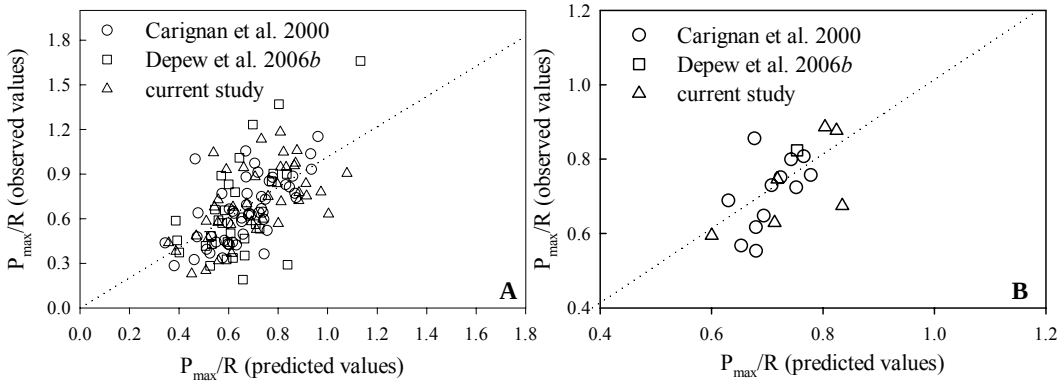

Fig. 2.10 (A) shows observed vs predicted values of P_{max}/R by model 8 (Table 2.4) for the individual data from three studies: Carignan et al. (2000) (circles), Depew et al. (2006*b*) (squares), and the present study (triangles up); (B) shows observed vs predicted values of P_{max}/R by model 15 (Table 2.4) for the site averaged data from three studies, Carignan et al. (2000) (circles), Depew et al. (2006*b*) (squares), and the present study (triangles down).

We did not measure DOC routinely in Lake Ontario and Hamilton Harbour and were not able to analyze its effect on individual metabolic rates ratios in our own data, however the analysis of Carignan et al. (2000) data has shown that DOC failed to explain a significant portion of variation in individual P_{max}/R ratios. Moreover, their DOC specific community respiration rates (community respiration per unit of DOC) were not correlated with either DOC or Chl *a* but did correlate positively with TP concentrations ($p = 0.011$, $n = 51$). However, in their data, it was found that DOC correlates negatively with Z_{eu}/Z_m ($p = 0.006$, $n = 51$)

2.4.5 Variations in site-averaged rates of P_{max} and R and their ratios (inter-site comparisons)

Our site average rates of P_{max}, R and P_{max}/R ratios were significantly ($p < 0.05$) positively correlated with either Chl *a*, TP, or the proportion of microplankton in the total phytoplankton, despite the small sample size (6 sites if 2003 and 2004 are treated independently for Hamilton Harbour and Lake Ontario). In the pooled dataset ($n = 19$), P_{max} and R had strong positive bivariate correlations with Chl *a* and TP (models 9, 10, 11 and 12; Table 2.4) or were related to both of them in multiple regression (models 13 and 14; Table 2.4). Mean P_{max}/R ratios for each site were significantly (and negatively)

correlated with Z_{eu}/Z_m (model 15, Table 2.4) and positively with TP ($p = 0.043$, $n = 19$). A correlation between P_{max}/R and Chl *a* in the pooled data ($p = 0.01$, $n = 18$; Fig. 2.8B) was only obtained if one data point in the Carignan et al. (2000) data with the extreme value (lake Chertsey that had the lowest Chl *a* and the highest P_{max}/R at the same time) is dropped out. The bivariate correlation between P_{max}/R and Chl *a* can also be obtained ($p = 0.01$, $n = 22$) if one can extend the range of Chl *a* values in our pooled dataset by adding data from three eutrophic bays of Lake Victoria (Silsbe 2004). Multiple regression analysis showed that Chl *a*, TP, and DOC did increase the percentage of explained variation compared to Z_{eu}/Z_m alone but the gain was not sufficient to make any of the additional predictor variables significant. Thus, P_{max}/R can be predicted from Z_{eu}/Z_m alone (Fig. 2.10B).

DOC was not correlated with P_{max}/R in Carignan et al. (2000) and in the pooled dataset either. DOC also failed to add significantly to the explanation of either P_{max} or R rates when controlling for both Chl *a* and TP. Despite the fact that average rates of R exhibited a weak but statistically significant correlation with DOC in Carignan et al. (2000) data ($p = 0.025$; $R^2 = 0.408$; $n = 12$) and in our pooled dataset ($p = 0.043$; $R^2 = 0.257$; $n = 19$), this was due to the co-linearity between DOC and either Chl *a* or TP observed in both datasets. The relationships between R and DOC become insignificant when controlled for the effects of either Chl *a*, TP, or both Chl *a* and TP. Also, in both datasets, average DOC specific respiration rates were not correlated with DOC but were related to TP (Carignan et al. 2000 data: $p = 0.033$, $n = 12$; pooled dataset: model 16, Table 2.4). In our pooled dataset ($n = 19$), average rates of R were correlated with the proxies of the trophic status: Chl *a* ($R^2 = 0.869$) or TP ($R^2 = 0.877$) or with both Chl *a* and TP ($R^2 = 0.916$). There was a strong correlation between average rates of R and P_{max} in the Carignan et al (2000) data ($R^2 = 0.898$, $n = 12$) and in the pooled data ($R^2 = 0.951$; see model 17, Table 2.4).

2.5 Discussion

Our systems, even without literature additions, were widely variable in physical structure (fully mixed to shallowly stratified), water transparency (high to low transparency), Chl *a* and TP concentrations (oligotrophic to moderately eutrophic) and Chl *a* plankton size structure (micro-, nano- and pico-fractions were all dominant at times). Metabolic rates and ratios varied widely, and the total range of P_{max}/R was almost one order of magnitude and the range of P_{max} and R was even greater. PCA showed that algal biomass (Chl *a*), TP, and the proportions of larger (microplankton) and smaller (picoplankton) phytoplankton were the most important variables associated with the net community production (NCP) and P_{max}/R. The relative importance of smaller phytoplankton, proportions of nanoplankton and picoplankton exerted a secondary effect. The nature of the effects was consistent with some previous findings that an elevated trophic status as indexed by higher Chl *a* and TP (del Giorgio and Peters 1994) and a predominance of larger algal size fractions (Smith and Kemp 2001) are associated not only with higher production rates but also higher production/respiration balance. If there is a differential partitioning of gross production and respiration between smaller cells (production < respiration) and larger cells (production > respiration) as it was reported (Williams 1981; Blight et al. 1995), then pico- and microplankton should have respectively low and high P_{max}/R ratios. The present study seems to be the first demonstration for lakes that P_{max}/R is dependent on size distribution of primary producers.

The individual P_{max}/R ratios were higher in eutrophic Hamilton Harbour than those in our oligotrophic sites. There are two reasons why Hamilton Harbour has higher P_{max}/R ratios. The first reason is because of its structure of phytoplankton community that had the lowest proportion of picoplankton and the largest proportion of microplankton. If light saturated rates of photosynthesis respond to intracellular quotas of nutrients (Senft 1978; Raven 1997) and larger phytoplankton cells have an advantage in nutrient storing capacity over the smaller cells (Stolte and Riegman 1995), then microplankton cells should have higher photosynthetic efficiency than the smaller cells (Williams

1981; Blight et al. 1995). The second reason why P_{max}/R ratios were high in Hamilton Harbour is because of the lower bacteria to phytoplankton biomass ratio in the harbour. The bacteria to phytoplankton biomass ratio is lower in eutrophic waters than in oligotrophic waters (Biddanda et al. 2001), and contribution of bacteria to total planktonic respiration is the lowest in eutrophic waters and increases along the decreasing productivity gradient (Biddanda et al. 1994, 2001).

Predictive regression relationships between individual P_{max} and Chl *a* and between R and Chl *a* were very strong, and almost as strong with TP. This again supports the previous findings of the close association between trophic status and metabolic rates (del Giorgio and Peters 1994; Krause-Jensen and Sand-Jensen 1998; Pace and Prairie 2005). The relationships with Chl *a* were significantly different for P_{max} and R, and when combined they predicted that P_{max}/R should be an increasing power function of Chl *a*. This was confirmed by the direct regression of P_{max}/R on Chl *a*. The dependence of P_{max}/R on Chl *a* might be understood as reflecting possibly greater efficiency of the algae themselves or a decreased activity of heterotrophic relative to autotrophic organisms, possibly due to a decreased proportion of allochthonous contributions to respiration in more eutrophic systems. It might also suggest a looser coupling of production and consumption at the scale of individual observations. In a coupled system the rates of production and consumption are balanced, while in an uncoupled or looser coupled systems those rates are different resulting in the accumulation or loss of phytoplankton biomass. Phytoplankton employ a number of mechanisms that help them temporarily escape consumption (Strom 2002). Grazers are coupled with their phytoplankton prey and change their feeding behaviour in response to such defense mechanisms, but they need some time for the adjustment (Calado et al. 1998). Also, event driven changes in algal growth rates caused by sudden changes in physical environment or nutrient availability may not always be balanced by an immediate corresponding change in grazing rates because the later depends not only on the feeding rates of each single grazer (functional response) but also on the grazers biomass (numerical response) (Strom 2002) and time is needed for biomass to catch up with the changes. All these may uncouple production from

consumption leading to the temporal variability of algal biomass as depicted on Fig. 2.2A and 2.3A, e.g. algal blooms (Fig. 2.2A) or abrupt changes in Chl *a* (Fig. 2.3A).

There was a strong relationship between R and P_{max} in my data too, and the former can be predicted from the latter by a power relationship with exponent less than unity. All these observations support previous suggestions that higher trophic status (Chl *a*, TP and absolute production rates) should be associated with higher production/respiration balance. Introduction of additional data from the literature (Carignan et al. 2000 and Depew et al. 2006*b*) supported the conclusions from my data.

Although significant, the relationships between P_{max}/R and Chl *a* had low coefficient of determination (R^2), suggesting additional factors were important. Using multiple regression on the pooled data set, we found evidence that Z_{eu}/Z_m and TP together with Chl *a* had significant influences. The nature of the partial relationships with TP and Z_{eu}/Z_m support previous suggestions about how phosphorus might stimulate bacterial respiration (Roberts and Howarth 2006; Farjalla et al. 2006) and increase degradability of DOC (Schindler et al. 1992), and how Z_{eu}/Z_m might select for phytoplankton with different P_{max}/R efficiencies (Harris 1978, Cushing 1989). The dependence of P_{max}/R on Z_{eu}/Z_m is of particular interest as most of the recent plankton metabolic studies overlooked this important variable. The ratio of Z_{eu}/Z_m is the proportion of the mixed layer depth which sustains photosynthesis, and it has been demonstrated that variations in this ratio have a powerful selection pressure on primary producers growing in the mixed layer and influence their population dynamics (e.g. Harris et al. 1980; Horn and Paul 1984; Alpine and Cloern 1988). It has also been previously shown that the balance between P_{max} and R (e.g. R/P_{max} ratio) is taxon specific and varies amongst major algal groups (Geider and Osborne 1989; Langdon 1992). Therefore, Z_{eu}/Z_m must determine the conditions for the survival and abundance of certain algal groups with different P_{max}/R efficiency. The mechanism underlying the selective force of Z_{eu}/Z_m may be the differences in specific maintenance respiration rates of each algal group (R/P_{max}) and consequent differences in the average irradiance level in the epilimnion needed to sustain algal growth (Harris 1978; Hecky and Guildford 1984; Cushing 1989).

Even the multiple regression model consisting of Chl *a*, TP and Z_{eu}/Z_m still explained only 36% of the variation in P_{max}/R (model 8, Table 2.4), suggesting either that P_{max}/R is hard to measure consistently or that the ratio is complex and there are more factors involved. One of those factors might be DOC, for which we did not have individual values, but at least in Carignan et al. (2000) data it did not seem to be an important predictor.

The instantaneous values of P_{max}/R will reflect multiple influences including transitory imbalances between producers and consumers and it is not surprising they are hard to predict with high precision. Using site-averaged data and the pooled data set we were able to test the relationships governing season average behaviour. These showed an excellent relationship between R and P_{max}, in the form of power relationship with exponent less than unity (model 17, Table 2.4). R and P_{max} both increased with Chl *a* and TP, but unlike individual data, their slopes of P_{max} and R on either Chl *a* or TP were not significantly different suggesting a tighter coupling between P_{max} and R. The P_{max} vs. Chl *a* and R vs. Chl *a* relationships predict that P_{max}/R should be slowly increasing along the productivity gradient as the latter is a power function of Chl *a* with an exponent less than unity (0.183). The observed P_{max}/R vs Chl *a* did have the right slope but was only significant if one point was excluded and even then the relationship was weak. Instead, the P_{max}/R ratio was most strongly related to Z_{eu}/Z_m. Neither Chl *a*, TP or DOC explained significant additional variation. This may suggest that on the larger scale (seasonal), the succession of phytoplankton and, therefore, algal taxonomic properties seem to be more powerful than the lake trophy effect in determining P_{max}/R. Although the relationship with Z_{eu}/Z_m did not have a large R^2, it was highly significant and provides the first wide scale support for the idea that the physical environment does select for phytoplankton communities of varying efficiency as expressed by P_{max}/R (Harris 1978). This selection may well operate at least partly through selection for plankton size as our own site-averaged data, despite their small number (n = 6), showed that the rates of P_{max}, R and their ratios (P_{max}/R) had statistically significant positive

correlations with the proportion of microplankton in the total phytoplankton, but we lack enough data to test this at the season average, inter-system scale with the larger sample size.

The failure to observe a strong P_{max}/R vs Chl *a* relationship for site-averaged data may simply reflect the more limited range of the data compared to individual data. Consideration of data from even more eutrophic systems (e.g. Lake Victoria; Silsbe 2004) and the inclusion of these data into our analysis support this idea. Averaged data also show tighter coupling between P_{max} and R compared to individual ones, suggesting the relationship in the individual data is somewhat dependent on episodes of uncoupling (e.g. algal bloom or clear water phase), and there was certainly evidence of this in the seasonal variation at our main study sites; while the production (P_{max}) and consumption (R) integrated over the entire season are more tightly related to each another, e.g. phytoplankton blooms may escape consumers that consequently catch up later when the blooms subside (algae are mostly eaten not exported). Higher trophic status and productivity were associated with higher P_{max}/R in our data and might be expected based on the literature, but over a limited range of Chl *a* and on season average the effect may not be strong.

Over the range of conditions covered here, there were no significant evidence that DOC was correlated with P_{max}, R or their ratio if the effects of Chl *a* and TP were accounted for by multiple regression. Also, an observed tight relationship between site-averaged rates of consumption (R) and production (P_{max}) suggests that the former is based mostly on the autochthonous carbon production. Thus, there were no evidence that DOC and, by inference, allochthonous inputs were having any strong influence on metabolism. This is consistent with some other previous studies demonstrating the lack of correlation between DOC and total plankton respiration (e.g. del Giorgio and Peters 1994; Biddanda et al. 1994; Cimbrelis and Kalff 1998). On the other hand, there are studies suggesting that DOC is a significant predictor of R when considered alone or in multiple regression together with Chl *a* (e. g. Pace and Prairie 2005); however, those studies did not control for TP and the significant effect of DOC in their data might be due to either co-linearity between DOC and TP or due to large

proportion of sites with high TP and moderate DOC concentrations. Under high phosphorus concentration bacterioplankton can become substrate limited (DeBruyn et al. 2004). Moreover, we found that the DOC-specific R was strongly related to TP. Also, in the multiple regression of R on both Chl *a* and TP for either individual or site average data, the latter was able to add significantly to the predictions of R already achieved by Chl *a* and the direction of its effect was similar to that of Chl *a*. This suggests that productivity (Chl *a*) and phosphorus (P) supply exert positive but somewhat separate effect on plankton metabolism. Bacteria have higher P to carbon content than that of either autochthonous or allochthonous carbon (Fagerbakke et al. 1996), and it could be that higher P concentrations help bacteria to increase a DOC utilization (Caron et al. 2000; Roberts and Howarth 2006) and thus stimulate bacterial respiration (Roberts and Howarth 2006; Farjalla et al. 2006). The dependence of DOC-specific R on TP rather than on DOC also means that in our range of lakes the bacterioplankton are not limited by DOC but P, and suggests (i) an increasing role of bacterial respiration along the increasing production gradient, (ii) DOC is present in concentrations higher than required to meet the bacterial demand and its utilization is limited by low availability of P, and (iii) Bacterial respiration proceeds at its highest rate determined by nutrients and particularly P and not DOC. Over a wider range of DOC and TP the situation might differ, as indeed the literature suggests (Hanson et al. 2003; Pace and Prairie 2005) but for low to moderate DOC waters it does not appear that DOC and allochthonous subsidies are very important to the plankton respiration and autotrophic-heterotrohic potential.

In the mostly oligotrophic-mesotrophic range covered here, autotrophic-heterotrophic potential (P_{max}/R) seems to be under mainly physical control on the seasonal time scale. Climate change may alter the physical environment affecting water temperatures, transparency and mixing depths in lakes (e.g. Fee et al. 1996) and is likely to cause systematic changes in P_{max}/R. However, it seems that changes in Z_{eu} and Z_m will have a greater direct impact on P_{max}/R than expected changes in water temperature (T). Our own data suggest that P_{max}/R is independent of T because both P_{max} and R

are correlated positively with T (p = 0.001 and p = 0.000 respectively, n = 41) and their rate of increase with increasing incubation T are very similar. However, we did observe a significant positive correlation between *in situ* T and the ratios of microplankton (p = 0.001, n = 41) in the total plankton and no correlation between *in situ* T and the proportions of picoplankton. Thus, future warming of the SML will likely affect the phytoplankton size-distribution favoring the increased proportion of large cells (microplankton) that have larger export potential than the smaller cells. Increased water stability and reduced vertical mixing in lakes due to warmer temperatures will affect the Z_{eu}/Z_m ratio and have a positive effect on P_{max}/R (see model 15, Table 2.4). A high P_{max}/R implies the potential for production to largely outstrip consumption in the most favorable part of the water column, generating a surplus for export, storage and utilization elsewhere in the water column. Depending on the physical structure of water column, this may promote heterogeneity of conditions for consumers, loading of organic matter to the lake hypolimnia, and other important ecological effects. The negative correlation between P_{max}/R and Z_{eu}/Z_m observed here suggests that inter-system variation of the two variables may have offsetting effects on the PMB_m of the SML, with higher P_{max}/R offset by mixing of the production through a deeper and less well illuminated SML. To test this requires additional measurements to define the depth-integrated rates of production, and is the subject of a following Chapter.

Chapter 3

Balance between plankton photosynthesis and respiration in Great Lakes sites of contrasting trophic status and dissolved organic carbon concentration.

3.1 Abstract

Planktonic metabolic balance (PMB_m) of the surface mixed layer was calculated as the ratio of areal rates of gross photosynthesis (AGP) to community respiration (AR), and estimated in the summertime for four Laurentian Great Lakes coastal sites of contrasting physical, optical and nutrient regime: western Lake Ontario, Hamilton Harbour, Georgian Bay and Woods Bay. The applied methods were oxygen light-and-dark bottle and ^{14}C methods. It was observed that PMB_m was net autotrophic in most of the cases (73% of the observations). Within- and inter-system variations in PMB_m were heavily dependent on both a ratio of light-saturated photosynthesis to community respiration (P_{max}/R) and a ratio of euphotic to mixing depths (Z_{eu}/Z_m). It was found that although dissolved organic carbon (DOC) was an important predictor of metabolic balance in lakes, the physical environment, biomass, and total phosphorus (TP) concentrations can be equally or more important to metabolic balance on various time scales. While short-term (individual) within-system variations in PMB_m were driven by the interplay of chlorophyll *a* (Chl *a*), TP and Z_{eu}/Z_m ratio, its inter-lake long-term (site-averaged) variability had a different behaviour. Average ratios of AGP/AR were dependent only on DOC or single physical parameters such as Z_{eu} or Z_m, while PMB_m determined as the ratio between average AGP and average AR was controlled by the joint effect of DOC, TP and Chl *a*. DOC affected average AGP/AR ratios primarily via its control over the light environment; it had a depressing effect on AGP rates but did not control rates of AR. ^{14}C method when performed with short incubations and acidification technique may provide estimates that are close to gross photosynthesis.

3.2 Introduction

Recent work has shown that heterotrophic metabolic balance is common in lakes, especially where dissolved organic carbon (DOC) is high, suggesting an important role for allochthonous subsidy (Cole et al. 2000; Prairie et al. 2002; Hanson et al. 2003). The tendency to heterotrophy may also decrease as trophic status increases (Carignan et al. 2000; Wetzel 1992) but over the oligotrophic to mesotrophic range, the influence of DOC seems greater (Prairie et al. 2002). The physical environment, particularly the optical and mixing depths, have also been considered important determinants of metabolic balance (Sverdrup and Allen 1936; Harris 1978; Cushing 1989).

Large, oligo-mesotrophic, lakes with relatively low DOC, such as the Laurentian Great Lakes (LGL), might be expected to tend towards autotrophy because of the low DOC, long water renewal times, and weaker coupling to the terrestrial catchments. Understanding of plankton processes in the LGL has emphasized mostly autochthonous processes, with phytoplankton production as the foundation of the pelagic food web (e.g. Schelske and Hodell 1995; Leggett et al. 1999). In contrast, there are recent reports indicating frequent or even characteristic heterotrophic balance in Lake Superior (Biddanda et al. 2001; Russ et al. 2004) and to a lesser extent in Lake Michigan (Biddanda and Cotner 2002; Urban et al. 2005) and Erie, with results from Lake Erie more variable (Ostrom et al. 2005; Depew et al. 2006*b*). Large lakes tend to have stronger physical forcing than the small lakes that have formed most of our knowledge about metabolic balance to date, and they also have spatial differentiation between nearshore and offshore zones (Boyce 1977; Wetzel 2001). The somewhat disparate conclusions about metabolic balance in the LGL may in part reflect an under-sampling of the within-lake or temporal variability that can result from these features of large lakes.

While studies of gas concentrations in small lakes have given strong evidence of persistent heterotrophic balance in many cases (Bachmann et al. 2000; Hanson et al. 2003; Cole et al. 2000), direct measurements of metabolic activities (e.g. Carignan et al. 2000) are more laborious to make. Particularly in large lakes, our knowledge to date depends on relatively sparse measurements and/or

indirect inferences from geochemical variables such as stable oxygen isotopes. Both direct measurements and geochemical methods depend on various assumptions and require careful interpretation, but direct methods can offer a better possibility to explore the links between metabolic balance and potential physical and biological controlling factors because of the immediate and in some ways less ambiguous measurement of photosynthetic and respiratory fluxes they provide.

Computations of lake metabolism are sensitive to the methods used (Carignan et al. 2000; González et al. 2002). If PMB_m is calculated from the oxygen exchange, it favors to the net autotrophy, contrary, if it computed from the ^{14}C uptake rate and oxygen consumption, it favors to the net heterotrophy (Carignan et al. 2000; González et al. 2002). Therefore, much of the uncertainty in the comparison of PMB_m derived from ^{14}C and oxygen methods is the relationship between light-saturated rates of carbon assimilation (P_{opt}) and gross oxygen evolution (P_{max}). Gross photosynthesis (P_{max}) should be measured as oxygen evolution (Falkowski and Raven 1997). The proximity of P_{opt} to gross photosynthesis depends on the incubation time (Laws et al. 2000; Marra 2002), and it was suggested that the short-term ^{14}C uptake might represent the gross photosynthesis (e.g. Dring and Jewson 1982; Fahnenstiel and Carrick 1988). Therefore, in this study we wanted to find out if a short-time (1-h) ^{14}C uptake measures gross photosynthesis measured as P_{max} or something between P_{max} and net community photosynthesis ($NCP = P_{max} - R$).

Apart from the methodological differences, the existing contradictory views on what control PMB_m in lakes (e.g. del Giorgio and Peters 1994 vs. Carignan et al. 2000) may be explained by the different ways PMB_m was defined. For example, Carignan et al. (2000) in their statistical analysis used the average of AGP/AR ratios and found only weak but statistically significant relationship between PMB_m and physical environment, namely variations in photic and mixing depths. Del Giorgio and Peters (1994) calculated PMB_m as the ratio between average AGP and average AR and have found that both trophic status and DOC were important determinants of the metabolic balance.

Here we use biweekly measurements to characterize the variability of plankton community metabolism in two LGL coastal sites of contrasting physical, optical, and nutrient regime, and test the importance of physical forcing (especially mixing and optical depth variations) in determining the metabolic balance. With additional but less frequent measurements from other LGL coastal sites, and data gleaned from the literature, we want to examine the relative roles of allochthonous inputs (as indexed by DOC concentration), physical environment (particularly mixing vs optical depth) and trophic status in determining plankton metabolic balance in lakes. In this paper, we also want to examine the relationship between P_{opt} and P_{max} to see if ^{14}C method with short incubations can give estimates close to the gross photosynthesis or not. Therefore, in this paper we want to address the following questions: (i) will a short-term 1-hour ^{14}C uptake (P_{opt}) represent gross photosynthesis (P_{max}) or not? (ii) will PMB be dependent on both the ratio of Z_{eu}/Z_m and P_{max}/R ratio? (iii) what environmental variables affect PMB_m? (iv) what is the difference between PMB_m determined as the average of ratios and as the ratio between averages in terms of controlling factors? and, (v) what is the potential mechanism through which DOC can affect lake metabolic balance?

3.3 Materials and Method

3.3.1 Design and study sites

Intensive work to elucidate the short-term temporal variability of metabolism in LGL plankton communities used a relatively oligotrophic, transparent, high-energy coastal site (Lake Ontario, location: 43°17.3'N, 79°43.9'W) and a more sheltered, turbid, eutrophic site (Hamilton Harbour, location: 43°17.3'N, 79°50.4'W) (Fig. 3.1). The Lake Ontario site, like many others around the LGL, is part of a nearshore zone subject to major upwelling and downwelling events (Blanton 1975; Rao and Murthy 2001*a*, *b*), has relatively low DOC (Scully et al. 1996; Smith et al. 2004) and TP in the oligotrophic range (Nicholls et al. 2001; Millard et al. 2003). Hamilton Harbour is also subject to important physical forcing including extreme fluctuations in water movement and exchange with Lake Ontario (Barica et al. 1989, Wu et al. 1996) but has higher concentrations of DOC (Scully et al.

1996; Smith et al. 2004) and TP (Charlton and Le Sage 1996). Comparison between these sites additionally tests the relative importance of trophic status (as indexed by TP and Chl *a*) vs DOC as determinants of metabolic balance (Carignan et al. 2000; Prairie et al. 2002). If DOC is the dominant influence then Hamilton Harbour should be more heterotrophic than Lake Ontario, but if trophic status is more important then the difference should be reversed.

For a broader sampling of trophic status and DOC conditions in the LGL, we did limited sampling at two additional sites in Georgian Bay (Lake Huron) (Fig. 3.1): Georgian Bay site (location: 45°07.8'N, 80°05.4'W) and Woods Bay site (location: 45°08.5'N, 80°00.1'W). The former is a coastal site and more transparent and oligotrophic with higher DOC than Lake Ontario, while the later is coloured inshore site with water quality largely influenced by the inflow from the Moon River and has DOC somewhat higher than Hamilton Harbour but is oligotrophic in TP and Chl *a*.

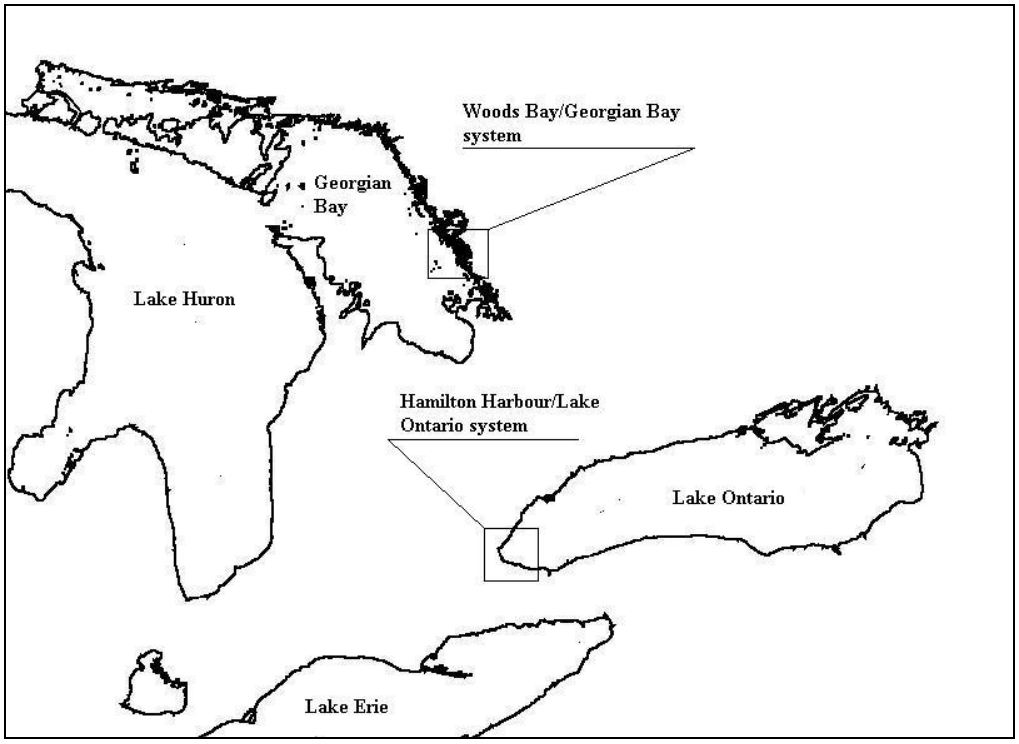

Fig. 3.1 Map of the Laurentian Great Lakes indicating two sampling systems.

3.3.2 Field methods

Lake Ontario and Hamilton Harbour stations were sampled bi-weekly from May to September of 2003 and 2004 with one additional sampling in October 2004. Woods Bay and Georgian Bay were sampled four times but water for metabolic rates was collected only twice in the beginning (June) and in the end (August) of summer 2004. Water temperature profiles were measured with either a YSI 600 or YSI 6600 and used to determine the depth of the mixed layer. The incident photosynthetically active radiation (PAR) was recorded with a LiCor underwater quantum sensor (Li-COR) at subsurface and at 1-m intervals to the depth corresponding to 5-10% of subsurface PAR. Samples of water at each station were collected with an integrated water sampler from the surface to the top of thermocline. The integrated water sampler was a 16-m long polyvinyl chloride (PVC) pipe (collection tube) with a specific weight and a PVC water locking mechanism at the bottom of the tube. Water samples were pre-screened with the 200-µm nylon mesh (Nytex®) to remove the larger zooplankton, collected in dark 20-L carboys placed inside the coolers and delivered to the laboratory for metabolic rate measurements.

3.3.3 Analytical methods

Concentrations of TP, Chl *a* and dissolved inorganic carbon (DIC) were measured in the beginning of each incubation experiment. Samples for TP were taken at the beginning of each experiment and stored at -20°C pending analysis by the ascorbate method, following persulfate digestion (Wetzel and Likens 2000). Procedures for Chl *a*, DIC and carbon assimilation rates were similar to that described by Depew et al. (2006*a*). We did not measure DOC in Lake Ontario and Hamilton Harbour because of the assumption that DOC is a conservative parameter and its temporal variations in these LGL sites are small, and we can always assume data from the literature. However, we measured DOC concentrations in Georgian Bay and Woods Bay. DOC samples were collected as the filtrate of water samples passed through precombusted Whatman GF/F filters (0.7-µm pore size) and measured with High Temperature Carbon Analyzer (Dohrman-Rosemount DC-190).

3.3.4 Metabolic rate measurements

The oxygen light-and-dark bottle method was used to derive volumetric rates of the community respiration (R) and light-saturated gross photosynthesis (P_{max}). The type of incubation bottles and procedure for this method was similar to that described in Depew et al. (2006*b*) with only two exceptions; bottle incubation times and incubation chambers were different. The incubations were performed in the temperature controlled incubators (Percival, Boone IOWA 50036). The light source of this incubator consisted of 14 fluorescent lamps, which provided an average irradiance of 330 μmol photons m^{-2} s^{-1} that was enough to meet the requirements for light-saturated photosynthesis (Bocaniov unpublished data). The light bottles were incubated for 6 hours, while incubation time for dark bottles was different: 6 hours (Hamilton Harbour and Woods Bay) and 18 hours (Lake Ontario and Georgian Bay). Rates of R and P_{max} were calculated as the difference in dissolved oxygen concentrations between initial and dark bottles (respiration) and between light and dark bottles (gross photosynthesis). The coefficient of variation (CV) of DO measurements yielded an average analytical precision of 0.04%. Similar to Depew et al. (2006*b*), analytical precision of the titrations was the greatest if the samples were titrated within a few hours of fixation and within 15 minutes of acidification.

The ^{14}C method employed measurements of production rates during 1-h incubations at different light intensities in the light gradient incubator with 18 different irradiance levels similar to that described in Hiriart et al. (2002). The methodology for this method followed the procedures described in Smith et al. (2005). As we used acidification technique to get rid of inorganic ^{14}C, rates of carbon assimilation were reported as the production of a new organic material (particulate and dissolved organic carbon). Primary production rates versus light intensity data were fit to the equation of Jassby and Platt (1976) using a curve-fitting program to construct a photosynthesis-irradiance relationship (P-I curve) and derive from this the photosynthetic parameters normalized to Chl *a*, such as P^B_m (Chl *a* normalized carbon uptake rate at light saturation), α^B (the slope of P-I curve at the onset of photosynthesis) and their ratio I_k (P^B_m/ α^B) that is the minimal light requirements for the maximal

rate of photosynthesis. The rates of carbon assimilation at light saturation (P_{opt}) were calculated as the product of $P^B m$ and Chl *a*.

3.3.5 Calculations and data manipulation

The mixed layer depth was defined as when the temperature gradient starts exceeding 0.01 °C cm^{-1} and overall temperature change over 1 m depth was more than 1 °C (Carignan et al. 2000). The light extinction coefficient (k_{PAR}) was calculated as the slope of a linear regression of the natural logarithm of mean light intensity against depth (Kirk 1994), and used to calculate the euphotic zone determined in this study as a zone extending to 1% of the incident irradiance.

Depth integrated rates of *in situ* carbon assimilation (P_{int}, mmolC m^{-2} d^{-1}) were calculated with the help of the Fee model (Fee 1990) using the photosynthetic parameters derived from the P-I curve (^{14}C method) and 70% of the theoretical cloudless value of solar radiation (Fee et al. 1992; Millard et al. 1996). To convert P_{int} rates to gross photosynthesis expressed in oxygen units (AGP, $mmolO_2$ m^{-2} d^{-1}), the apparent gross photosynthetic quotients (PQ*) were applied. The PQ* was directly calculated as the ratio of P_{max} to P_{opt}. Values of PQ*, R and Z_m were calculated for each day of the sampling season by the interpolation of the results of two closest sampling days. Daily rates of *in situ* areal community respiration (AR, $mmolO_2$ m^{-2} d^{-1}) were calculated by multiplication of the volumetric respiration rates (R) by the depth of the mixed layer (Z_m) for each day with the assumption that the volumetric *in situ* respiration rates were similar to those measured in the dark bottles and they were the same throughout the mixed layer (e.g. Urban et al. 2005). Seasonal rates of gross photosynthesis ($\sum P_{int}$, mmolC m^{-2}; $\sum$AGP, $mmolO_2$ m^{-2}) and community respiration ($\sum$AR, $mmolO_2$ m^{-2}) were calculated separately for 2003 and 2004 by integration of calculated daily rates for every single day over the sampling periods from May 10 to September 3 inclusive.

Apart from our own data, the analysis included the examination of the literature data as well as pooled datasets where we combined both our own and literature data. We used data from the following studies with the type of lakes and number of the sampled systems (*n*) indicated in brackets:

del Giorgio and Peters 1994 (southern Quebec lakes; n = 20), Carignan et al. 2000 (oligotrophic Canadian Shield lakes; n = 12), Hanson et al. 2003 (Northern Highland Lake district of Wisconsin and the Upper Peninsula of Michigan lakes; n = 25), and Depew et al. 2006*b* (oligotrophic east basin of Lake Erie; n = 1), For the literature data of Depew et al. (2006*b*), only those data were taken into consideration that were obtained within a similar season to my sampling season, namely from 30 April to 25 September 2002. As in the later study, rates of AGP and AR were corrected for lake volume; we used uncorrected rates to be consistent with the results of our work and other metabolic rates studies used in our data analysis. Mean values of Depew et al. (2006*b*) data are reported in Tables 3.2 and 3.3. For the inter-site comparisons, in our own data, the mean value for each of our sites was calculated, with separate means for each year of observation in Hamilton Harbour and Lake Ontario. For literature data (Carignan et al. 2000; Depew et al. 2006*b*), all the values reported for each given lake were averaged and considered as one independent data-point. To convert P_{int} rates expressed in carbon units in del Giorgio and Peters (1994) work to AGP rates expressed in oxygen units we used a PQ* of 2 based on the present study results where we compared light-saturated rates of gross oxygen evolution (oxygen method) and carbon assimilation (^{14}C method). For the work of Carignan et al. (2000), we recalculated metabolic rates from carbon to oxygen units using reported values for the assumed photosynthetic and respiration quotients. Apart from analyses of our own data or data from individual literature studies, we also analyzed two combined data sets: pooled 1 dataset (including Carignan et al. 2000, Depew et al. 2006*b*, and our own data) and pooled 2 dataset (del Giorgio and Peters 1994, and Hanson et al. 2003 in addition to pooled 1 data). The former dataset was used to examine the effect of controlling factors on the average ratios of AGP/AR (average ratios), while the latter was used to examine the ratio between average AGP and average AR (ratio between averages). We could not include data from del Giorgio and Peters (1994) and Hanson et al. (2003) into our pooled 1 dataset, as those studies did not report either average ratio for metabolic balance or individual AGP/AR rates.

3.3.6 Statistical analysis

All data were $\log_{10}$ transformed before the statistical analysis to ensure equal variances. The statistical analyses were performed on individual as well as lake-averaged data using SYSTAT statistical software. All regression parameters were considered being significant at $p \leq 0.05$ levels. Ordinary least-squared regressions were used for the predictive purposes, and reduced major axis regressions for the analysis of two dependent variables. Metabolic rates were treated as dependent variables while the others as independent ones. To test if the slopes of two regression lines are significantly different or not, the Student *t*-test statistic was used. For comparison of more than two slopes, the *F*-test statistic was applied. Principal components analysis (PCA) was performed on the site-averaged data from pooled 2 dataset. PCA was based on correlation matrix without rotation. Ordination was based on selected lake-averaged data including Chl *a*, TP, DOC, AGP and AR.

3.4 Results

3.4.1 Physical-chemical variations at intensive sites

The thickness of epilimnion (Z_m, m) in Lake Ontario was very variable ranging from 19 to 1.2 with a mean value of 12.4 ± 6.6 (± st. dev.). The variability in Z_m (m) in 2003 was quite similar to that in 2004 depicted on Fig. 3.2B. In Hamilton Harbour, the stratification was stable during the summer with a very distinct position of thermocline and a relatively shallow epilimnion of a few meters. The timing and degree of thermal stratification in 2003 were quite similar to that observed in 2004 (Fig. 3.3B). Water columns at the Woods Bay and Georgian Bay sites were mixed to the bottom of the lakes during both times of water collection.

The euphotic depth (Z_{eu}, m) in Lake Ontario was much larger than that measured in Hamilton Harbour (Table 3.2) and showed a seasonal trend with distinct minimums during the times of early and late summer algal blooms, and a mid summer maximum when Chl *a* concentrations were low with Fig. 3.2B depicting this for 2004. Its Z_{eu} was larger than its physical depth most of the time

except the time when the algal blooms occurred. In contrast to Lake Ontario, Hamilton Harbour had a very shallow Z_{eu} with much less fluctuations and with values slowly decreasing from spring towards autumn with Fig. 3.3B showing this for 2004. Georgian Bay station had a euphotic depth two times deeper that that of Woods Bay (Table 3.2). If the former had its Z_{eu} larger than the physical depth of the station, the latter had its Z_{eu} slightly less than the station physical depth.

Concentrations of Chl *a* (mg m^{-3}) ranged from 3.47 to 22.97 in Hamilton Harbour and from 0.59 to 4.21 in Lake Ontario with the summer mean concentration in Hamilton Harbour being fivefold higher than in Lake Ontario (Table 3.2). The seasonal cycles of Chl *a* in Hamilton Harbour in both years were abrupt with three distinct peaks occurring approximately at intervals of one month (Fig. 3.3A). In Lake Ontario, Chl *a* concentrations showed similar pattern with two peaks in the beginning (June) and the end of the summer (late August) with a midsummer low chlorophyll values (Fig. 3.2A). Woods Bay and Georgian Bay had larger concentrations of Chl *a* in the early summer than in the end of the summer. Measured TP concentrations (mmol m^{-3}) in Hamilton Harbour were in meso-eutrophic range, while those of the other sites were in oligotrophic range with a larger degree of oligotrophy observed in Georgian Bay and Woods Bay than in Lake Ontario (Table 3.2). DOC concentrations (g m^{-3}) were larger in Hamilton Harbour than that in Lake Ontario (Table 3.2). Georgian Bay had DOC concentration slightly higher than Lake Ontario, while Woods Bay had the highest DOC concentration among the sites (Table 3.2). DIC concentrations (g m^{-3}) were in the range of between 22.0 and 32.71 in Hamilton Harbor, and between 20.43 and 23.55 in Lake Ontario with the means of 26.22 ± 2.5 and 22.08 ± 0.85 respectively. Both stations in Georgian Bay had much lower DIC concentrations with the means of 1.94 ± 0.21 (Woods Bay) and 12.20 ± 1.79 (Georgian Bay).

Table 3.1 Nomenclature of selected often-used terms.

Term	Definition (units)
$\sum$AGP	Seasonal rate of gross photosynthesis: from May 10 to Sept 3 ($mmolO_2\ m^{-2}$)
$\sum$AR	Seasonal rate of community respiration: from May 10 to Sept 3 ($mmolO_2\ m^{-2}$)
$\sum P_{int}$	Seasonal rate of carbon assimilation: from May 10 to Sept 3 ($mmolC\ m^{-2}$)
$\sum$R	Seasonal rate of community respiration: from May 10 to Sept 3 ($mmolO_2\ m^{-2}$)
AGP	Areal rate of gross photosynthesis ($mmolO_2\ m^{-2}\ d^{-1}$)
AR	Areal rate of community (total plankton) respiration ($mmolO_2\ m^{-2}\ d^{-1}$)
Chl *a*	Chlorophyll *a* ($mg\ m^{-3}$)
DOC	Dissolved organic carbon ($g\ m^{-3}$)
I_k	Minimal light requirements for the maximal rate of photosynthesis ($\mu mol\ m^{-2}\ s^{-1}$)
k_{PAR}	Light attenuation coefficient of PAR (m^{-1})
NCP	Net community production: $NCP = P_{max} - R$ ($mmolO_2\ m^{-3}\ h^{-1}$)
PAR	Photosynthetically available radiation ($\mu E\ m^{-2}\ s^{-1}$)
P^B_m	Chl *a* normalized carbon uptake rate at light saturation ($mgC\ mgChl\ a^{-1}\ h^{-1}$)
PCA	Principal components analysis (none)
P_{int}	Areal rate of carbon assimilation ($mmolC\ m^{-2}\ d^{-1}$)
P_{max}	Light saturated rate of gross oxygen evolution ($mmolO_2\ m^{-3}\ h^{-1}$)
PMB_m	Plankton metabolic balance of the mixed layer: AGP/AR (none)
P_{opt}	Rates of carbon assimilation at light saturation ($mmolC\ m^{-3}\ h^{-1}$)
PQ*	Apparent gross photosynthetic quotient (moles O_2/moles C) (none)
R	Community respiration ($mmolO_2\ m^{-3}\ h^{-1}$)
SML	Surface mixed layer (none)
TP	Total phosphorus ($mmol\ m^{-3}$)
Z_{eu}	Euphotic or optical depth (m)
Z_m	Vertical mixing depth (m)
α^B	Slope of P-I curve at the onset of photosynthesis ($mgC\ mgChl\ a^{-1}\ E^{-1}\ m^2$)

Table 3.2 Mean (standard error) summer limnological characteristics for the surface mixed layer of the study sites. The physical station depth (m) is indicated in square brackets, and number of observations for each site is indicated by "*n*" and shown in angle brackets.

Lake[1]	Mixing depth (m)	Euphotic depth (m)	Z_{eu}/Z_m	Chlorophyll ($mg\ m^{-3}$)	Total phosphorus ($mmol\ m^{-3}$)	DOC ($g\ m^{-3}$)
HH [19], <*n* = 19>	8.7 (1.3)	6.1 (0.2)	1.01(0.14)	10.90 (1.1)	0.96 (0.08)	4.2 (0.4)
LO [19], <*n* = 18>	12.4 (1.6)	21.4 (1.5)	2.81(0.65)	1.98 (0.2)	0.31 (0.02)	2.6 (0.1)
WB [6], <*n* = 2>	6.0 (-)	5.4 (0.5)	0.89(0.09)	3.31* (1.7)	0.24* (0.01)	4.9* (0.5)
GB [6], <*n* = 2>	6.0 (-)	11.3 (1.7)	1.89(0.28)	0.90* (0.03)	0.13* (0.002)	2.9* (0.4)
LE** <*n* = 34>	13.0(1.4)	14.7(0.9)	1.47(0.13)	2.13(0.4)	0.32 (0.17)	3.5 (0.2)

[1] Hamilton Harbour (HH), Lake Ontario (LO), Woods Bay (WB), Georgian Bay (GB), and Lake Erie (LE).

* Determinations of mean and st. error are based on 4 observations (DOC) and 6 observations (Chl *a*, TP).

** Lake Erie data were obtained from Depew et al. (2006*b*) and averaged over the time interval from April 30 to September 25, 2002.

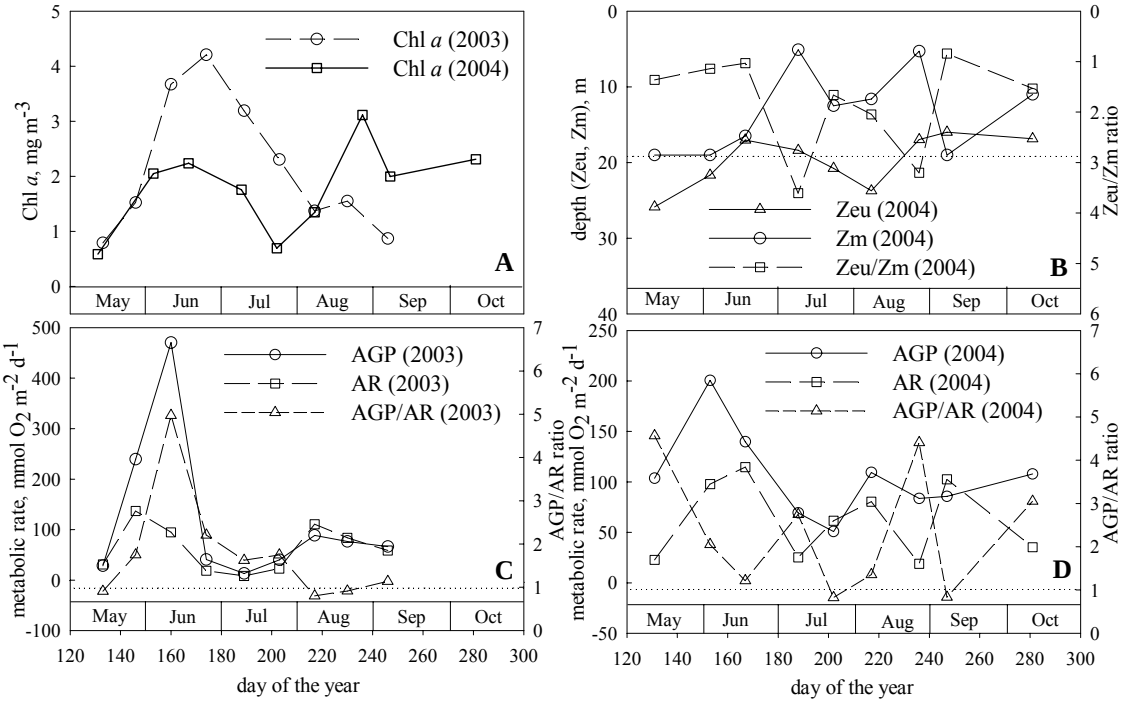

Fig. 3.2 (A) Chl *a* concentrations (mg m^{-3}) in Lake Ontario (LO) in 2003 (circles) and 2004 (squares); (B) euphotic depth (Z_{eu}, m) (triangles), mixing depth (Z_m, m) (circles) and Z_{eu}/Z_m ratio (squares) in LO in 2004; dotted line indicates station physical depth; (C) areal rates of gross photosynthesis (AGP, $mmolO_2$ m^{-2} d^{-1})(circles) and community respiration (AR, $mmolO_2$ m^{-2} d^{-1}) (squares) and AGP/AR ratio (triangles) in LO in 2003; dotted line indicates metabolic equilibrium conditions when AGP equals AR; (D) areal rates of AGP (circles) and AR (squares), and AGP/AR ratio (triangles) in LO in 2004; dotted line indicates metabolic equilibrium conditions.

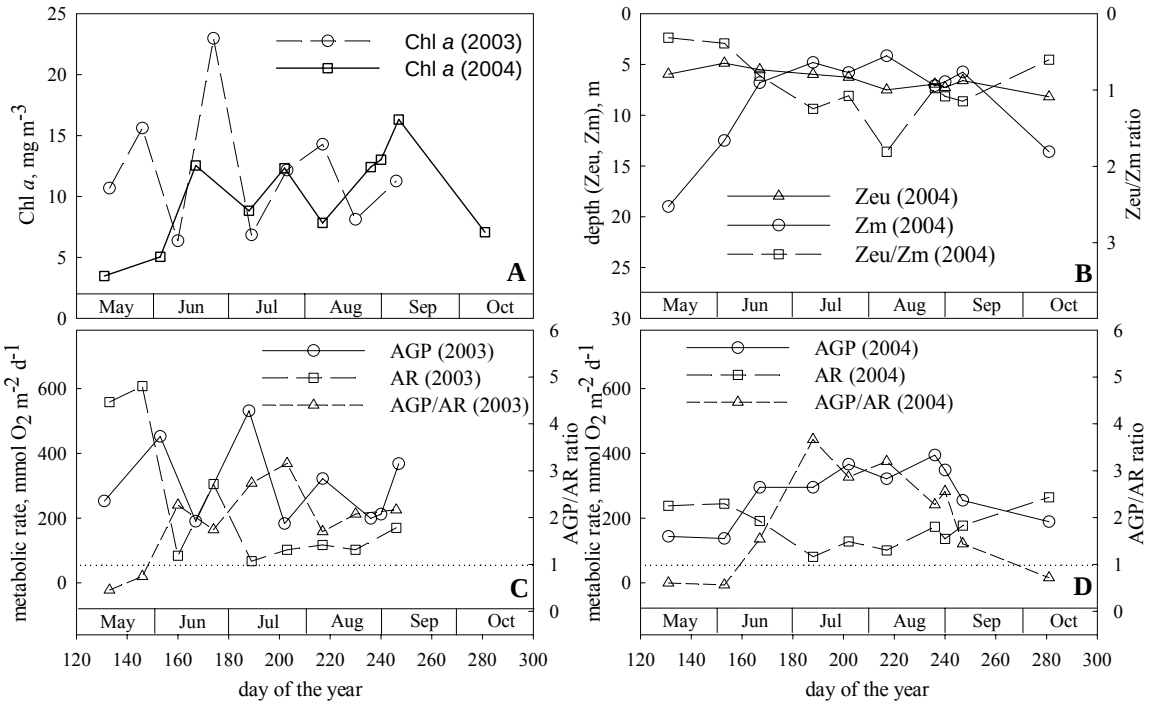

Fig. 3.3 (A) Chl *a* concentrations (mg m^{-3}) in Hamilton Harbour (HH) in 2003 (circles) and 2004 (squares); (B) euphotic depth (Z_{eu}, m) (triangles), mixing depth (Z_m, m) (circles) and Z_{eu}/Z_m ratio (squares) in HH in 2004; dotted line indicates station physical depth; (C) areal rates of gross photosynthesis (AGP, $mmolO_2$ m^{-2} d^{-1})(circles) and community respiration (AR, $mmolO_2$ m^{-2} d^{-1}) (squares), and AGP/AR ratio (triangles) in HH in 2003; dotted line indicates metabolic equilibrium when AGP equals AR; (D) areal rates of AGP (circles) and AR (squares), and AGP/AR ratio (triangles) in HH in 2004; dotted line indicates metabolic equilibrium conditions.

3.4.2 Results of oxygen light-and-dark bottle method

Rates of P_{max} ($mmolO_2$ m^{-3} h^{-1}) in Hamilton Harbour were significantly different and much higher those measured in Lake Ontario (Table 3.3). They ranged from 3.578 to 16.917 in Hamilton Harbour, and from 0.116 to 2.826 in Lake Ontario. Mean P_{max} in Woods Bay was almost threefold of that in Georgian Bay (Table 3.3). Rates of R ($mmolO_2$ m^{-3} h^{-1}) in Hamilton Harbour were 4.5 higher than rates in Lake Ontario. Average R rates in Woods Bay and Georgian Bay were respectively larger and smaller that that of Lake Ontario (Table 3.3). Ratios of P_{max}/R in Hamilton Harbour were approximately 60% higher than in the other systems (Table 3.3).

Table 3.3 Mean summer (standard error) characteristics of metabolic rates: P_{max} and R ($mmolO_2\ m^{-3}\ h^{-1}$), P_{int} ($mmolC\ m^{-2}\ d^{-1}$), AGP and AR ($mmolO_2\ m^{-2}\ d^{-1}$), and AGP/AR ratio (average of ratios). See Table 3.1 for the definitions of terms used. See Table 3.2 for number of observation (*n*) for each specific site.

Lake[1]	P_{max}	R	P_{int}	AGP	AR	AGP/AR
HH	7.41 (0.72)	1.05 (0.10)	148.9 (9.9)	287.0 (24.5)	202.3 (34.4)	1.92 (0.23)
LO	0.94 (0.14)	0.22 (0.02)	55.9 (13.5)	111.8 (25.0)	62.4 (9.6)	2.06 (0.32)
WB	1.50 (0.58)	0.30 (0.06)	20.4 (7.0)	65.0 (24.2)	43.8 (9.0)	1.43 (0.26)
GB	0.53 (0.09)	0.13 (0.04)	15.8 (4.0)	39.3 (6.1)	18.6 (5.1)	2.18 (0.27)
LE*	0.69 (0.08)	0.16 (0.02)	n/a	51.8 (5.4)	44.2 (6.9)	1.78 (0.27)

[1] Hamilton Harbour (HH), Lake Ontario (LO), Woods Bay (WB), Georgian Bay (GB), and Lake Erie (LE).

* Lake Erie data were obtained from Depew et al. (2006*b*) and averaged over the time interval from April 30 to September 25, 2002.

3.4.3 Results of ^{14}C method (photosynthetic parameters: α^B, I_k, P^B_m and P_{opt}) and k_{PAR}

Mean α^B value ($mgC\ mgChl^{-1}\ \mu mol^{-1}\ m^{-2}$) found in Lake Ontario was slightly smaller that of Hamilton Harbour (Table 3.4). Woods Bay had a lower mean value of α^B than that of Georgian Bay (Table 3.4). Mean values for I_k ($\mu mol\ m^{-2}\ s^{-1}$) were higher in Lake Ontario and Hamilton Harbour and lower in Woods Bay and Georgian Bay (Table 3.4). It was observed that P^B_m values ($mgC\ mgChl^{-1}\ h^{-1}$) in oligotrophic Lake Ontario were almost always lower than those of eutrophic Hamilton Harbour. The average P^B_m value in Lake Ontario was about two thirds of that in Hamilton Harbour with Georgian Bay and Woods Bay sites having the lowest values amongst all four sites (Table 3.4). Mean rate of P_{opt} ($mmolC\ m^{-3}\ h^{-1}$) was the highest in Hamilton Harbour, intermediate in Lake Ontario and Woods Bay sites, and the lowest in Georgian Bay (Table 3.4). Values of k_{PAR} (m^{-1}) were the highest in Woods Bay, smaller in Hamilton Harbour and Georgian Bay, and the lowest in Lake Ontario (Table 3.4).

Table 3.4 The range and the mean ± st. error (in brackets) for the key photosynthetic parameters: P^B_m (mgC mgChl a^{-1} µmol $^{-1}$ m^2), α^B (mgC mgChl a^{-1} E^{-1} m^2), I_k (µmol m^{-2} s^{-1}), P_{opt} (mmolC m^{-3} h^{-1}), and k_{PAR} (m^{-1}). See Table 3.1 for the definitions of terms used. The letter "*n*" stands for the number of observations.

Lake	P^B_m	α^B	I_k	P_{opt}	k_{PAR}
Hamilton Harbour (*n* = 19)	2.4 - 7.8 (4.6 ± 0.4)	4.8 – 13.0 (9.8 ± 0.6)	70 – 168 (131 ± 5)	1.5 - 5.8 (3.8 ± 0.3)	0.56 – 1.13 (0.77 ± 0.03)
Lake Ontario (*n* = 18)	1.5 - 6.3 (3.1 ± 0.3)	3.9 – 16.0 (8.5 ± 0.9)	75 - 156 (103 ± 6)	0.1 – 1.71 (0.5 ± 0.1)	0.12 – 0.33 (0.23 ± 0.01)
Woods Bay (*n* = 2)	1.5 – 2.3 (1.9 ± 0.4)	5.5 – 7.2 (6.3 ± 0.8)	77 - 88 (82 ± 5)	0.3 – 0.6 (0.5 ± 0.2)	0.78 – 0.96 (0.87 ± 0.09)
Georgian Bay (*n* = 2)	2.0 – 3.7 (2.9 ± 0.9)	7.2 – 12.6 (9.9 ± 2.7)	79 – 82 (81 ± 1.8)	0.2 – 0.3 (0.2 ± 0.1)	0.35 – 0.48 (0.42 ± 0.06)

3.4.4 Comparison of the P_{opt} and P_{max}

Overall, there was a strong positive relationship between light saturated rates of carbon assimilation and gross oxygen evolution (models 1 and 1**, Table 3.5; see also Fig. 3.4). My own data suggested average PQ* of approximately 2 (gross PQ*; range: 1.1 to 3.3) and 1.6 (net PQ*; range: 0.45 to 2.8). However, combination of our own data with those of Depew et al. (2006*b*) yielded a mean gross and net PQs* of 1.7 and 1.27, respectively (*n* = 74). The re-analysis of the regression models of P_{max} and NCP (NCP = P_{max} – R, $mmolO_2$ m^{-3} h^{-1}) on P_{opt} for the same combined data (models 2** and 3, Table 3.5) gave PQs* of 1.59 (gross) and 1.22 (net).

3.4.5 Areal photosynthesis and respiration rates

Instantaneous rates of carbon assimilation (P_{int}, mmolC m^{-2} d^{-1}) in Lake Ontario were variable ranging from 6.64 to 266.35, while those rates in Hamilton Harbour fluctuated within a more restricted range from 58.43 to 217.73. Georgian Bay system had rates of P_{int} ranging from 13.34 to 27.37 in Woods Bay and from 11.79 to 19.88 for Georgian Bay. Mean P_{int} rates were the largest in

Table 3.5 Linear regression models using $\log_{10}$-transformed data and relating individual rates of P_{max} ($mmolO_2$ m^{-3} h^{-1}) and P_{opt} (mmolC m^{-3} h^{-1}). Models 1 and 1** are based on our own data, while models 2, 2** and 3 are based on the combined data (our own data plus Depew et al. 2006*b* data). The ± symbol stands for the standard errors of the regression parameters. The following abbreviations are used: the coefficient of determination (r^2), the *p*-value (*p*), and a number of observations (*n*).

Model	Dependent variable	Regression	r^2	*p*	*n*
1	P_{max}	$0.30\pm0.02 + 0.95\pm0.04\cdot[P_{opt}]$	0.950	0.000	41
1**	P_{max}	$0.30\pm0.02 + 0.98\pm0.04\cdot[P_{opt}]$			
2	P_{max}	$0.192\pm0.02 + 1.004\pm0.05\cdot[P_{opt}]$	0.862	0.000	75
2**	P_{max}	$0.202\pm0.03 + 1.081\pm0.04\cdot[P_{opt}]$			
3	NCP	$0.086\pm0.02 + 1.116\pm0.05\cdot[P_{opt}]$	0.877	0.000	74

** reduced major axis model regression (Model II)

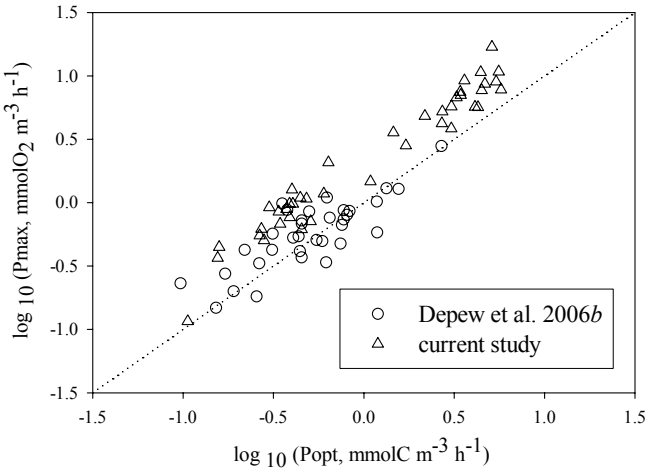

Fig. 3.4 Relationship between maximum rate of oxygen evolution (P_{max}, $mmolO_2$ m^{-3} h^{-1}) measured by oxygen bottle method and maximum rate of carbon assimilation (P_{opt}, mmolC m^{-3} h^{-1}) measured by ^{14}C method. Current study (triangles) and Depew et al. 2006*b* data (circles).

Hamilton Harbour, smaller in Lake Ontario and Woods Bay, and the smallest in Georgian Bay (see Table 3.3). Rates of AGP ($mmolO_2$ m^{-2} d^{-1}) were 2.5 times larger in Hamilton Harbour than in Lake Ontario (Table 3.3) and ranged from 137.23 to 531.21 in Hamilton Harbour (Fig. 3.3C, D) and from 13.08 to 470.34 in Lake Ontario (Fig. 3.2C, D). Mean value of AGP rates in Woods Bay was approximately twice of that in Georgian Bay (Table 3.3). Rates of AR ($mmolO_2$ m^{-2} d^{-1}) ranged from

8.00 to 136.80 in Lake Ontario (Fig. 3.2C, D) and from 66.91 to 607.17 in Hamilton Harbour (Fig. 3.3C, D) with the mean value in the harbour being threefold of that in the lake (Table 3.3). Mean rates of AR in Woods Bay and Georgian Bay were the smallest among all four systems (Table 3.3).

Individual rates of AGP were correlated (bivariate correlations) positively with Chl *a* and TP (R^2 = 0.634 [model 4, Table 3.6] and R^2 = 0.556 respectively; n = 40) and negatively with Z_{eu}/Z_m (R^2 = 0.380; n = 41). Similar to AGP, individual AR rates were also correlated (bivariate correlations) positively with Chl *a* and TP (R^2 = 0.424 and R^2 = 0.535 [model 5, Table 3.6] respectively; n = 40) and negatively with Z_{eu}/Z_m (R^2 = 0.653; n = 41). Multiple regressions consisting of both Chl *a* and TP showed that only Chl *a* was a significant variable in predicting AGP and only TP was significant in predicting AR.

Similar to individual rates, site-averaged rates of AGP and AR were significantly and positively correlated with either Chl *a* or TP despite the small sample size (n = 6). I found the similar results in other data sets too: del Giorgio and Peters (1994), Hanson et al. (2003), pooled 1 and pooled 2 data sets. AGP rates were better predicted from Chl *a* (e.g. pooled 1 and 2 data: model 6-1 and 6-2, Table 3.6) while best predictor of AR rates was TP (e.g. pooled 1 data: model 7, Table 3.6) or both TP and Z_m (e.g. pooled 1 data: model 8, Table 3.6).

It was found that in all datasets (including pooled 1 and pooled 2 datasets), for both individual and mean data, regression slopes of AGP and AR rates on either Chl *a* and TP within a given dataset were not significantly different, meaning that AGP/AR ratios should not significantly change along the trophic gradient.

Table 3.6 Linear regression models using $\log_{10}$-transformed data and relating rates of AR, AGP and their ratio to different water property characteristics. For the multiple regressions, the independent variables are listed in a decreasing order of explained variance. See Table 3.1 and 3.5 for the meanings of the terms, symbols and abbreviations (±, r^2, p, and n) used. The following data were used for regression analyses: our own individual data (models 4, 5, 13 and 15), pooled 1 dataset (individual data: models 9, 14 and 16; site-averaged data: models 6-1, 7, 8, 10 and 11), and pooled 2 dataset (site-averaged data: models 6-2, 12 and 17).

Model	Dependent variable	Regression	r^2	p	n
4	AGP	1.79±0.06 + 0.63±0.08·[Chl *a*]	0.634	0.000	40
5	AR	2.24±0.06 + 0.94±0.14·[TP]	0.535	0.000	40
6-1	AGP	1.41±0.11+ 0.67±0.21·[Chl *a*]	0.388	0.004	19
6-2	AGP	1.34±0.07 + 0.55±0.08·[Chl *a*]	0.426	0.000	64
7	AR	2.15±0.11 + 1.13±0.17 [TP]	0.731	0.000	19
8	AR	1.48±0.13 + 1.02±0.10·[TP] + 0.79±0.13·[Z_m]	0.916	0.000	19
9	AR	-0.01±0.09* + 0.89±0.05·[AGP]	0.695	0.000	126
10	AR	-0.30±0.11 + 1.05±0.07·[AGP]	0.939	0.000	19
11	AGP	2.28±0.21+ 1.22±0.19·[Chl *a*] – 1.96±0.44·[DOC]	0.726	0.000	19
12	AGP	1.87±0.06 + 0.91±0.06·[Chl *a*] – 1.06±0.10·[DOC]	0.799	0.000	64
13	AGP/AR	-0.54±0.06+0.97±0.08·[P_{max}/R] + 0.59±0.05·[Z_{eu}/Z_m]	0.840	0.000	41
14	AGP/AR	-0.51±0.03+0.94±0.03·[P_{max}/R]+ 0.57±0.03·[Z_{eu}/Z_m]	0.881	0.000	126
15	AGP/AR	-0.11±0.15*+0.35±0.12·[Z_{eu}/Z_m] + 0.32±0.15·[Chl *a*] – 0.30±0.22·[TP]*	0.270	0.008	41
16	AGP/AR	-0.19±0.08 + 0.38±0.08·[Chl *a*] - 0.36±0.11·[TP] + 0.28±0.09·[Z_{eu}/Z_m]	0.206	0.000	126
17	AGP/AR[1]	-0.09±0.15*-0.96±0.13·[DOC]+0.70±0.12·[Chl *a*] - 0.63±0.16·[TP]	0.559	0.000	64

* not significant at the $p \leq 0.05$ level; [1] ratio of averages.

There was a strong positive relationship between individual rates of AR and AGP in our own data (p =0.000, R^2 = 0.639, n = 41). Similar strong relationships between instantaneous AGP and AR

have been found across different data sets, e.g. Carignan et al. 2000 (p = 0.000, R^2 = 0.635, n = 51), Depew et al. 2006*b* (p = 0.006, R^2 = 0.212, n = 34) and pooled 1 data (R^2 = 0.695; model 9, Table 3.6). Comparing the slopes of the regression lines of AR on AGP in three independent studies (current study; Carignan et al. 2000; and, Depew et al. 2006*b*) has shown that all three models were not significantly different (F-statistic; F_{cal} =1.968 < F_{tabl} = 3.12, df_{pooled} = 120) and therefore they form similar relationships between instantaneous AR and AGP.

The relationship between AGP and AR becomes even stronger if site averaged rates are considered, e.g. current study (p = 0.000, R^2 = 0.981, n = 6), Carignan et al. 2000 (p = 0.001, R^2 = 0.659, n = 12) and pooled 1 data (R^2 = 0.939; model 10, Table 3.6). However the relationship between AGP and AR was weaker in the studies that included lakes with high DOC concentrations, e.g. Hanson et al. (2003) (p = 0.003, R^2 = 0.320, n = 25) and del Giorgio and Peters (1994) (p = 0.004, R^2 = 0.380, n = 20). However, the last two studies did hold strong relationships between AR and AGP for their low to moderate DOC sites. For example, if we split data of Hanson et al. (2003) into two more or less equal subsets of low DOC sites (DOC < 8 mg L^{-1}, n = 13) and high DOC sites (DOC > 8 mg L^{-1}, n = 12), there was a significant correlation between AR and AGP rates in the low DOC sites (p = 0.000, R^2 = 0.784) and no correlation in the high DOC sites. The AR vs. AGP relationship can also be improved in del Giorgio and Peters work (1994) if three sites with the highest DOC concentrations (>7 mg L^{-1}) are dropped from the analysis (p = 0.000, R^2 = 0.631, n = 17).

The PCA (Fig. 3.5 and 3.6), that was based on the site averaged data from five independent studies (pooled 2 dataset), shows the positions of sampled sites in the principal components space and visualizes the relationship amongst Chl *a*, TP, DOC, AGP and AR. It is seen that the positions of our sampling sites were not different from those of other studies (Fig. 3.5). The first component axis (PC1) was mostly determined by trophic status and to some extent by DOC while the second component (PC2) was largely determined by DOC concentrations only (Table 3.7). The PCA has shown that rates of AGP were loaded on both PC1 and PC2, while rates of AR were only loaded on

PC1 (Table 3.7; Fig. 3.6). This means that across several studies and many systems (n = 62) AR rates were only associated with the trophic status, while rates of AGP were associated with both trophic status and DOC.

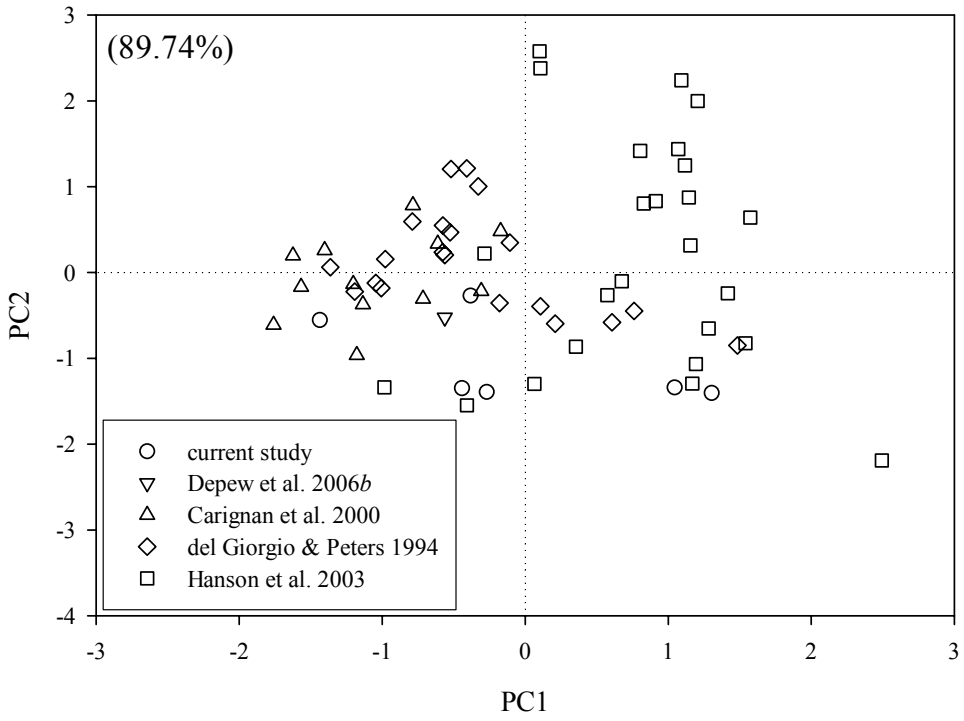

Fig. 3.5 Principal components ordination of the sampling sites based on site-averaged data for selected parameters: Chl *a*, TP, DOC, AGP and AR. Total variance explained by two components is indicated in the parenthesis in the top left corner. Current study (circles), Depew et al. 2006*b* (triangle down), Carignan et al. 2000 (triangles up), del Giorgio and Peters 1994 (diamonds), and Hansson et al. 2003 (squares).

Table 3.7 Components loadings derived from the principal components analysis (PCA). Components were extracted from a correlation matrix based on the log-base10-transformed data. Results are shown for non-rotated loading matrix.

Variable	PC 1	PC 2
Chl *a*	0.940	0.077
TP	0.946	0.050
DOC	0.532	0.828
AGP	0.709	-0.659
AR	0.885	-0.106
eigenvalue	3.346	1.140
% variance	66.93	22.81

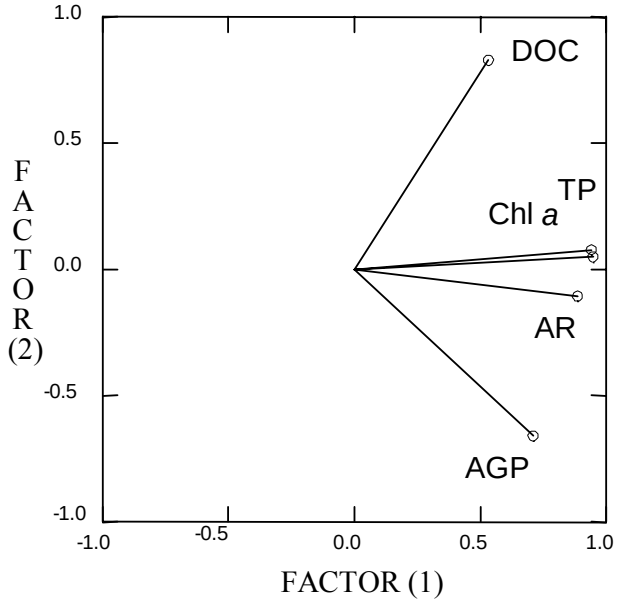

Fig. 3.6 Factors loadings plot for the PCA performed on site-averaged data (pooled 2 dataset) (Table 3.7 and Figure 3.5) and based on the following variables: Chl *a*, TP, DOC, and areal rates of gross photosynthesis (AGP) and community respiration (AR).

There was no statistically significant correlation between DOC and site averaged AR in any dataset except pooled 2 data (p = 0.003, R^2 = 0.132, n = 64) but the latter was due to a correlation

between DOC and TP (p = 0.000, R^2 = 0.258). In all datasets, the best predictor for average AR was TP. Multiple regressions containing DOC and TP as independent variables showed that in all datasets except Carignan et al. (2000) and pooled 1, DOC failed to add significantly to the predictions of AR achieved by TP. In Carignan et al. (2000) and pooled 1 datasets, the significant effect of DOC was due to its correlation with Z_m over which AR were integrated; the addition of Z_m to the model already containing TP and DOC drove DOC out of the model.

DOC failed also to explain a significant portion of variation in site-averaged volumetric rates of R in del Giorgio and Peters (1994) data. It was correlated with R in the data of Carignan et al. (2000) (p = 0.025; n = 12) or in our pooled 1 data set (p = 0.027; n = 19) but this was due to co-linearity between DOC and TP in the data of the former (p = 0.018; R^2 = 0.445) and of the latter (p = 0.05; R^2 = 0.208). Partial correlation analysis showed that there was no statistically significant correlation between site-averaged DOC and R if control variable is TP in both data sets. However, there was a significant relationship between DOC and R in the work of Hanson et al. (2003) that included sites with much higher TP concentrations over the same DOC range than in all other studies under consideration.

Similar to the PCA results, multiple regressions containing DOC, Chl *a* and TP as independent variables performed for all data sets mentioned above pointed out that apart from Chl *a*, DOC was a powerful predictor of site averaged AGP. The effect of TP on AGP in the presence of DOC and Chl *a* was not significant except for our pooled 1 data where it had only a marginal significance (p = 0.047). DOC and Chl *a* had respectively negative and positive effects on the rates of AGP. The addition of DOC to the linear regression models containing Chl *a* as a single independent variable increased strongly the percentage of the explained variance in AGP compared to Chl *a* alone, e. g. the percentages of variance in AGP explained by Chl *a* alone vs. that explained by both Chl *a* and DOC were the following: 73.8 vs. 94.3 (del Giorgio and Peters 1994); 19.3 vs. 73.2 (Carignan et al. 2000); 22.2 vs. 76.3 (Hanson et al. 2003); 38.8 vs. 72.6 (pooled 1 data: models 6-1 and 11, Table

3.6; see also Fig. 3.7A), and 42.6 vs. 79.9 (pooled 2 data: models 6-2 and 12, Table 3.6; see also Fig 3.7B).

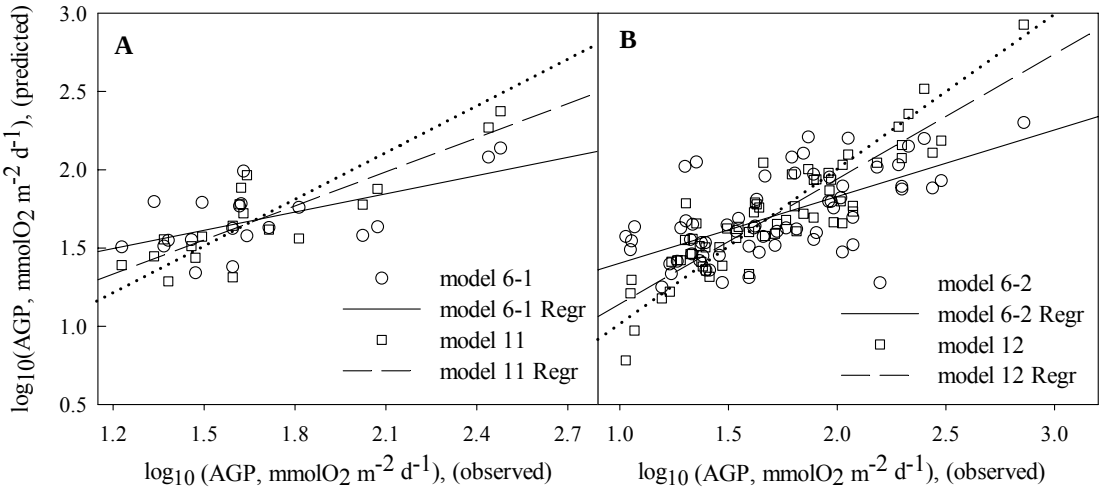

Fig. 3.7 (A) observed vs predicted values of AGP by models 6-1 and 11 (Table 3.6): model 6-1 (circles) and model 11 (squares); dotted line is 1:1 line; (B) observed vs predicted values of AGP by models 6-2 and 12 (Table 3.6): model 6-2 (circles) and model 12 (squares); dotted line is 1:1 line.

3.4.6 Seasonal rates of photosynthesis and respiration

Seasonal rates of AGP (ΣAGP, $mmolO_2\ m^{-2}$), AR (ΣAR, $mmolO_2\ m^{-2}$) and P_{int} (ΣP_{int}, $mmolC\ m^{-2}$) were determined for Lake Ontario and Hamilton Harbour only and separately for each sampling season (2003 and 2004) over the entire sampling season (May 10 to September 3 inclusive). There were only little variations in ΣAGP and ΣAR between 2003 and 2004. Rates of ΣAGP were the following: 14,590 (LO, 2003); 14,475 (LO, 2004); 36,867 (HH, 2003) and 34,617 (HH, 2004). Rates of ΣAR in Lake Ontario were approximately half of ΣAGP rates: 7,562 (LO, 2003) and 7,714 (LO, 2004); while in Hamilton Harbor the share of ΣAR in ΣAGP was larger reaching 60 to 70 percent: 25,209 (HH, 2003) and 21,614 (HH, 2004). Rates of ΣP_{int} were as follows: 8,245 (LO, 2003); 6,000 (LO, 2004); 19,374 (HH, 2003) and 18,643 (HH, 2004).

3.4.7 Ratio between areal rates of photosynthesis and respiration

The individual AGP/AR ratios varied over the course of the sampling season. In Lake Ontario, their trends were more or less similar in both years. In 2003 (Fig. 3.2C), AGP/AR ratios were below unity in the spring (mid May), then peaked during the algal bloom (late May to mid June) and declined afterwards to the values slightly above or below unity (August to September). In 2004 (Fig. 3.2D), AGP/AR ratios were high in the spring (May) and declined towards mid summer with a peak during the late summer algal bloom (late August). The seasonal dynamics of AGP/AR ratios in Hamilton Harbour was similar between 2003 and 2004 years (Fig. 3.3C, D). The harbour surface mixed layer (SML) was net heterotrophic (AGP/AR < 1) in May and early June and became net autotrophic (AGP/AR > 1) during the stratified period (mid June to September) and became net heterotrophic again in the autumn (early October). The observed ratios of AGP to AR in Georgian Bay and Woods Bay were above unity and were higher in the former (Table 3.3).

Short-term variations in AGP/AR ratios were only correlated (simple linear regressions) positively with either P_{max}/R ($p = 0.000$; $n = 41$) or Z_{eu}/Z_m ($p = 0.009$; $n = 41$). A multiple regression has shown that both of them were significant variables in predicting AGP/AR ratios (0.000, $R^2 = 0.840$, $n = 41$), and thus, instantaneous AGP/AR can be well predicted if we know both P_{max}/R and Z_{eu}/Z_m (model 13, Table 3.6; Fig. 3.8). Similar to our data, multiple regression containing P_{max}/R and Z_{eu}/Z_m as independent variables could explain 96.5%, 84.5% and 88.1% in variability in individual AGP/AR in data of Depew et al. (2006*b*), Carignan et al. (2000), or in the pooled 1 data (model 14, Table 3.6).

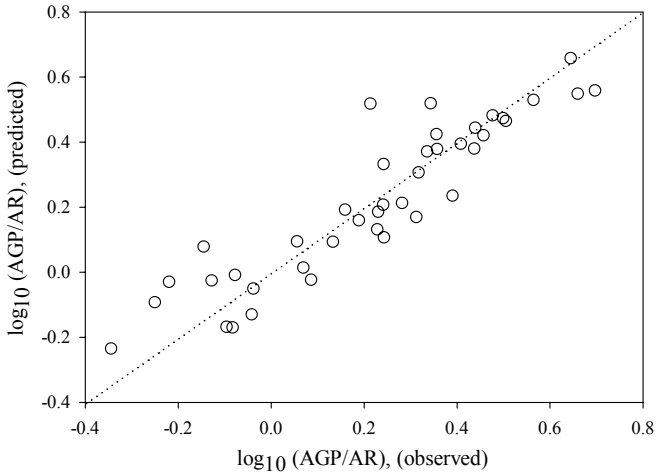

Fig. 3.8 Observed vs predicted values of AGP/AR by model 13 (Table 3.6) for the individual data (n = 41); dotted line is 1:1 line.

Despite the fact that a simple regression analysis showed no relationship between individual AGP/AR and proxies of the trophic status, a multiple regression analysis indicated that AGP/AR was controlled by the joint effect of trophic status (Chl *a*, TP) and variations in physical environment (Z_{eu}/Z_m). Our own data (n = 41) showed that in predictions of PMB_m two variables were significant, Z_{eu}/Z_m and Chl *a* (model 15, Table 3.6) while pooled 1 dataset that included more observations (n =126) has indicated that all three variables were significant predictors (model 16, Table 3.6) with Chl *a* and Z_{eu}/Z_m having positive and TP having negative effects on metabolic balance.

Our average AGP/AR ratios were higher in lower DOC systems (e.g. Lake Ontario and Georgian Bay) and lower in higher DOC systems (e.g. Hamilton Harbour and Woods Bay) (Table 3.3). Our pooled 1 data set (n = 19) have shown that average AGP/AR ratios were not correlated with the trophic status but had a negative correlation with DOC ($\log_{10}$[AGP/AR] = 0.465±0.069 – 0.367±0.121·$\log_{10}$[DOC], p = 0.007, R^2 = 0.353) and a positive one with either Z_m (p = 0.041) or Z_{eu} (p = 0.005). The way DOC affected AGP/AR was similar to that of physical factors, Z_m and Z_{eu}. A multiple regression containing DOC, Z_m and Z_{eu} as independent variables showed that DOC did not

explain any significant variation explanation beyond what Z_{eu} and Z_m did. Either Z_{eu} or Z_m were able to drive DOC away from the multiple regression models but their contributions to the predictions of PMB_m were similar to DOC except individual data of Carignan et al. (2000) where either Z_{eu} or Z_m was a significant variable and DOC not.

Overall, ratios between average AGP and average AR (ratios between averages) were slightly larger in more oligotrophic and lower DOC systems (but also a more shallower system, $Z_{eu}>Z_m$) than in eutrophic and higher DOC systems (that was also a deeper system, $Z_{eu}\approx Z_m$): 1.93 (LO, 2003), 1.88 (LO, 2004), 1.46 (HH, 2003) and 1.60 (HH, 2004). They were also larger in Georgian Bay (2.11) than in Woods Bay (1.49). According to our data, ratios between averages were positively correlated with Chl *a* (p = 0.029; n = 6) while Carignan and others (2000) data suggested a negative correlation with TP (p = 0.016; n = 12) and a positive one with Z_{eu} (p= 0.009; n = 12) only. However, our pooled 1 data set (n = 19) yielded results (simple linear regressions) where ratios between averages were correlated positively with Z_{eu}/Z_m (p = 0.034) and Chl *a* (p = 0.020), and negatively with either TP (p = 0.008) or DOC (p = 0.039). But if we look at our pooled 2 data set (n = 64), then AGP/AR ratios between averages were only correlated negatively with DOC ($\log_{10}[AGP/AR] = 0.389\pm0.099 - 0.671\pm0.127\cdot\log_{10}[DOC]$; p = 0.000, R^2 = 0.312) or positively with Z_m (p = 0.023). It is worth mentioning that it was not possible to examine the effect of Z_{eu}/Z_m on metabolic balance as the data on Z_{eu} were not reported by either del Giorgio and Peters (1994) or Hanson et al. (2003). Unlike simple regressions, a multiple linear regression for our pooled 2 data containing Z_m, DOC, Chl *a*, TP as independent variables showed that only last three variables were significant with a negative effects of DOC and TP, and a positive effect of Chl *a* on AGP/AR ratios between averages (model 17, Table 3.6). Based on the semi-partial correlation analysis of model 17 (Table 3.6), a unique contribution towards explanation of metabolic balance is slightly higher for DOC (42.8%) than that of Chl *a* (23.7%) and lower for TP (11.0%).

3.5 Discussion

3.5.1 Photosynthetic parameters: α^B, I_k and P^B_m

Our mean values of I_k for Hamilton Harbour and western Lake Ontario were lower than those observed by Millard et al. (1996) for eastern and central Lake Ontario stations but close to I_k values reported by Carignan et al. (2000) for the oligotrophic Shield Lakes, and within the range of values compiled by Harris (1978). Mean values of I_k for Woods Bay and Georgian Bay were lower than those of Lake Ontario. Mean α^B values reported in this study were almost twice as high when compared to those observed by Millard et al. (1996) and Millard et al. (1999) for Lake Ontario and Bay of Quinte. The difference might be explained by the use of different types of light sources used in the incubation experiments, as the spectral match of lamp irradiance and the algal absorption spectrum is an important factor determining the value of α^B (Markager and Vincent 2001). Our P^B_m values for Lake Ontario and Georgian Bay were within the mean values reported by others for Lake Ontario or other oligotrophic systems (Millard et al. 1996; Carignan et. al. 2000). Mean value of P^B_m rates for Hamilton Harbour was only slightly above those reported by Millard et al. (1999) for two stations at the eutrophic Bay of Quinte: Upper Bay and Middle Bay. Rates of P^B_m in Woods Bay were lower compared to other sites, but they were not unreasonably low and were within the range of values reported for ELA and SAQ (Saqvaqjuac) lakes (Fee et al. 1987; Welch 1985).

3.5.2 Rates of areal Photosynthesis and Respiration

Our P_{int} estimates in Lake Ontario were consistent with the previous studies (e.g. Glooshenko 1974; Millard et al. 1999) while those in Hamilton Harbour were close or slightly higher than rates reported for the eutrophic Bay of Quinte (Lake Ontario) by Millard et al. (1999). Our rates of P_{int} estimated for Woods Bay and Georgian Bay were similar to those observed by Watson et al. (1975) for Georgian Bay and were close to the rates of production in small and oligotrophic southern Quebec lakes (del Giorgio and Peters 1994).

AGP and AR rates are well correlated for low to moderate DOC systems (e.g. pooled 1 dataset) but this breaks down in higher DOC systems (e.g. del Giorgio and Peters 1994; Hanson et al. 2003), implying a change in degree of coupling (Hanson et al. 2003). A relationship between AGP and AR was also stronger for site averaged than for instantaneous rates. This suggests a tighter coupling of metabolic rates on a seasonal scale and a looser coupling on the scale of individual observations. A weaker relationship between AGP and AR in the studies that included high DOC lakes (e.g. del Giorgio and Peters 1994; Hanson et al. 2003) could be explained by the fact that the higher DOC concentrations are more efficient in decoupling AR from AGP. There are also other possible reasons why coupling between AGP and AR are weaker in those two studies: (i) the effect of under-sampling as the studied systems were sampled only a few times (e.g. del Giorgio and Peters 1994) or only once in the season over a very short time of 2-4 days only (e.g. Hanson et al. 2003) when production and consumption were probably not coupled; and (ii) different methodology to estimate AGP and AR were applied; our pooled 1 dataset was all based on the direct measurements of oxygen to estimate production and respiration, while del Giorgio and Peters (1994) and Hanson et al. (2003) were using different methodologies.

Both individual and mean rates of AGP and AR were correlated with the proxies of the trophic level (Chl *a* or TP). If the rates of photosynthesis and respiration are coupled and both correlated with Chl *a*, this would suggest a dependence of bacterial metabolism on the phytoplankton production especially in low DOC systems. There are several recent papers suggesting that even in the systems that are dominated by allochthonous carbon, the autochthonous carbon may be an important substrate for bacterial growth (e.g. Bukaveckas et al. 2002; Kritzberg et al. 2004). Hanson et al. (2003) had also suggested that at low DOC concentrations community respiration was based on phytoplankton production as they found that the rates of gross photosynthesis and respiration were comparable. Correlations of AGP and AR with either Chl *a* or TP are rather similar and suggest little change in their ratio over productivity gradient, so both instantaneous and average AGP/AR ratios are

not trophic related. This implies that some other factors such as DOC or changes in the physical environment (Z_{eu}, Z_m) may be important.

DOC may increase volumetric R where nutrients are high enough (e.g. Hanson et al. 2003) but various data sets agree that it does not control AR because of the coincident changes in Z_m. DOC affects Z_m in small lakes (Christensen et al. 1996; Fee et al. 1996) over which AR rates are integrated and this effect overrides the stimulation effect of DOC on bacterial respiration in the systems where nutrients are abundant.

If DOC does not affect AR but is correlated negatively with the PMB_m as some studies suggested (e.g. Prairie et al. 2002; Hanson et al. 2003), then, it should have an effect on AGP. Both the multiple regression analyses and PCA results have shown that DOC does depress AGP and significantly improves the relationships between AGP and Chl *a*. AGP is mainly a product of P_{max} and Z_{eu}, and in Chapter 2 we have shown that DOC does not affect P_{max} when controlled for the trophic status. Therefore, the negative impact of DOC on primary production is due to its light-attenuation properties and shading effect (Jones 1992) that decrease Z_{eu}. This is also supported by the fact that the addition of Z_{eu} into the multiple regression model of AGP vs Chl *a* and DOC removed DOC from the model in our pooled 1 dataset (n = 19). Del Giorgio and Peters (1994) and Hanson et al. (2003) did not report values for Z_{eu}, so we could not examine the effect of DOC on the latter. Our findings that DOC limits primary production are consistent with the previous studies (Jackson and Hecky 1980; Jones 1992; Carpenter et al. 1998).

3.5.3 Ratios of AGP to AR: average ratio vs. ratio between averages

In our study we report two ratios, an average ratio of AGP/AR and a ratio of average AGP to average AR (ratio between averages). The ratio between averages puts more emphasis on periods of high production and/or R, and thus the seasonal mass ratio of AGP to AR, while average ratio emphasizes most frequent ratio and thus the most typical production to respiration balance likely to be

encountered at any moment. Both ratios are meaningful depending on the purpose of their use; if we want the most frequent value in the AGP/AR distribution (average ratio) or we want to know the amount of production per unit of respiration, a value that is influenced by cases of high or very low production (ratio between averages). These two ratios are not exactly the same. For example, Hamilton Harbour 2003 data: 1.89 (average ratio) and 1.28 (ratio between averages). Their seasonal dynamics may differ. In the summer time, we could expect that there will be an approximate balance between production and consumption (AGP≈AR) in the SML most of the time (Fahnenstiel and Scavia 1987), and the big imbalances will occur in episodes such as a spring bloom (AGP>AR) or a clear water phase (AGP<AR). These episodic events are infrequent so the average ratio will tend to reflect the average condition, with AGP/AR being near unity except some cases where significant allochthonous subsidies (DOC) may affect it. Thus, for the average ratio, we do not expect strong variations with the trophic status. By contrast, the ratio between averages is likely to reflect the productivity of the system, with potential export production (AGP>AR) expected to be larger in more eutrophic systems (e.g. Cotner and Biddanda 2002). Where bacterial metabolism constrained by low nutrient and DOC availability we may also expect a greater prevalence of export production.

3.5.4 Ratios of AGP to AR (short-term variations)

Individual ratios of AGP/AR for SML were positively correlated with either P_{max}/R or Z_{eu}/Z_m. In Chapter 2, it was argued that the PMB_m was mostly a product of P_{max}/R and Z_{eu}/Z_m with only a small influence from the light response factor, $f1$. Strong correlations of AGP/AR with both P_{max}/R and Z_{eu}/Z_m observed in this study have proved that the $f1$ factor we defined is only a minor influence as we said it would be. The positive relationship between AGP/AR and Z_{eu}/Z_m is due to the fact that phytoplankton cells are confined to a shallower part of euphotic zone where light conditions are more favorable for growth. The larger Z_{eu}/Z_m ratio the higher average light intensity in the mixing layer, and thus better conditions for photosynthesis and growth. Some previous studies found similar results. For example, Grobbelaar (1985) used a phytoplankton production model of Grobbelaar

(1981) and Grobbelaar et al. (1984) to show the presence of a strong linear relationship between Z_{eu}/Z_m ratios and the productivity of a biomass (mg m^{-3} h^{-1}) in the water column. The dependence of PMB_m on both P_{max}/R and Z_{eu}/Z_m ratios stresses the importance of physical factors such as Z_{eu} and Z_m that play significant roles in the total planktonic production/respiration balance.

Short-term variations in AGP/AR had multiple regression relationships with Chl *a*, TP and Z_{eu}/Z_m of expected directions. The dependence of individual AGP/AR on Chl *a* in the presence of TP and Z_{eu}/Z_m indicates that instantaneous variations in metabolic balance depends on the looser coupling between production and respiration. The PMB_m is larger when production is able to escape from consumers (e.g. algal bloom conditions), and it is smaller when consumers finally catch up (e. g. clear-water phase). The positive effect of Z_{eu}/Z_m on AGP/AR is obvious as larger ratios mean higher light availability in Z_m that favours production over respiration. The negative effect of TP on PMB_m in the presence of Chl *a* and Z_{eu}/Z_m reflects the increasing role of bacterial biomass and respiration along the increasing gradient in TP concentrations. However, the R^2 of multiple regression relationship with Chl *a*, TP and Z_{eu}/Z_m is low, so the relationship is weak and other factors must be important too. This supports the idea that average ratios are not strongly linked to trophic status and related parameters. It is also worth mentioning that in the model 15 (Table 3.6) representing only our own data and consisted of high-energy sites, fluctuations in the physical environment (Z_{eu}/Z_m) explained more variance compared to the trophic status (Chl *a*); while in model 16 (Table 3.6) based on our pooled 1 dataset that also included a large proportion of small lakes (>40%), the physical environment was able to explain less variance than the trophic level did (Chl *a* or TP).

Overall, our individual AGP/AR ratios had a mean of 1.97 and were not different from those found in other similar studies, e.g. 1.8 (Carignan et al. 2000) and 1.99 (Depew et al. 2006*b*). Our short-term AGP/AR were mostly >1 for our low to moderate DOC sites, but within our data we did see lower AGP/AR where DOC was higher (e.g. Hamilton Harbour and Woods Bay). The persistence of AGP/AR ratios above unity and therefore net autotrophy in both oligotrophic and eutrophic sites

documented in our study as well as a coupling between AGP and AR on both short-term scale and seasonal scale support the classical view on lake metabolism that planktonic photosynthesis is sufficient to sustain the pelagic food web during the stratified summer period in the coastal zones studied here but also in the sites of other studies (Carignan et al. 2000; Depew et al. 2006*b*; Staehr and Sand-Jensen 2007).

3.5.5 Ratios of AGP to AR (inter-sites comparison)

Making comparison between two stations within each system (Hamilton Harbour vs. Lake Ontario and Woods Bay vs. Georgian Bay, it was found that the average ratios of AGP/AR were lower in the sites with the higher DOC and TP concentrations (Table 3.2 and 3.3). According to Prairie et al. (2002), DOC concentrations between 4 and 6 $mg \cdot L^{-1}$ (10 mg L^{-1}; Hanson et al. 2003) correspond to metabolic equilibrium, and lakes with DOC below this threshold tend to be autotrophic with AGP/AR above unity (Prairie et al. 2002). This also implies that lakes with lower DOC should be more autotrophic than those with higher DOC. Our sampling sites had DOC concentrations below that threshold and there is no surprise that they were found to be autotrophic with the sites with lower DOC having a larger degree of autotrophy. In this regard, our results followed the DOC theory of Prairie et al. (2002) and were in general agreement with the work of Carignan et al. (2000) and Hanson et al. (2003). Because almost all of Great Lakes are low to moderate DOC, this is a strong evidence for summertime autotrophy in the SML of the Laurentian Great Lakes.

Our data have shown that average ratios of AGP/AR were not related to Chl *a* or TP so they are not trophic-related. Instead, they were related to DOC but the way the latter affected average AGP/AR was similar to that of the physical factors, Z_m or Z_{eu}. This suggests again that DOC affects metabolic balance via fluctuations in the physical environment (Z_{eu}/Z_m) rather than through its impact on P_{max}/R (see Chapter 2).

Concentrations of DOC do correlate negatively with Z_{eu}/Z_m ratios in the work of Carignan et al. (2000) and in our pooled 1 data (p = 0.033, n = 12 and p = 0.008, n = 19, respectively). By affecting Z_{eu}/Z_m, DOC has a negative effect on AGP/AR ratios as the latter are directly proportional to Z_{eu}/Z_m. It may seem that higher DOC gives lower Z_{eu}/Z_m and lower Z_{eu}/Z_m gives higher P_{max}/R (see Chapter 2) that must cancel out the effect of DOC on PMB_m. However, the effect of DOC on Z_{eu}/Z_m overrides the consequent effect of Z_{eu}/Z_m on P_{max}/R. It is possible to re-express Z_{eu}/Z_m and P_{max}/R as the functions of DOC (by expressing Z_{eu}/Z_m as a function of DOC, and P_{max}/R as a function of Z_{eu}/Z_m with a substitution of the later with its functional relationship with DOC) based on our pooled 1 site-averaged data ($0.658[DOC]^{-0.734}$ and $0.57[DOC]^{0.274}$ respectively). The PMB_m is mainly a product of Z_{eu}/Z_m and P_{max}/R, and the multiplication of $0.658[DOC]^{-0.734}$ and $0.57[DOC]^{0.274}$ gives the following function $0.375[DOC]^{-0.46}$ which shows that increasing DOC should have a decreasing effect on PMB_m supporting the idea that the depressing effect of DOC on Z_{eu}/Z_m has an overriding power over the consequent stimulation effect of Z_{eu}/Z_m on P_{max}/R.

According to our data, AGP/AR ratios between averages had multiple regression relationship with Chl *a* (positive) and with DOC and TP (negative). While the positive and negative effects of Chl *a* and TP (respectively) are clear as the contribution of the former to photosynthesis is larger than to respiration along the increasing productivity gradient and the latter stimulates heterotrophic respiration, the negative impact of DOC on AGP/AR ratios is due to its light-attenuation properties (shading effect) that decreases Z_{eu}/Z_m ratio.

3.5.6 Comparison of the P_{opt} with P_{max}

Overall, there was a good relationship between carbon assimilation rates and gross photosynthesis measured as the oxygen evolution (models 2 and 2**, Table 3.5; Fig. 3.4). The average PQ* over many measurements (our data plus Depew et al. 2006*b* data; n = 76) was higher than a commonly accepted value of 1.2 but it was not unreasonably high as PQ depends on the nature of the principal photosynthetic products and can vary from near unity when carbohydrates are synthesized to as high

as 3 during synthesis of lipids (Wetzel 2001). Many studies have reported values for PQ* of similar magnitude (Bell and Kuparinen 1984; Megard et al. 1985; Fahnenstiel and Carrick 1988). PQ is also dependent on the nitrogen source, and PQ values of 1.2 and 1.6 would be expected respectively for ammonium and nitrate assimilation (Williams et al. 1979). Our average gross PQ* of 1.7 ± 0.08 (mean ± std. error) was not significantly different from 1.6 (one-sample *t*-test), a usually accepted PQ value when nitrate is the dominant nitrogen source (Williams et al. 1979). The average ratio of P_{max} to P_{opt} and the slope of the regression of P_{max} on P_{opt} (model 2*, Table 3.5) gave two different assessments of the typical PQ* value, and it is worth mentioning that they agree fairly well. If we assume a PQ for balanced growth to be 1.4 that is an average between 1.2 (dominant nitrogen source: ammonium; Williams et al. 1979) and 1.6 (dominant nitrogen source: nitrate; Williams et al. 1979), then our average net PQ* (=1.27) is slightly lower than the accepted PQ for balanced growth.

Our mean PQ* calculated over many estimates (n = 76) was in the PQ physiological range for nitrate assimilation growth but was still significantly larger than the traditionally accepted average value of 1.2. However, we did not measure what was the dominant nitrogen source. It might also be that ^{14}C method measures something slightly less than the gross photosynthesis. We used short incubations and total carbon fixation method so mechanisms like dissolved organic production and food web-based recycling of fixed carbon will not be important. By elimination, this suggests that internal recycling of respired carbon may be important. When this happens, less dissolved inorganic carbon needs to be taken up from the environment. There are many reasons why ^{14}C uptake may somehow underestimate gross photosynthesis. This can be due to (i) the existence of various pathways through which ^{14}C fixed by phytoplankton is transformed to DOC and DOC is rapidly oxidized (respired) to CO_2 (Sakshaug et al. 1997); (ii) the presence of the inhibitory contaminants in our tracer solution ($NaH^{14}CO_3$) as the commercially available ^{14}C stock solutions may contain such contaminants (e.g. Fitzwater et al. 1982); or, (iii) a slow rate of diffusion of the radioactive isotope in and out of the cells (Yacobi et al. 2007).

3.5.7 Importance of sampling frequency in lake plankton metabolism studies

Recent metabolic studies have shown that the heterotrophic conditions are a common feature in the SML of many lakes (Prairie et al. 2002; Hanson et al. 2003; but see Carignan et al. 2000). However, many of those studies draw their conclusions from very low-frequency measurements for a given lake (e.g. del Giorgio and Peters 1994; Hanson et al. 2003) without estimating a seasonal balance AGP and AR. Our results have shown that the dynamics of PMB_m are very different over a temporal scale, especially in oligotrophic system. For example, Lake Ontario can be found to be strongly net autotrophic (e.g. June 2003) or slightly heterotrophic (e.g. August 2003) but with the overall seasonal photosynthesis exceeding seasonal respiration. Therefore, the under-sampling might miss the pulses of high primary production such as algal blooms (e.g. early summer 2003 in Lake Ontario) and underestimate a production/respiration balance leading to a false impression of the prevalence of the net heterotrophic conditions. A recent study of metabolic balance in Lake Erie with more frequent sampling (Depew et al. 2006*b*) has shown that the balance was predominantly close to unity ($AGP/AR \approx 1$) with occasional high autotrophic conditions ($AGP/AR >> 1$) during a stratified season (July to September 2002). Another recent lake metabolic study of the nutrient-rich shallow Danish lake with the continuous measurements of production/respiration balance in the SML found that PMB was annually balanced with net autotrophy observed in the summer (mid May to mid September) and net heterotopy outside of that time range (Staehr and Sand-Jensen 2007). Therefore, conclusions about plankton metabolism may not be correct if they are based on low sampling frequency data. However, our conclusion about the frequency of measurements was influenced by the results of PMB_m in large lakes that are not in steady state and always in transition in response to atmospheric forcing, while small lakes can be different as they can be viewed as satisfying steady state assumptions during stratified season.

Chapter 4

Photosynthesis, respiration and stable oxygen isotope dynamics in plankton systems of contrasting trophic status and physical stability.

4.1 Abstract

The natural abundance of stable oxygen isotopes ($^{18}O/^{16}O$) has been used to infer system metabolism (P to R ratios) in lakes and rivers but only rarely with any comparison against independent methods. In this study, the eutrophic and thermally stratified Hamilton Harbour was compared against the oligotrophic and physically dynamic western Lake Ontario to determine whether useful information on P, R and P/R could be obtained at different levels of system productivity and disturbance. Independent measurements of P and R were made by incubating plankton samples in bottles and compared against estimates from a stable isotope model, adjusted for wind-driven gas exchange. The $\delta^{18}O$ of dissolved oxygen ($\delta^{18}O$-DO) in the surface mixed layer (SML) was typically below atmospheric equilibrium and DO above saturation over the spring to early fall observation period. The SML of Hamilton Harbour was predicted to be usually net autotrophic (P>R) by both the isotope model and the bottle incubations, while absolute rates of P from the isotope model correlated well with bottle estimates in the harbour and some other relatively sheltered sites that were sampled occasionally. Isotope model estimates for R in the harbour were not well correlated with bottle estimates, but were of comparable magnitude on average and differences were explicable in terms of physical forces and the different time scales of response for the two methods. By contrast, the isotope model in Lake Ontario gave internally inconsistent results (e.g. negative absolute rates of P and R) and poor agreement with independent estimates of P, R and P/R despite superficially plausible estimates for P/R. The low productivity and strong physical disturbance in Lake Ontario appeared to confound the biological signals in the isotope signatures and invalidate the steady-state isotope

model. The hypolimnion of the harbour presented another type of paradoxical behaviour, as the seasonal development of DO depletion was not accompanied by the progressive isotope enrichment expected from respiratory fractionation. The Lake Ontario and harbour hypolimnion results both appear to show that simple steady state models that assume constant fractionation processes and ignore physical dynamics are of limited applicability to lakes.

4.2 Introduction

Biological processes in aquatic ecosystems such as photosynthesis (P) and respiration (R) play a crucial role in regulating fluxes of many important elements. Amongst those elements, oxygen (O_2) is probably the most fundamental parameter of lakes and rivers (Wetzel 2001), and its cycle is the largest biogeochemical cycle in aquatic systems (Luz et al. 2002). The dynamics of oxygen concentrations are governed by a balance between rates of P and R (Wetzel 2001). Photosynthesis produces organic matter and releases oxygen whereas aerobic respiration consumes organic matter and uses oxygen. Oxygen production usually predominates in the light while oxygen consumption predominates in the dark.

The balance between P and R rates (P/R) lies at the basis of an understanding of carbon flow and food web structure in aquatic ecosystems. Ecosystems, where total planktonic respiration exceeds photosynthesis ($P<R$ or $P/R<1$) are net heterotrophic; they are net consumers of organic carbon and oxygen. Contrary, ecosystems where photosynthesis exceeds respiration ($P>R$ or $P/R>1$) are net autotrophic; they are net producers of organic carbon and oxygen. In a balanced system, respiration and photosynthesis are equal, but natural systems are open systems and are rarely in balance (Russ et al. 2004). P/R ratios more than 1 can be a result of excessive nutrient loading and occur when the amount of autochthonous organic carbon produced by photosynthesis is larger than that consumed by respiration. Respiration may exceed photosynthesis in nutrient poor or light-limited waters with inputs of allochthonous organic carbon (Carignan et al. 2000).

Our understanding of carbon flow and of the P/R ratios is still limited and is the subject of an ongoing debate in oceanography and limnology (del Giorgio and Peters, 1994; del Giorgio et al., 1997; Carignan et al., 2000; Prairie et al. 2002; Hanson et al. 2003). The apparent contradiction between the results of Carignan et al. (2000) and del Giorgio and Peters (1994) was probably in the uncertainties of the applied *in vitro* methods, oxygen light-and-dark bottle method (OLDB) and ^{14}C assimilation technique. Although these two methods have been used for several decades, some questions remain whether those methods can provide reasonable estimates of photosynthetic and respiration rates representative of the *in situ* conditions (Howarth and Michaels 2000). A significant part of the controversy concerns problems that are common to *in vitro* based methods. These problems include containment and manipulation effects, proper storage and incubation conditions, artificial light source with different wavelengths, the uncertainties with the choice of proper incubation time, lack of both mixing and hydrostatic pressure as well as nutrient fluxes inside the bottles that are common for natural systems (Howarth and Michaels 2000). In principle, any measurement of a water sample in a closed glass bottle, even when carried out *in situ*, will not guarantee a primary production value which reflects that of the water of the site of collection. The absence of turbulence, which influences the amount of nutrients, light, excretion products, and CO_2, could conceivably change primary production inside the bottle. Furthermore, the glass surface of the bottle is a substrate for bacteria and some algal species, which grow rapidly under these circumstances (Howarth and Michaels 2000). Therefore, in order to get real estimates of P and R rates, they must be measured under *in situ* conditions without any bottle incubations and artificial laboratory conditions; although it has been done successfully (Fahnenstiel and Carrick 1988).

Over the past decade, stable isotopes have shown to be powerful tools in a wide range of applications in aquatic sciences. Natural abundance isotopic signatures have proven to be useful in unraveling food-web pathways or tracing organic matter and nutrient sources (Fry 2006). More recent applications involved the use of stable isotopes in unconfined, field experiments where certain

isotopes can be used as tracers for metabolic rates or their ratio measurements. One of such recent applications is the use of natural abundance of oxygen stable isotope ($^{18}O/^{16}O$) of dissolved oxygen ($\delta^{18}O$-DO) to determine the ratios of P to R in freshwater ecosystems. The first application of this method and its approach was described by Quay et al. (1995).

The literature review has shown that ^{18}O method using natural abundances in $\delta^{18}O$-DO to calculate plankton P/R ratios was applied to mostly oligotrophic environments (e.g. Quay et al. 1995; Russ et al. 2004; Ostrom et al. 2005) with one exception, the eutrophic west basin of Lake Erie (Ostrom et al. 2005). To date, there are no reported applications of this method to more productive systems than the western basin of Lake Erie. The current study of Hamilton Harbour (western Lake Ontario) is the first application of this method to a higher productivity system than western Lake Erie.

In the literature regarding lentic systems, to date, there are no direct comparisons of the results of ^{18}O method based on the natural abundance of oxygen and its isotopic signature with any of the traditional methods except one study comparing ^{18}O method with the oxygen diel method in a shallow channelized stream with a mean depth of 15-20 cm (Tobias et al. 2007). Are they meaningful and valid as we think they are? To draw any conclusion about the meaning of this method, the results of ^{18}O method need to be directly compared to other methods. Thus, the main aim of this study was to compare ratios of photosynthesis to respiration derived from two methods, ^{18}O and one of the traditional methods that is a bottle incubation method based on Fee model for calculation *in situ* photosynthesis and dark bottle incubations for calculation of the plankton respiration rates (thereafter called as “bottle method” or “bottle estimates”).

Moreover, the studies reporting the ratios of plankton photosynthesis to respiration (e.g. Quay et al. 1995; Russ et al. 2004; Ostrom et al. 2005) did not make any attempt to estimate the absolute rates of P and R. However, it is possible to calculate absolute rates of P and R if one knows the magnitude of the gas exchange rates between atmosphere and water surface. The estimates of gas exchange are not new in aquatic science and have already been applied in many lake metabolism

studies (e.g. Cole et al. 2000*a*; Hanson et al. 2003). Therefore, we decided to calculate gas exchange rates and apply them to the steady state model to estimate absolute rates of P and R (a similar approach used by Tobias et al. (2007) in their recent stream metabolism study) to see if P and R are in the reasonable range and their seasonal dynamics follow those predicted by the traditional method.

The results of ^{18}O method are sensitive to isotopic fractionation factor during respiration (α_r) and the interpretation of the variations in oxygen isotopic composition requires knowing the representative community α_r (Kiddon et al. 1993). The latter depends on the nature of planktonic community because of the high variability in the individual α_r values (Kiddon et al. 1993), and therefore needs to be measured. There is no existing literature on measurements of bottle-derived plankton community α_r in the large freshwater systems (e.g. LGL) except those measured in Lake Erie (Wang 2005). The α_r measurement is tedious involving incubations several days long, and there is a growing tendency to use the assumed values for α_r, especially for those systems where the literature data do not exist, e.g. LGL. For example, Russ et al. (2004) and Ostrom et al. (2005) used α_r (=0.977) measured for lake Kinneret (Luz et al. 2002) in their studies of Lake Superior and Lake Erie. Can we justify the use of lake Kinneret's value of α_r for the LGL assuming a similar plankton composition? The lake Kinneret differs from the temperate LGL in many parameters. For example, it is small (170 km^2) and shallow (mean depth of 24 m) subtropical warm monomictic lake (13-30ºC) (Hadas and Pinkas 1995; Hart et al. 2000) circulating in the winter (late December to February) and strongly stratified from April to November with an anoxic hypolimnion (Hart et al. 2000); it is higher in nutrient concentrations (meso-eutrophic lake) with the biomass in the eutrophic range, e. g. the annual averages (from 1972 to 1993) of chlorophyll ranged from 127 to 247 mg m^{-3} (Berman et al. 1995); moreover, it is rather a storage reservoir than a natural lake and undergoes annual fluctuations in water levels of 1-4 m (Hambright et al. 1994). If the limnological parameters are not the same, then one can expect different plankton composition and therefore different values for α_r. What if the α_r measured in the Lake Kinneret are different by several ‰ from those of large lakes (e.g. LGL)? Can

we trust the ^{18}O model results with α_r=0.977 showing the predominance of heterotrophic conditions in the large oligotrophic and low DOC clear water lakes? Therefore, one of the goals of our study was to measure the isotopic fractionation during respiration in Lake Ontario as well as in Hamilton Harbour.

4.3 Materials and Method

4.3.1 The $\delta^{18}O$ of DO as a tracer of biological productivity

Oxygen has three stable isotopes with the following abundances: ^{16}O (99.763 %), ^{17}O (0.0375 %) and ^{18}O (0.1995 %). Because of the higher abundance and the greater mass difference, the ratio of $^{18}O/^{16}O$ is usually used and reported as delta value. Delta value (δ) is used to express the isotopic composition in terms of per mil (‰) deviation from Standard Mean Ocean Water (SMOW) or Vienna Standard Mean Ocean Water (VSMOW).

The $\delta^{18}O$-O_2 is a unique biological tracer that can be used in a determination of P/R ratios. Under the assumption that mixing and water movement are not important, there are primarily three processes affecting the $\delta^{18}O$: air-water gas exchange, respiration and photosynthesis. Gas exchange drives the $\delta^{18}O$-DO towards 24.2‰. Photosynthesis produces O_2 with the $\delta^{18}O$ of the lake water (H_2O) which is variable among lakes and produces O_2 that is depleted in $\delta^{18}O$ relative to O_2 derived from air-water gas exchange. During respiration, the ^{16}O-^{16}O uptake rate is higher than the ^{18}O-^{16}O uptake rate, and therefore respiration increases the $^{18}O/^{16}O$ of the remaining DO causing the enrichment of $\delta^{18}O$-DO. Thus, when gas exchange dominates over photosynthesis and respiration, DO is close to the saturation and the $\delta^{18}O$-DO is ~24.2‰. When photosynthesis exceeds respiration, DO will be supersaturated and $\delta^{18}O$-DO will be <24.2‰. If respiration dominates over photosynthesis, then DO will be unsaturated with $\delta^{18}O$ being higher or lower than 24.2‰ (Quay et al. 1993; Wang and Veizer 2000). All these give a unique opportunity to distinguish different oxygen fluxes and quantify the rates of primary production and respiration.

4.3.2 Study sites

The main system selected for this study was Hamilton Harbour vs. adjacent western Lake Ontario, where two stations have been selected to provide two different conditions in thermal structure, biomass, inorganic nutrient status and dissolved organic carbon (DOC) concentrations. Apart from the main system, two additional sites were sampled in Lake Huron: Georgian Bay and Woods Bay. The locations of the stations and their physical depths are shown in Table 4.1. More detailed information can be found in Chapter 2 and Chapter 3.

4.3.3 Field methods

Stations of the main system were visited approximately at biweekly intervals from early May to early September in 2003 and to early October in 2004. A more intense sampling (every second day) was conducted in the last week of August 2004. Georgian Bay and Woods Bay stations were visited 4 times, but the present study includes only data from 2004 visits (June and August trips) when ^{14}C and oxygen light-and-dark bottle incubation were run to compare the results with ^{18}O method. During each visit, 2 water samples for $\delta^{18}O$-DO were taken from the upper (2 m) and lower parts of the surface mixed layer. The second sampling depth was a few meters deeper than 2 m depth depending on the thickness of the surface mixed layer. However, during the conditions of full mixing in early spring when water column was isothermal and well mixed, the sampling depth for $\delta^{18}O$-DO was only 2 m. The water samples for $\delta^{18}O$-H_2O were routinely taken at the depth of 2 m. In the Hamilton Harbour site, we also collected hypolimnetic water from one depth in the middle of hypolimnion (depth: 12-16 m) to determine the isotopic compositions of both DO and H_2O.

Table 4.1 Locations and physical depths of sampling sites.

Station	Location	Latitude North, Longitude West	Station depth, m
Hamilton Harbour	W. Lake Ontario	43°17.3'N, 79°50.4'W	19
Lake Ontario	W. Lake Ontario	43°17.3'N, 79°43.9'W	19
Woods Bay	E. Georgian Bay (Lake Huron)	45°08.5'N, 80°00.1'W	6
Georgian Bay	E. Georgian Bay (Lake Huron)	45°07.8'N, 80°05.4'W	6

Table 4.2 List of selected notations often-used in the current Chapter.

Notation	Definition (units of measurements)
[DO%]	fractional concentration of DO (DO%/100)
DO	dissolved oxygen concentration (mg L^{-1})
DO%	percent of oxygen saturation in respect to equilibrium with air (%)
Chl *a*	chlorophyll *a* concentration (mg m^{-3})
PAR	photosynthetically available radiation (E m^{-2} d^{-1})
P	gross photosynthesis
P_{max}	light-saturated rates of gross photosynthesis ($mmolO_2$ m^{-3} h^{-1})
R	dark community respiration ($mmolO_2$ m^{-3} h^{-1})
SC	specific conductivity (mS cm^{-1})
SML	surface mixed layer (m)
T_w	*in situ* temperature of the surface mixed layer at measured depth (degree C)
T_{ws}	*in situ* water surface temperature (degree C)
k_{O2}	oxygen transfer velocity (m d^{-1})
VP	average volumetric P in the SML ($mmolO_2$ m^{-3} d^{-1}) based on Fee model
^{18}O-VP	average photosynthesis in the SML ($mmolO_2$ m^{-3} d^{-1}) derived from ^{18}O method
VR	bottle-based respiration rates in the surface mixed layer ($mmolO_2$ m^{-3} d^{-1})
^{18}O-VR	average respiration in the SML ($mmolO_2$ m^{-3} d^{-1}) derived from ^{18}O method
Z_m and Z_{eu}	surface mixed layer depth (Z_m, m) and euphotic depth (Z_{eu}, m)
α_r	isotopic fractionation effect during respiration
δ^{18}O-DO	$^{18}O/^{16}O$ ratio of dissolved oxygen (‰ vs. SMOW)
$\delta^{18}O$-H_2O	$^{18}O/^{16}O$ ratio of lake water (‰ vs. SMOW)

All water samples were collected in duplicates using a 10-L Niskin sampling bottle. Collection of water for determination of the isotopic composition of DO and H_2O followed the protocol of Emerson et al. (1991; 1999). Samples for δ^{18}O-DO analysis were collected in pre-evacuated 60-mL (for epilimnetic water) and 125 mL (for hypolimnetic samples when we expected low DO concentrations) serum bottles. Blue butyl septa (Bellco Glass 2048-11800) and aluminum crimp seals were used to seal the bottles (Wassennar and Koehler 1999). A new 21-gauge needle was used each time a septum was to be punctured to prevent the coring of the septum. The water samples were treated with 0.1 ml of saturated $HgCl_2$ to stop all biological activities. Samples for δ^{18}O-H_2O were collected in 40-mL plastic bottles. All samples for isotopic analysis of DO and H_2O were placed in the ice-filled cooler and taken to the laboratory for storage at 4° C pending further analysis. Water samples for DO were taken from the same Niskin bottle as δ^{18}O-DO water and were collected in 300-mL BOD bottles, fixed with the Winkler reagents immediately after collection and transported to the lab under *in situ* temperature in the coolers filled with the lake water to minimize the change in temperature. In the lab samples were stored in the temperature-controlled incubator under *in situ* temperature pending further analysis for DO. Dissolved oxygen concentrations, temperatures and specific conductivity were measured *in situ* with the YSI multi-parameter water quality datalogger (YSI 600XLM) equipped with the Rapid Pulse Clark-type oxygen sensor (accuracy: ±0.2 mg L^{-1}), conductivity probe (accuracy: ±0.004 mS cm^{-1}), temperature (accuracy: ±0.15ºC) and depth (accuracy: ±0.12 m) sensors. While the calibration of conductivity and pre-calibration of oxygen sensor were done in the lab, the final calibrations of the oxygen and depth sensors were done in the field under *in situ* conditions. Before each deployment, the profiler was allowed to run in the lake for at least 20 min to equilibrate with the water temperature and stabilize the DO readings. After retrieval of the water profiler, the readings of dissolved oxygen were validated by measuring DO in 100% water-saturated air. Chlorophyll *a* (Chl *a*) concentrations were determined from the integrated water sample collected over the entire depth of the SML.

To provide data to estimate the vertical thermal structure and the approximate position of the thermocline between sampling days, two thermistor strings were built and moored by the Canadian Center for Inland Waters (CCIW, Burlington, Ontario) in the summer of 2004 (from early June to October) at two our sampling sites: Lake Ontario and Hamilton Harbour stations. Each string held 11 temperature data loggers (HOBO Water Temp Pro; Onset Computer Corporation), which sampled at 10 min intervals. All sampling times were synchronized to have simultaneous measurements of temperatures along the entire water profile. The thermistors are temperature and time accurate to 0.2ºC and 1 min month^{-1} respectively, and have a resolution of 0.02 ºC. The thermistors were positioned at the fixed spacing. Hamilton Harbour string had temperature sensors at the following depths (m): 1, 3, 4, 5, 6, 7, 8, 9, 11, 16, and 21; and Lake Ontario one: 2, 4, 5, 6, 7, 8, 9, 10, 12, 14, and 17.

Meteorological data such as surface water temperature, average wind speed and wind directions were measured at two shore-based weather stations operated by the CCIW. One station designated for Hamilton Harbour was 3-m high and located on the CCIW break-wall (latitude: 43º17'50'' N; longitude: 79º48'50'' W), while the second one designated to collect information for Lake Ontario had 10 m height and was located on Burlington Pier (latitude: 43º17'50'' N; longitude: 79º47'30'' W). The following instruments were used: Campbell Scientific 107B temp probe with RH (air temperature), Vaisala model HMP35CF probe (relative humidity), Campbell Scientific 107B temp probe (surface water temperature), R.M. Young model 05103 wind monitor (wind speed and direction at the Hamilton Harbour site), Met One wind speed sensor (014A) and wind direction sensor (024A) (wind speed and direction at the Lake Ontario site), and Vaisala model PTA427 barometric pressure sensor (barometric pressure). Surface water temperatures were measured every 2 min and the wind speed and direction every 5 sec with the averaging of the data over 10 min intervals. Determination of the wind direction was done based on the following coordinate system: north (N) = 0º or 360º, east (E) = 90º, south (S) = 180º, and west (W) = 270º. We defined twelve 30º-wind-

direction sectors: NNE (0-30º), NE (30-60º), ENE (60-90º), ESE (90-120º), SE (120-150º), SSE (150-180º), SSW (180-210º), SW (210-240º), WSW (240-270º), WNW (270-300º), NW (300-330º) and NNW (330-360º). In the text, terms "westerly winds" and "easterly winds" will refer to the wind-direction sectors of 225-315º and 45-135º, respectively. Wind directions were considered to be low persistence (persisted for 1 day or so or less) and high persistence (persisted for 3 days or more). The PAR data was obtained from CCIW where a Li-Cor Biosciences quantum sensor (LI-190SA) was mounted on the roof of the CCIW building.

4.3.4 Measurements of the fractionation factor associated with respiration (α_r)

To determine isotopic fractionation during dark respiration, several series of dark incubation experiments were run. The water samples from both stations were incubated in a series of 8-L bottles under *in situ* temperatures in the dark. The incubation time ranged depending on the station and the amount of the planktonic biomass measured as Chl *a* and was usually 3 days for the Hamilton Harbour station and 4 days for the Lake Ontario station to assure that the detectable changes in δ^{18}O-DO can be measured. The δ^{18}O-DO and O_2 concentrations were measured in the beginning and in the end of each incubation experiment. A modified, high-precision Winkler method (Carignan et al. 1998) was used to determine DO concentration. The procedure for collection and analysis of water samples for δ^{18}O-DO followed the same protocol as it was done for the *in situ* samples. From the measured δ^{18}O-DO and DO, a value of α_r was determined by the use of the Rayleigh fractionation relationship following Broecker and Oversby (1971):

$$(4.1) \qquad R_t / R_o = \left(O_{2t} / O_{2o}\right)^{(\alpha_r - 1)}$$

where R is the measured isotopic composition $^{18}O/^{16}O$ of DO, O_2 is the oxygen concentration (DO), o and t represent conditions in the beginning and in the end of the experiment.

4.3.5 Analytical methods

The isotopic analyses of the samples for δ^{18}O-DO and δ^{18}O-H_2O were done at the University of Waterloo Environmental Isotope Laboratory. The δ^{18}O-DO was analyzed by using a continuous flow gas chromatograph isotope ratio mass spectrometer (CF-GCIRMS). A headspace of helium (UHP, Praxair) was added to the sample by simultaneously injecting the gas and withdrawing the corresponding volume of liquid. After equilibration an aliquot of the headspace gas was introduced to the Micromass Isochrom isotope ratio mass spectrometer through the reference gas line of a Gilson autosampler modified to accommodate the equipment required for δ^{18}O-DO analysis (Wassenaar and Koehler 1999). The precision on δ^{18}O-DO measurements was ±0.3‰. Water samples were analyzed for their $^{18}O/^{16}O$ ratio by the standard CO_2 equilibration technique (Epstein and Mayeda 1953; Fritz et al. 1986). A modified, precise Winkler method (Carignan et al. 1998) was used to determine DO concentrations of *in situ* water samples. The titrations were performed within 24 hours of water collection and 15 min of acidification using an automatic Mettler Toledo DL50 titrator. The standardization of thiosulfate was done on the same day as titrations. The average precision of the Winkler method was 4 $\mu gO_2\ L^{-1}$. Duplicate water samples for Chl *a* analysis were filtered under low vacuum through 0.7-µm pore-size GF/F glass fiber filters (AMD inc., Mississauga) then stored at –20°C for later analysis by fluorometry after 20-h extraction in 90% acetone in the dark at –20°C (Hiriart et al. 2002).

4.3.6 Statistical methods

All data for the statistical analyses were $\log_{10}$-transformed to stabilize the variances. The statistical analysis was performed with SYSTAT statistical software for Windows (Version 10.2). The linear regression analysis was used for least squared regressions (Model I) with a significance level of 5% or less ($p \leq 0.05$).

4.3.7 Determination of P/R ratios

Under the assumption that there is no mixing with sub-SML water or the effect of mixing is negligible, it may be assumed that three processes primarily control the concentration and isotopic composition of DO: photosynthesis, respiration and gas exchange at the air-water interface (Quay et al. 1995). The rate of change of DO can be represented by the following equation (Quay et al. 1995):

$$\frac{d(O_2)}{dt} = \frac{G}{Zm}\left(O_{2s} - O_2\right) - R + P \qquad (4.2)$$

where $d(O_2)/dt$ is the change in the concentration of O_2 over time, G is the gas transfer rate, Z_m is the mean depth of the surface mixed layer, O_{2s} is DO concentration at atmospheric saturation, O_2 is DO concentration of the water sample, R is the rate of respiration and P is the rate of photosynthesis.

Similarly, the rate of change for isotopic composition of DO over the same period of time can be expressed by the following equation (Quay et al. 1995):

$$\frac{d\left({}^{18:16}O\right)}{dt} = \frac{G}{Zm}\alpha_g \left\{\left(O_{2s}\,{}^{18:16}O_a \cdot \alpha_s\right) - O_2\,{}^{18:16}O\right\} + P\cdot{}^{18:16}O_w \cdot \alpha_p - R\cdot{}^{18:16}O \cdot \alpha_r \qquad (4.3)$$

where, $^{18:16}O$ is the oxygen isotope ratio of DO, α_g is a fractionation factor associated with gas transfer and equal to 0.9972 at 10˚C (Knox et al. 1992), $^{18:16}O_a$ is the isotopic ratio of atmospheric oxygen, α_s is the fractionation factor associated with the gas solubility in water and equal to 1.0007 at 28˚C (Benson and Krause 1984), $^{18:16}O_w$ is the isotopic composition of water, α_p is the ratio of the photosynthetic reaction rates of $H_2{}^{18}O$ to $H_2{}^{16}O$ and equal to 1.000±0.003 (Guy et al. 1993), α_r is the fractionation factor associated with respiration.

Finally, assuming steady state conditions, P/R ratios can be calculated from the measured values of O_2 and δ^{18}O-DO (Quay et al. 1995) using Eq. 4.2 and 4.3:

(4.4) $$P:R = \left({}^{18:16}\mathrm{O}\cdot\alpha_r - {}^{18:16}\mathrm{O}_g\right)/\left({}^{18:16}\mathrm{O}_w\cdot\alpha_p - {}^{18:16}\mathrm{O}_g\right)$$

where, ${}^{18:16}\mathrm{O}_g$ represents the ratio of the net air-water fluxes of ${}^{18:16}\mathrm{O}$ and ${}^{16:16}\mathrm{O}$ and can be found as:

(4.5) $${}^{18:16}\mathrm{O}_g = \frac{\alpha_g\cdot\left[{}^{18:16}\mathrm{O}_a\cdot\alpha_s - \left(\mathrm{O}_2/\mathrm{O}_{2s}\right){}^{18:16}\mathrm{O}\right]}{\left[1-\left(\mathrm{O}_2/\mathrm{O}_{2s}\right)\right]}$$

4.3.8 Determination of absolute P and R rates from ^{18}O method

Absolute rates of photosynthesis and respiration can be derived from Eq. 4.2 and 4.3 if the oxygen gas transfer rate (G) and Z_m are known. Rates of P can be calculated as:

(4.6) $$P = \frac{a\cdot c - b}{d - c}$$

(4.7) $$R = a + P$$

where $a = (G/Z_m)\cdot(O_{2s} - O_2)$; $b = (G/Z_m)\cdot\alpha_g\cdot(O_{2s}\cdot {}^{18:16}O_a\cdot\alpha_s - O_2\cdot {}^{18:16}O)$; $c = {}^{18:16}O\cdot\alpha_r$; and, $d = {}^{18:16}O_w\cdot\alpha_p$

4.3.9 Calculation of the oxygen transfer rate

The oxygen transfer rate is a product of multiplication of oxygen transfer velocity (k_{O2}, m d^{-1}) and the difference between oxygen concentration at atmospheric saturation (O_{2s}) and the actual concentration of the water sample (O_2). The latter can directly be measured in the field, and O_{2s} can be precisely calculated as a function of surface water temperature (T_{ws}), salinity (S) and atmospheric pressure, as given by Riley and Skirrow (1974). Therefore the main uncertainties in G are associated with defining value for k_{O2}. There are a number of predictive equations in the literature relating k_{O2} to the wind speed alone (e.g. Crusius and Wanninkhof 2003) or wind speed and Schmidt number (e.g. Wanninkhof 1992). Schmidt number (Sc) is a dimensionless number relating the ratio of inertial to

molecular diffusive forces and is used in gas exchange studies. Most of the existing work on lake metabolic studies using gas exchange has been done in small lakes and therefore calculations of k_{O2} were based on models derived from studies of small lakes. Hamilton Harbour and Lake Ontario are different from small lakes because of their sizes and the importance of physical forces, such as water movement and turbulence in the process of gas exchange. The small lake models usually do not take into account the variations in Schmidt number that depends on T_{ws} and in our study we observed substantial temporal variations in the latter from 4.2 to 23.2˚C in Lake Ontario and from 10.9 to 27.3˚C in Hamilton Harbour. Also, despite the fact that Hamilton Harbour has the size of a moderate lake (22 km^2), it does not fit a model for a static lake of similar size. It is very dynamic and subject to upwelling episodes and water exchanges with Lake Ontario (Barica 1989), with the water residence time only 90 days during the summer period. Therefore, in calculating k_{O2}, we decided to follow the approaches of two studies, small lake model of Crusius and Wanninkhof (2003) and ocean model of Wanninkhof (1992) to see which one can give reasonable and predictable values. The former source, depending on U_{10}, gives equations for k_{600} that is a k-value (CO_2 gas transfer velocity) normalized to Schmidt number = 600 (Sc_{600}) which is Sc of CO_2 at 20ºC in freshwater. To convert a gas transfer velocity from CO_2 to oxygen, we used the following relationship (MacIntyre et al. 1995):

$$(4.7) \qquad k_{o2} / k_{CO2} = (Sc_{O2} / Sc_{600})^{-\frac{1}{2}} = (Sc_{O2} / 600)^{-0.5}$$

Wanninkhof (1992) gives the following equation for k_{O2} (cm h^{-1}):

$$(4.8) \qquad k_{O2} = 0.31 \cdot U_{10}^2 \cdot \left(\frac{Sc}{660} \right)^{-0.5}$$

where 0.31 is a coefficient when short-term wind data are used, U_{10} is the wind velocity at 10 m height, Sc is the Schmidt number for oxygen and can be expressed as is a function of surface temperature (T_{ws}, ˚C) and salinity (S, ppt) according to:

$$(4.9) \qquad Sc = \left(0.9 + 0.1\frac{S}{350}\right) \cdot \left[1953.4 - 128.0T_{ws} + 3.9918T_{ws}^2 - 0.05009T_{ws}^3\right]$$

As wind at Hamilton Harbour site was measured at the height of 3 m, we used the empirical relationship of Kohler and Parmele (1967) to estimate wind at 10 m above the lake surface. Both weather stations were shore-based; therefore to estimate the wind speed at 10 m elevation above water surface at our stations, we used an approach from Fang and Stefan (1994):

$$(4.10) \quad U_{10m} = U_{10} \cdot F(fetch),$$

where U_{10} is a wind speed measured at 10 m height on land (m s^{-1}), and F(fetch) can be calculated as:

$$(4.11) \quad F(fetch) = \frac{\ln\frac{10}{z_{o2}} \cdot \ln\frac{\delta}{z_{o1}}}{\ln\frac{10}{z_{o1}} \ln\frac{\delta}{z_{o2}}} \cong \frac{5ZB + 4.6052}{3ZB + 9.2103}$$

where: z_{o1} is a roughness of land (assume 0.01 m; Kraus 1972); z_{o2} is a roughness of water surface (assume 0.0001 m; Ford and Stefan, 1980); δ is a thickness of wind boundary layer in meters over smooth surface that is a function of the fetch length (Elliott 1958); and ZB = 0.8 ln(fetch/2)-1.0718.

In estimating k_{O2}, we used a wind speed averaged over 72-h proceeding the actual time of water sampling (see Appendix A3) based on the assumption that the re-aeration rate of the SML in the harbour takes at least 3 days (assuming average Z_m = 6 m and k_{O2} = 2 m d^{-1}). Knowing from Emerson (1975) that gas exchange velocity in ocean is 1.9 to 8.8 m d^{-1} and from 0.6 to 1.9 in the lakes of US Great Lakes Basin, we expect typical values for k_{O2} to be somewhere within the range between 0.6 and 1.9 m d^{-1} or slightly larger than 1.9.

4.3.10 Determination of P and R from bottle method

Daily volumetric rates of photosynthesis averaged over Z_m were calculated with the help of the Fee model (Fee 1990). The approach is described in Chapter 3 and is based on the photosynthetic

parameters derived from P-I curve (^{14}C method), apparent photosynthetic quotient (PQ*), Z_m and the amount of incoming PAR. The only the difference was that in Chapter 3, PAR was assumed to be 70% of the clear sky solar radiation in accordance with the previous suggestions of Fee et al. (1992) and Millard et al. (1996), however, here we used the amount of actually measured PAR on the day of water sampling. Daily volumetric respiration rates were assumed to be similar throughout the SML and equal to those rates derived from dark bottle incubations.

4.4 Results

4.4.1 Thermal structure

In Hamilton Harbour, the summer stratification was stable in both years with a very distinct position of the thermocline, with Fig. 4.1*a* depicting thermal structure for 2004. However, it was observed that prevailing westerly winds and major water column perturbations in western Lake Ontario had a pronounced effect on the harbour thermal structure causing the fluctuations in the temperature isopleths. For example, Fig. 4.1*a* shows the largest oscillations in the temperature isopleths in the harbour happened during the upwelling episodes in western Lake Ontario (Fig. 4.1*b*). Unlike shallow SML in Hamilton Harbour, the thickness of the surface mixed layer in Lake Ontario was very variable and largely influenced by upwelling or downwelling episodes. The temporal loss of stratification (and followed by isothermal conditions) was observed during the pronounced upwelling episodes in both years with Fig. 4.1*b* depicting these for 2004. Temperature data from the thermistor strings in both systems (not shown here) supported the observation of thermal structure obtained from bi-weekly measured water profiles (Fig. 4.1*a*, *b*). Both Georgian Bay and Woods Bay stations did not have a well-defined thermocline and were mixed to the bottom at the times of both visits.

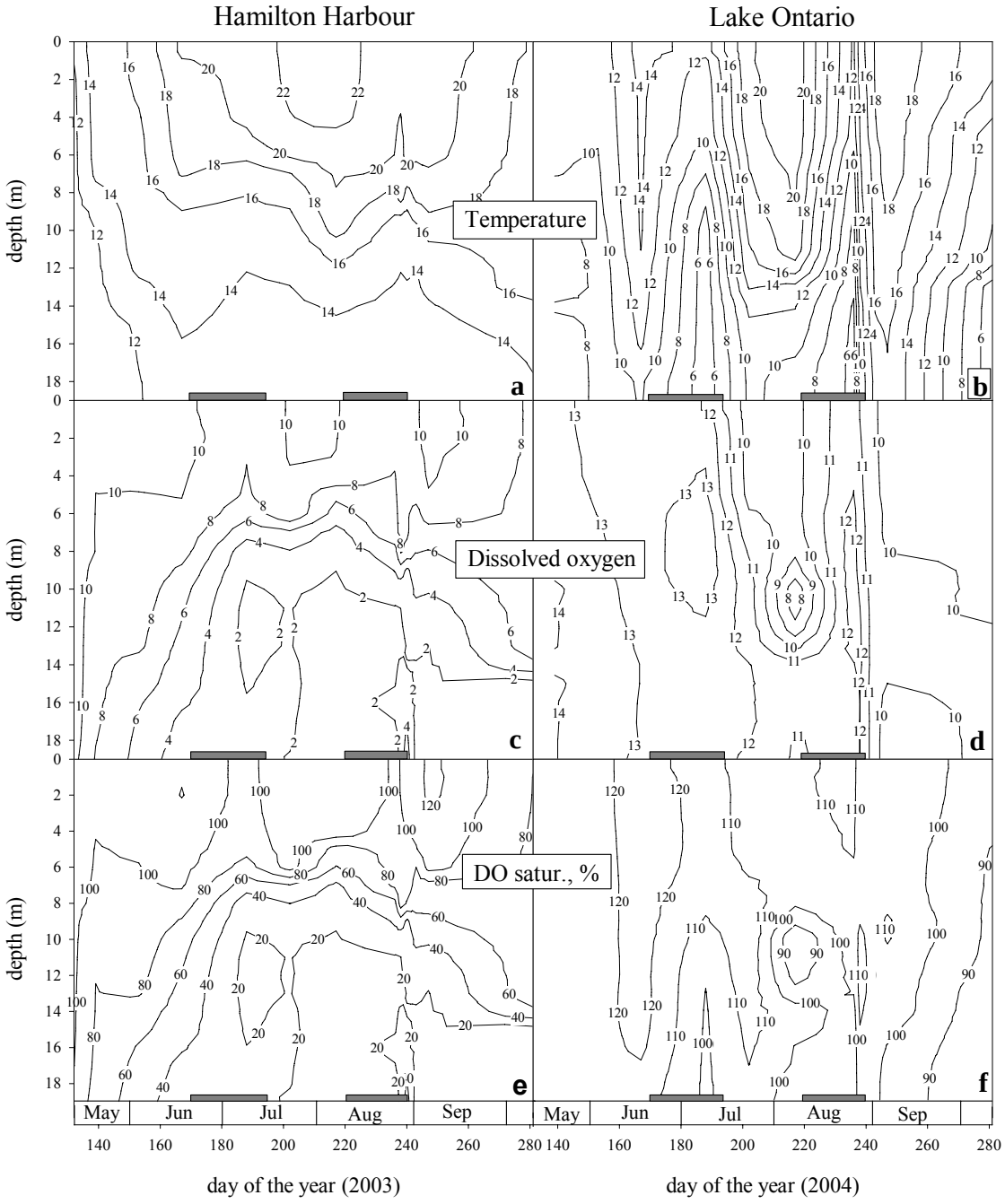

Fig. 4.1 Thermal and dissolved oxygen (DO) structure of water column in Hamilton Harbour and Lake Ontario determined from bi-weekly water profiles taken at the times of sampling from May 10 to October 7, 2004: (a) and (b) temperature (°C) isopleths for Hamilton Harbour (a) and Lake Ontario (b); (c) and (d) DO concentration (mg L^{-1}) isopleths for Hamilton Harbour (c) and Lake Ontario (d); (e) and (f) DO percent saturation (%) isopleths for Hamilton Harbour (e) and Lake Ontario (f). Horizontal gray bars correspond to the times of upwellings in western Lake Ontario.

4.4.2 Variations in chemical parameters

The SML in Lake Ontario had lower water temperature and specific conductivity (SpC, mS cm^{-1}) as well as higher DO concentration (mg L^{-1}) and oxygen percent saturation (DO%) than those in Hamilton Harbour (Table 4.3) with Fig. 4.1 depicting the differences in water temperature (T_w), DO and DO% for 2004. Average DO concentration in Hamilton Harbour hypolimnion was very low compared to SML (Table 4.3), while in Lake Ontario, hypolimnetic DO was similar or even larger than those of SML (Table 4.3). In Lake Ontario DO concentrations were the highest in the spring and had a slow decreasing trend from spring to fall. On average, the SML of Lake Ontario was degassing at the rate of 1 $mmolO_2\ m^{-3}\ d^{-1}$ that was equivalent to average areal rate of oxygen flux to atmosphere of 13 $mmolO_2\ m^{-2}\ d^{-1}$ (mean Z_m = 13 m). Concentrations of DO in Lake Ontario at 2 m depth were negatively correlated with T_w via simple regression ($p < 0.000$, $R^2 = 0.630$, n = 21), and negatively with T_w and positively with Chl *a* via multiple regression ($p < 0.000$, $R^2 = 0.739$, $n = 20$). DO% values in SML at different depths were almost always above saturation and were positively correlated with Chl *a* ($p = 0.013$, $R^2 = 0.311$, $n = 19$). DO in the SML of Hamilton Harbour were fluctuating up and down without a specific seasonal trend. DO% of the SML were usually above saturation except a few brief episodes when it dropped below 100%, with Fig. 1*e* depicting those episodes for 2004 (early July and end of August). DO concentrations in the harbour hypolimnion were low reaching hypoxic concentrations (< 2 mg L^{-1}) during the time of stable stratification (Fig. 4.1*c*). Georgian Bay had higher values in DO and DO% than those observed in Woods Bay (Table 4.3).

Table 4.3 Selected physical, chemical and isotopic properties of the water samples collected at 4 study sites. See text for the explanation of the terms used. For each variable we show the range of values and mean value ± standard deviation (both are shown in brackets). The letter "*n*" stands for the number of samples except the case with $\delta^{18}O\text{-}H_2O$ where *n* was different: 18 (Hamilton Harbour, SML), 10 (Hamilton Harbour, hypolimnion), 12 (Lake Ontario, SML), 4 (Woods Bay, SML) and 4 (Georgian Bay, SML).

	Hamilton Harbour		Lake Ontario		Georgian Bay	Woods Bay
	SML (n = 43)	hypolimnion (n = 20)	SML (n = 39)	hypolimnion (n = 7)	SML (n = 4)	SML (n = 4)
T_w, ºC	10.4 – 23.8 (18.7 ± 3.7)	11.3 – 18.8 (13.5±1.9)	4.2 – 23.2 (13.9 ±4.9)	4.8 – 23.1 (10.1 ± 6.7)	16.9 – 24.6 (19.9 ± 3.4)	19.1 – 25.3 (22.0 ± 2.5)
SpC, mS cm^{-1}	0.561 – 0.801 (0.671±0.08)	0.460 - 0.792 (0.572±0.108)	0.295 – 0.348 (0.307±0.012)	0.291 – 0.322 (0.305 ± 0.011)	0.117 – 0.161 (0.138 ± 0.022)	0.050 - 0.055 (0.053 ±0.002)
DO, mg L^{-1}	4.6 – 13.4 (9.5 ± 1.5)	0.4 – 6.6 (2.8 ± 1.8)	9.1 – 14.5 (11.4 ± 1.6)	9.1 – 13.7 (11.9 ± 1.6)	9.1 – 9.8 (9.4 ± 0.3)	7.7 – 9.2 (8.4 ± 0.7)
DO, % satur.	53.6 – 136.3 (102.7 ±17.3)	3.6 – 71.6 (27.0 ± 17.7)	87.9 – 127.1 (110.38 ± 8.0)	80.6 – 125.5 (105.5 ± 14.1)	100.1 – 111.6 (104.7 ± 5.2)	86.2 – 101.7 (97.0 ± 7.3)
$\delta^{18}O$-DO, ‰ vs. SMOW	15.3 – 27.07 (20.67 ± 2.86)	21.38 – 36.86 (26.80 ± 3.50)	20.87 – 25.93 (23.19 ± 1.03)	22.15 – 27.65 (23.72 ± 1.84)	22.18 – 24.61 (23.51 ± 0.91)	21.79 – 23.41 (22.51 – 0.67)
$\delta^{18}O\text{-}H_2O$, ‰ vs. SMOW	-8.02…-6.54 (-7.28 ± 0.45)	-7.70 …-6.77 (-7.08 ± 0.29)	-7.02…-6.3 (-6.67 ± 0.23)	not sampled	-8.2…-7.15 (-7.77 ± 0.47)	-9.16 …-7.74 (-8.59 ±0.68)

Hamilton Harbour hypolimnion was subject to occasional intrusions of lake water during upwelling episodes in western Lake Ontario, e.g. an episode that happened in late June/early July 2003 (Fig. 4.2) and coincided with the strong and high persistent westerly winds on June 25 - 30, 2003 (Fig. 4.3) and a consequent upwelling episode in western Lake Ontario (Fig. 4.4). The driving force for the lake water intrusion was probably the differences in water levels of the harbour and the lake, and the density differences between these two water bodies. Cold (6-8ºC; Fig. 4.4) and therefore dense Lake Ontario water entered Hamilton Harbour through Burlington Shipping Canal (10 m deep) directly to the harbour hypolimnia (depth ≥ 8 m; Fig. 4.2) that was warmer (13-15ºC; see Fig. 4.2 for temperature profile for June 23) and therefore less dense. Fig. 4.2 shows that on June 23, the harbour hypolimnion was warm and relatively well mixed with uniformly distributed high specific conductivity values across the water column and with some hypoxic conditions near the bottom. Strong westerly winds persisted from June 25 to June 30, 2003 (Fig. 4.3) caused the upwelling in western Lake Ontario (Fig. 4.4) and intrusions of low conductivity (see Table 4.3), cold and dense lake water into the harbour. As the result, the hypolimnion water temperature decreased (Fig. 4.2*a*; see water profiles for July 2 and 7) with a significant drop in conductivity (Fig. 4.2*b*; see July 2 and 7 data). The hypoxic water near the bottom was displaced by colder and richer in DO lake water (Fig. 4.2*c*) causing the layering of two water masses with the true hypolimnetic water with low DO concentrations being pushed up towards metalimnion and creating hypoxic conditions in the upper part of hypolimnion (Fig. 4.2*c*). It is interesting to see that the harbour hypolimnion was not uniform in respect to DO and had a steep gradient in conductivity for several days (e.g. from July 2 to July 7), meaning that it was not well mixed and homogenous as it is usually assumed for classical hypolimnion.

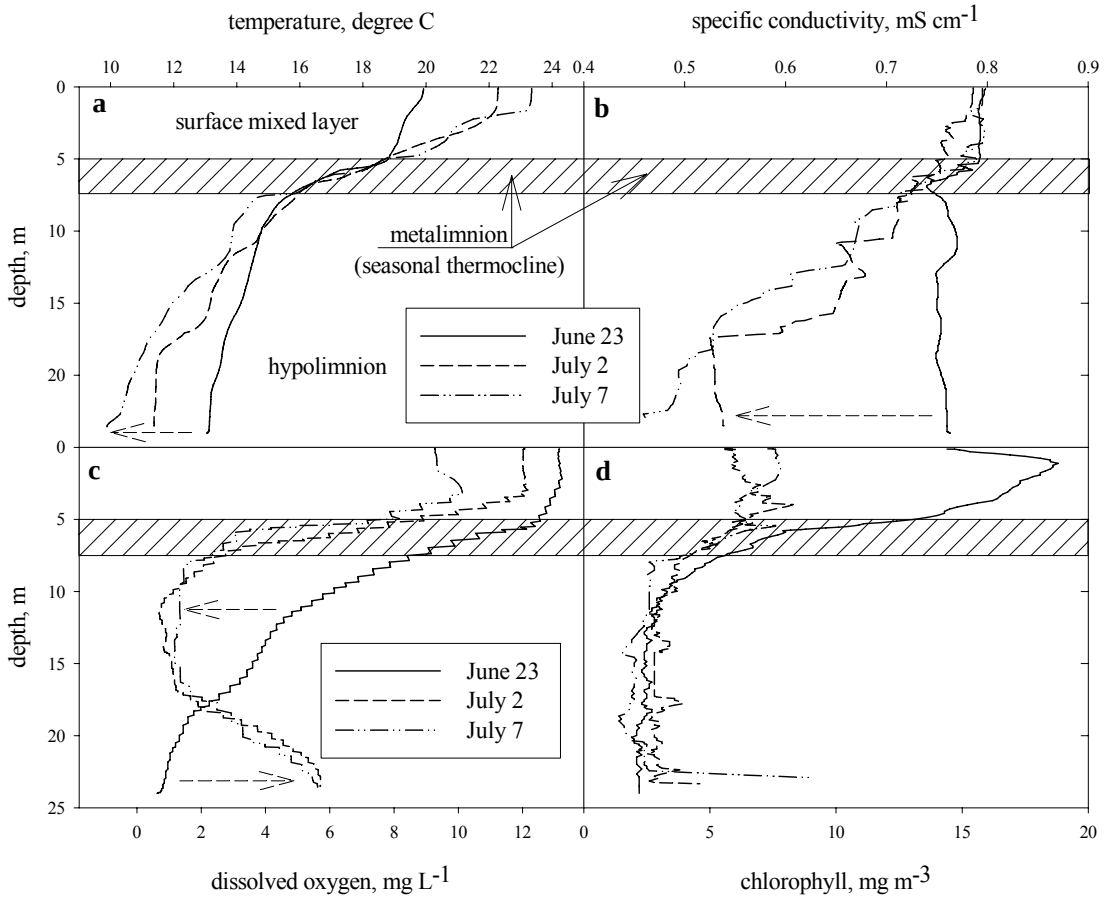

Fig. 4.2 Water profiles taken in Hamilton Harbour on three selected days in 2003 (June 23, 10:40 am; July 2, 11:20 am; and, July 7, 2:30 pm): (a) temperature (ºC), (b) specific conductivity (mS cm^{-1}), (c) dissolved oxygen (mg L^{-1}), and (d) chlorophyll (mg m^{-3}). Hatched area marks an approximate position of metalimnion determined from the seasonal thermocline. The SML is above this hatched area, and a hypolimnion is below. The short-dashed arrows indicate the direction of changes in environmental parameters in the hypolimnion from June 23 to July 7, 2003.

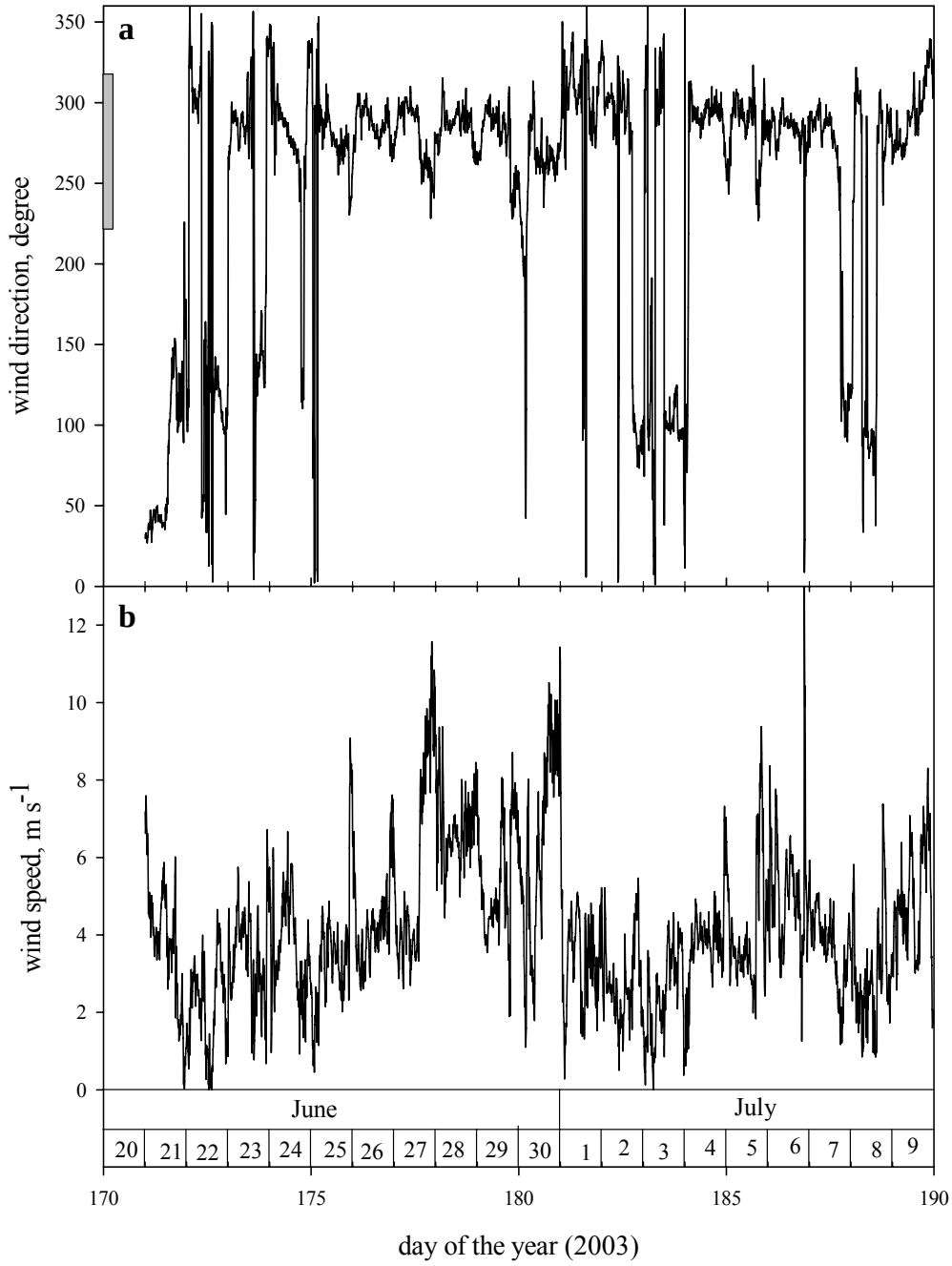

Fig. 4.3 Some selected meteorological data as measured at 3 m height at the Hamilton Harbour weather station: (a) wind direction (degree), and (b) average wind speed (m s^{-1}). A gray vertical bar on y-axis (see sub-plot "a") indicates westerly winds (wind sector: from 225 to 315 degrees).

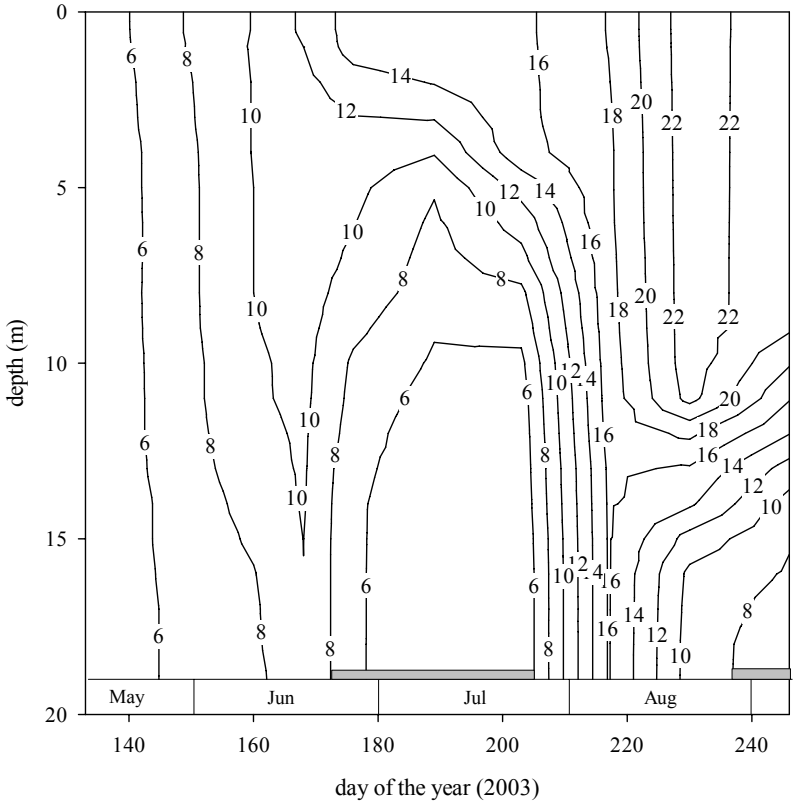

Fig. 4.4 Thermal structure of western Lake Ontario water column determined from bi-weekly water profiles taken at the time of sampling from May 13 to September 3, 2003. Horizontal gray bars correspond to the times of upwelling episodes.

Table 4.4 Estimates of isotopic fractionation effect during respiration (α_r) derived from bottle incubations* in two systems, Hamilton Harbour and Lake Ontario.

Date of experiment	Hamilton Harbour		Lake Ontario	
	n	α_r mean ± st.dev	*n*	α_r mean ± st.dev.
2003-Aug-05	2	0.984 ± 0.000	2	0.959 ± 0.040
2004-Jul-06	3	0.981 ± 0.000	2	0.983 ± 0.007
2004-Jul-20	2	0.990 ± 0.004	3	0.994 ± 0.005
2004-Aug-04	3	0.988 ± 0.002	1	0.993 ± n.a.
2004-Oct-07	3	0.987 ± 0.003		
overall average:		0.986 ± 0.003		0.982 ± 0.016

* Incubation times were 3 days (Hamilton Harbour) and 4 days (Lake Ontario).

4.4.3 Abundances in isotopic $^{18}O/^{16}O$ ratios

In both systems (Hamilton Harbour vs. adjacent Lake Ontario; Woods Bay vs. Georgian Bay), the less productive sites had higher δ^{18}O-DO concentrations compared to their more productive sites (Table 4.3). In most of the cases, the SML in Hamilton Harbour had a very pronounced and clear signal in δ^{18}O-DO values with the latter being below atmospheric saturation value of 24.2 ‰ (Fig. 4.5). The seasonal changes in δ^{18}O-DO of the SML in Lake Ontario were not as pronounced as for Hamilton Harbor. Nevertheless, here too, δ^{18}O-DO values were below atmospheric equilibrium value of 24.2‰ except early May and October when the lake was circulating (Fig. 4.5). In Hamilton Harbour hypolimnion, δ^{18}O-DO values were almost always above 24.2‰ but their inter- and intra-seasonal patterns were not constant (Fig. 4.5*c*, *d*). Unlike Hamilton Harbour hypolimnion where δ^{18}O-DO were well elevated compared to its SML (Table 4.3) indicating a predominance of respiration process, the δ^{18}O-DO in the lake hypolimnia were similar to those measured in SML (Table 4.3).

4.4.4. Isotopic and fractional saturation of DO

The positions of our water samples in respect to the oxygen abundance and its isotopic composition are visualized on a cross-plot of δ^{18}O-DO vs. oxygen fractional saturation ([DO%], [DO%] $=(DO\%)_{actual}/(DO\%)_{satur}$) (Fig. 4.6). The central point on the plot with [DO%] = 1 and δ^{18}O-DO = 24.2‰ is the equilibrium locus. The Lake Ontario SML samples (Fig. 4.6*b*) are mostly (with a few exceptions though) concentrated near the equilibrium locus in the area with δ^{18}O-DO values being slightly below 24.2‰ with [DO%]>1. However, there was a different situation with the Hamilton Harbour SML samples. Unlike Lake Ontario samples, the extent of both [DO%] and δ^{18}O-DO cycling were large and indicative of the eutrophic conditions. The harbour samples did not go through equilibrium locus as Lake Ontario samples did (Fig 4.6*a*, *b*). There is a clear trend in the harbour SML samples

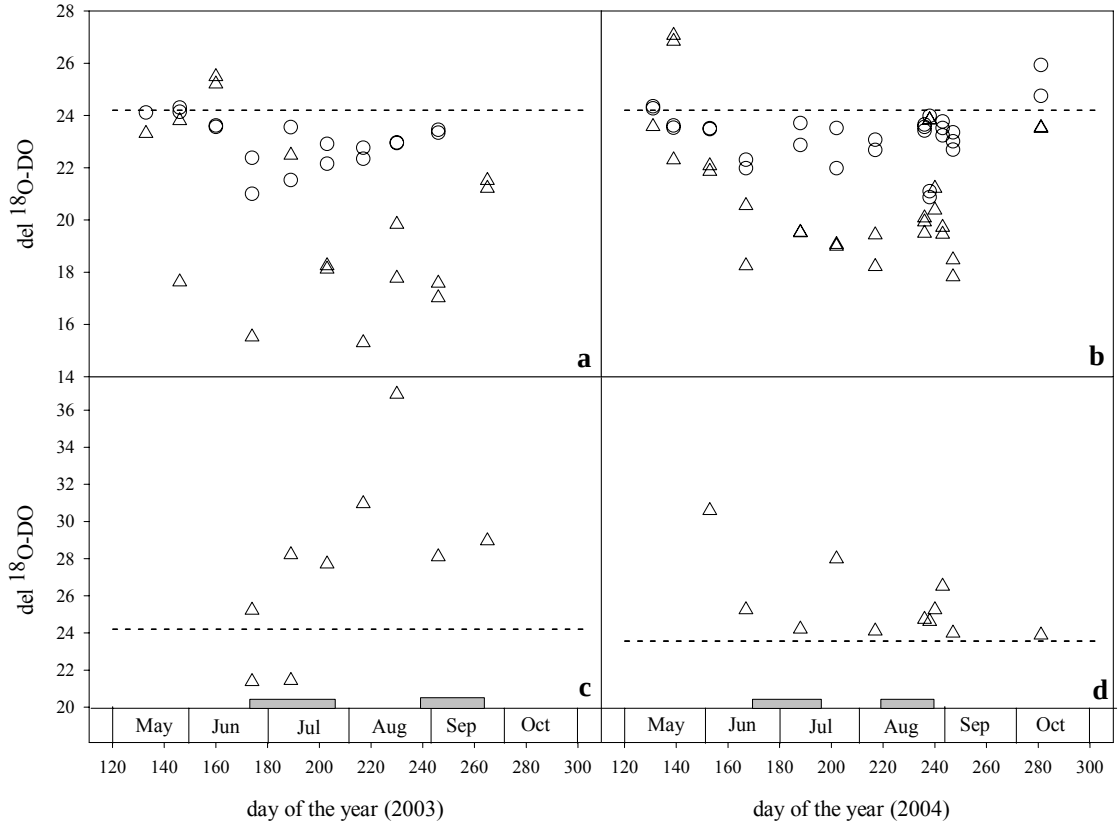

Fig. 4.5 The trend in $\delta^{18}O$ of dissolved oxygen ($\delta^{18}O$-DO, ‰ vs. SMOW) in Lake Ontario (circles) and Hamilton Harbour (triangles) over the sampling seasons of 2003 and 2004: (a) shows surface mixed layer (SML) in 2003, (b) SML in 2004, (c) and (d) samples from hypolimnetic water in 2003 (c) and 2004 (d). The dashed lines show values for $\delta^{18}O$-DO in equilibrium with the atmosphere (24.2 ‰). The horizontal gray bars indicate time of upwelling episodes in western Lake Ontario.

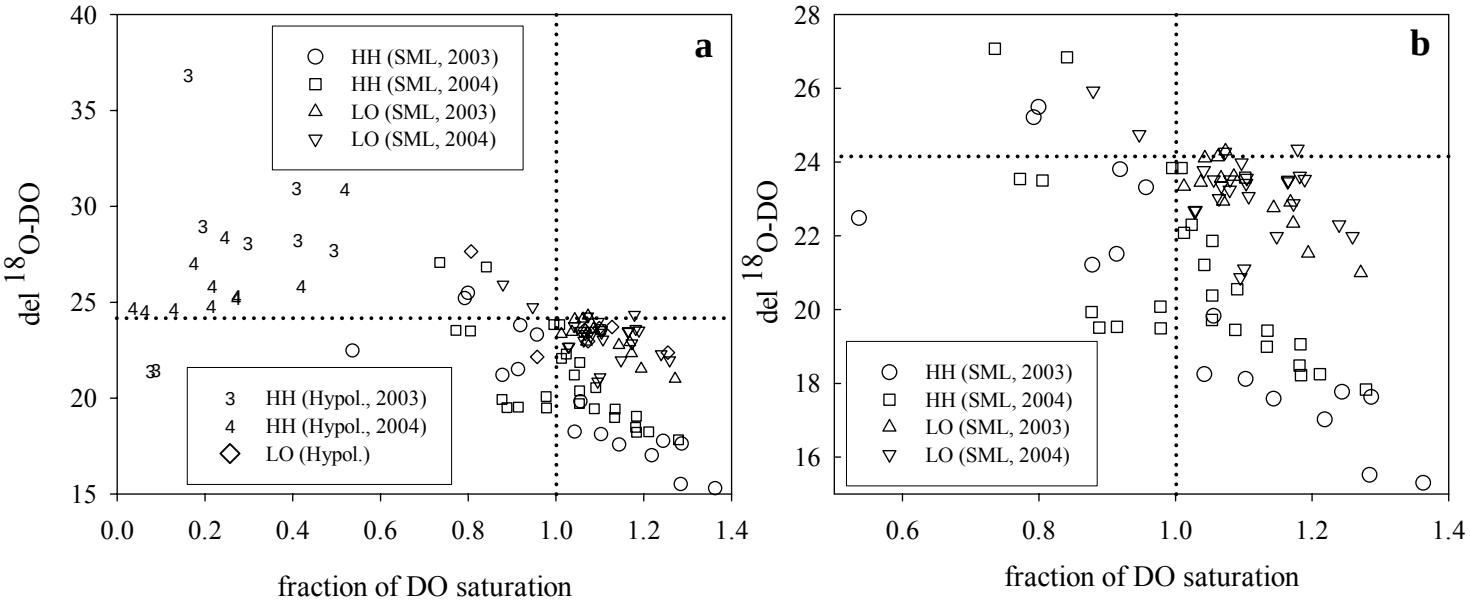

Fig. 4.6 Isotopic (δ^{18}O-DO, ‰ vs. SMOW) and fractional saturation of DO of all samples collected from the surface mixed layer (SML) and hypolimnetic waters in Lake Ontario (LO) and Hamilton Harbour (HH): (a) shows symbols indicating LO SML in 2003 (triangles up) and 2004 (triangles down), LO hypolimnetic water in 2003 and 2004 (diamonds), HH SML in 2003 (open circles) and 2004 (squares) and HH hypolimnetic water in 2003 ("3") and 2004 ("4"); (b) shows samples from SML for Lake Ontario and Hamilton Harbour but has a different scale with the symbols as in (a).

trend in the harbour SML samples in both years from lower [DO%] and higher δ^{18}O-DO values towards higher [DO%] and lower δ^{18}O-DO (see Fig. 4.6*a*, *b*) with the increase in biomass as measured by Chl *a* (not shown here). There was also an unexpected general trend in the harbour hypolimnetic samples to have lower δ^{18}O-DO values as [DO%] decreases (Fig. 4.6*a*) with the only one outlier (δ^{18}O-DO = 36.86‰ and [DO%] = 0.162) representing conditions on 18-Aug-2004 at 12 m depth.

The δ^{18}O of epilimnetic water (δ^{18}O-H_2O) in Hamilton Harbor were lower compared to those of Lake Ontario (Table 4.3). There was a very clear seasonal trend in δ^{18}O-H_2O in both systems (and in both years) from lower values in the spring towards higher values in the fall. The same is true for Georgian Bay and Woods Bay stations (see the range in Table 4.3) with late summer values having higher $^{18}O/^{16}O$ concentrations than the early summer ones. Hypolimnion in Hamilton Harbour had δ^{18}O-H_2O values somewhere between the values measured in SML of the harbour and the lake (Table 4.3).

4.4.5 Chl-a concentrations

In Hamilton Harbour, the Chl *a* concentrations integrated over the SML were variable ranging from as low as 3.5 to as much as 23.0 mg m^{-3} with the maximums occurring at approximately 1-month intervals. Usually, low Chl *a* concentrations were associated with minimum values in DO and DO%; while peaks in phytoplankton biomass were associated with the peaks in DO and DO%. It is worth noticing that biomass in the harbour SML was significantly reduced or washed out after the events of atmospheric forcing (strong wind episodes) and intrusions of lake water into the harbour (e.g. Fig. 4.2*d*; June 23 vs. July 2 data). In Lake Ontario, Chl *a* concentrations were between 0.6 to 4.2 mg m^{-3} with two clear peaks occurring in early and late summer with a midsummer minimum. Concentrations of Chl *a* in Woods Bay were 3.5 fold higher than those in Georgian Bay with an average values of 3.3 and 0.9 mg m^{-3}, respectively.

4.4.6 Fractionation factor during respiration

The α_r incubation experiments for Hamilton Harbour and Lake Ontario yielded respectively overall mean values of 0.986±0.003 and 0.982±0.016 (Table 4.4). The measured α_r value implies that O_2 consumed during respiration was approximately, on average, 14±3 ‰ (Hamilton Harbour) and 18±16% (Lake Ontario) more depleted than that of δ^{18}O-DO.

4.4.7 Oxygen exchange with the atmosphere

The calculated k_{O2} values (m d^{-1}) were dependent on the method used. Based on the approach of Wanninkhof (1992), Hamilton Harbour had k_{O2}(W) ranging from 1 to 8.3 with a mean and median (± st. dev.) respectively of 2.8±1.8 and 2.3±1. The method of Crusius and Wanninkhof (2003) gave k_{O2}(CW) of a wider range (0.24 – 9.7) with a similar mean and median values: 2.7±2.3 and 2.3±2.3. Overall, mean values of k_{O2} calculated for Lake Ontario were smaller: 1.11±0.55 (Wanninkhof 1992) and 0.83±1.03 (Crusius and Wanninkhof 2003) probably because of lower water temperatures in the lake. Both k_{O2}(W) and k_{O2}(CW) were highly correlated (R^2 = 0.885, n = 43; k_{O2}(CW) = 0.465[k_{O2}(W)]$^{1.6}$) but had a larger scatter at low values. However, k_{O2}(W) provided a better match of calculated photosynthetic rates with those rates calculated from the Fee model. The calculated k_{O2}(W) were used to define oxygen flux through water surface (F, mmolO_2 m^{-2} d^{-1}). Mean F in Lake Ontario and Hamilton Harbour were respectively 38±23 and 108±90. To estimate F in Georgian Bay system, k_{O2} values were assumed to be 1 in Woods Bay (as a more sheltered system), 2 (August-2004) and 3 (June-2004) in Georgian Bay (as a less sheltered system). The value of 3 for June-2004 was taken because of the breeze as well as a thunderstorm happened on the previous day.

4.4.8 P/R ratios

For the SML in Hamilton Harbour, the ^{18}O method (steady state model) predicts (Fig. 4.7) heterotrophic conditions (P/R<1) in the spring and early summer (May and early Jun) and in the fall (late September/early October), and the predominance of autotrophic conditions (P/R>1) during the rest of the summer (stratified season) with only a few brief episodes of heterotrophy occurring during

the changes in the harbour thermal structure and observed minimums in Chl *a* concentrations, and coincident with the westerly winds and upwelling episodes in western Lake Ontario (see Fig. 4.1*b* for 2004, and Fig. 4.4 for 2003). P/R ratios in the SML of Hamilton Harbour were usually higher in the top (2 m) than in the deeper layer of 3-5 m depth (Fig. 4.7). For Lake Ontario, the ^{18}O method did not work well giving some negative values of P/R ratios using the value of α_r measured for Lake Ontario (0.982±0.016). There are no published data on bottle-based α_r for the Laurentian Great Lakes except those measured in the oligotrophic east basin of Lake Erie (Wang 2005) with a seasonal average value of 0.982±0.011, the same value as ours, but with slightly lower standard error because of the larger number of estimates. Therefore, we decided to use an annual average α_r (α_r = 0.977) for Lake Kinneret (Luz et al. 2002) that was recently applied to larger water bodies such as Lake Superior (Russ et al. 2004) and Lake Erie (Ostrom et al. 2005). In this case, the steady state model predicts all P/R ratios to be positive with the predominance of heterotrophic conditions over the entire season with only a few brief episodes of autotrophy occurred in the top SML layer or in the deeper part (deep chlorophyll maximum layer).

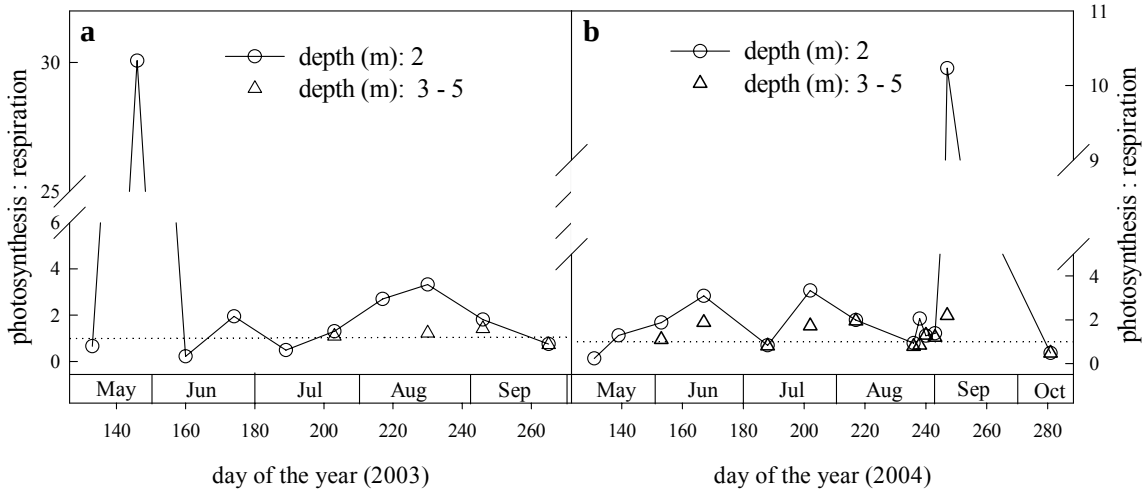

Fig. 4.7 The seasonal dynamics in the ratios of photosynthesis to respiration in Hamilton Harbour at different depths calculated from a steady state model and α_r = 0.986: (a) 2003, and (b) 2004.

4.4.9 Rates of respiration and photosynthesis

Rates of average *in-situ* photosynthesis (VP, $mmolO_2\ m^{-3}\ d^{-1}$) in the SML predicted by the bottle method based on Fee model (Fee 1990) ranged from 1.5 to 24.8 (mean: 9.4; median: 10.0) in Lake Ontario, and from 7.6 to 118.0 (mean: 43.8; median: 45.8) in Hamilton Harbour (Fig. 4.8*a*, *b*). The volumetric respiration rates of the SML (VR, $mmolO_2\ m^{-3}\ d^{-1}$) based on bottle derived incubation rates ranged from 1.2 to 9.2 (mean: 5.4; median: 5.4) in Lake Ontario, and from 6.1 to 59.2 (mean: 25.2; median: 24.3) in Hamilton Harbor (Fig. 4.8*c*, *d*). The mean ratios of VP/VR (=AGP/AR) in Lake Ontario and Hamilton Harbour were respectively 2.06±1.36 and 1.79±0.95. In Georgian Bay system, rates of VP and VR were respectively 10.8±5.7 and 7.3±2.1 (Woods Bay), 6.6±1.4 and 3.1±1.2 (Georgian Bay). Mean ratios of AGP/AR were 1.43±0.37 (Woods Bay) and 2.18±0.38 (Georgian Bay).

The ^{18}O method predicted that absolute rates of both photosynthesis and respiration in Lake Ontario were almost always negative though their ratios were positive (with only a few exceptions during the periods of stable stratification, e.g. 3-Sept-2003 and 3-Sept-2004 at 2 m depth). The absolute rates were still negative if we apply lower and higher gas exchange rates (in the reasonable range) to the steady state model. However, in more productive system, Hamilton Harbour, ^{18}O method predicted overall photosynthetic rates (^{18}O-VP, $mmolO_2\ m^{-3}\ d^{-1}$) between 3.8 and 135 (Fig. 4.8*a*, *b*) with a mean and a median values of 39.6 and 28.9 respectively; and overall respiration rates (^{18}O-VR, $mmolO_2\ m^{-3}\ d^{-1}$) ranged from 1.8 to 276 (Fig 4.8*c*, *d*) with a mean and median values of 40.9 and 19.31, respectively. If we drop one day (8-July-2003) that had extreme rates in respiration and photosynthesis ^{18}O-VR and ^{18}O-VP, then the mean values will be 29.2 (respiration), 34.8 (photosynthesis) and 1.73 for their ratios (^{18}O-VP/VR). There was a close coupling between rates of respiration and photosynthesis (Fig. 4.9) in the SML with the former exceeding the latter at times of the thermocline deepening in the harbour coincident with the prevalence of the strong westerly winds and upwelling episodes in western Lake Ontario.

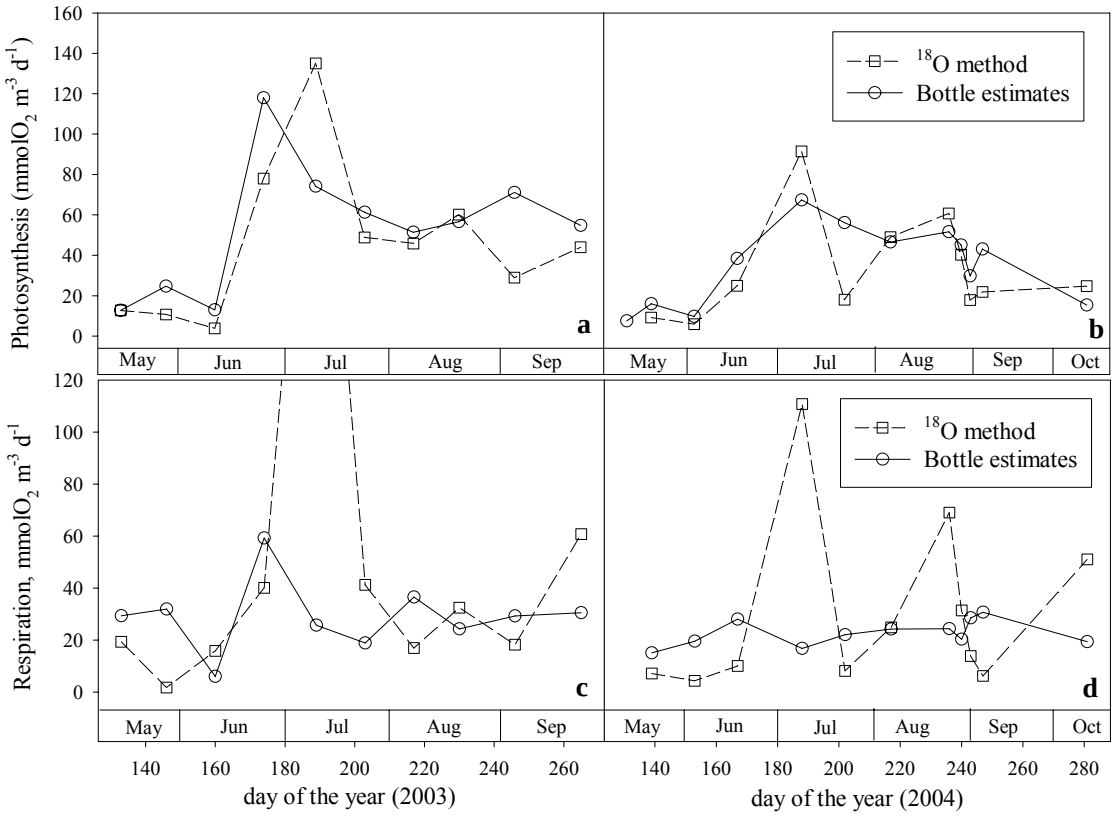

Fig. 4.8 (a) and (b) the seasonal dynamics in photosynthesis ($mmolO_2\ m^{-3}\ d^{-1}$) averaged over SML of Hamilton Harbour, and determined by ^{18}O method (squares) and bottle estimates (circles): 2003 (a) and 2004 (b); (c) and (d) the rates of respiration ($mmolO_2\ m^{-3}\ d^{-1}$) averaged over SML of Hamilton Harbour and predicted by ^{18}O method (squares) and bottle estimates (circles): 2003 (c), and 2004 (d). Panel "c": the rate on July-8-2003 predicted by ^{18}O method is 276.

Rates of ^{18}O-VR in Hamilton Harbour were correlated (n = 22) positively with T_w (p = 0.013) or negatively with Z_m (p = 0.016). A multiple regression model containing wind speed (WS, m s^{-1}) and T_w as independent variables was able to explain 78% variability in ^{18}O-VR. Rates of ^{18}O-VP were correlated positively with T_w (R^2 = 0.534) or negatively with Z_{mix} (R^2 = 0.594). Three variables, T_w, WS and Chl *a*, within a multiple regression model were able to explain more than 74% variability in volumetric photosynthesis and all of them were significant variables exhibiting positive effects. There

was no correlation between VR and ^{18}O-VR (Fig 4.8*c*, *d*), and between VP/VR and ^{18}O-VP/VR (Fig. 4.10). However, rates of VP and ^{18}O-VP were highly correlated (p = 0.000, R^2 = 0.752, n = 21; see also Fig. 4.8*a*, *b*). Ratios of ^{18}O-VP/VR were positively correlated with Chl *a* (p = 0.002, R^2 = 0.403, n = 22) and negatively with Z_m (p = 0.023, R^2 = 0.232, n = 22). Mean photosynthetic rates in Georgian Bay and Woods Bay based on ^{18}O method were respectively 1.49 and 5.3, while respiration rates were 0.75 and 8.1. The inclusion of Georgian Bay and Woods Bay sites improved the overall relationship between VP and ^{18}O-VP (p = 0.000, R^2 = 0.827, n = 25; see Fig. 4.11).

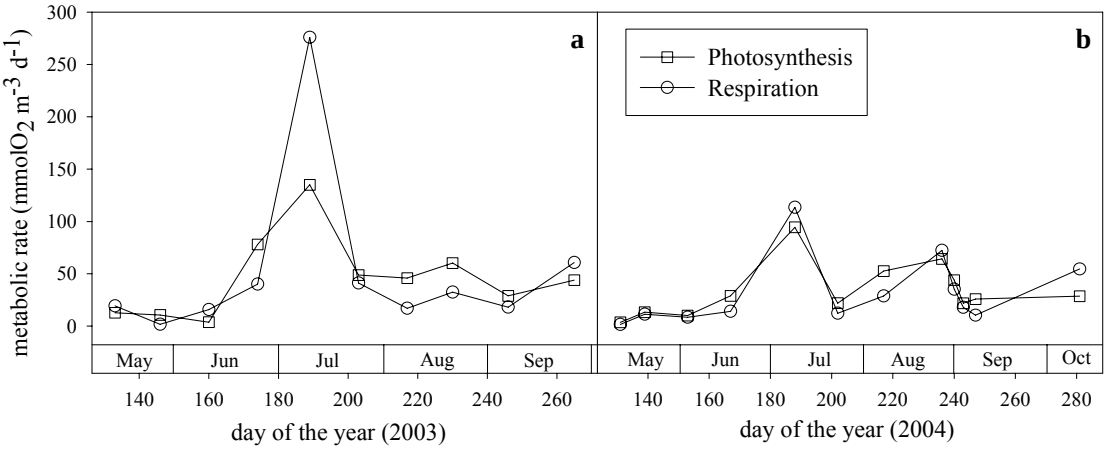

Fig. 4.9 The seasonal dynamics in rates ($mmolO_2$ m^{-3} d^{-1}) of photosynthesis (squares) and respiration (circles) in the SML of Hamilton Harbour as predicted by ^{18}O method: (a) 2003, and (b) 2004.

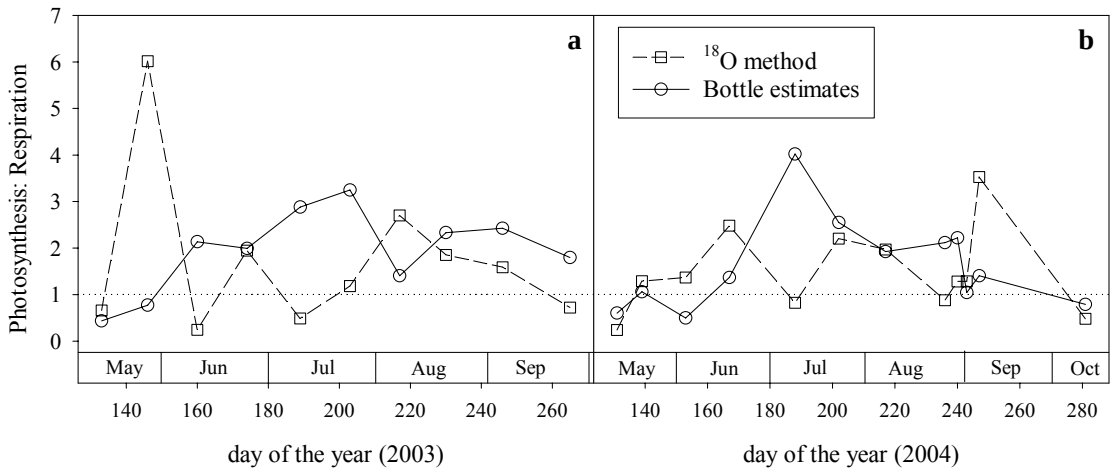

Fig. 4.10 Photosynthesis to respiration ratios (P/R=VP/VR=AGP/AR) of SML averaged rates in Hamilton Harbour predicted by ^{18}O method (squares) and bottle estimates (circles): (a) 2003, and (b) 2004. The dotted line shows the conditions of metabolic equilibrium when photosynthesis is equal to respiration.

Table 4.5 Comparative summary of photosynthesis to respiration ratios (mean ± st. dev.) in SML obtained by two different methods, ^{18}O and traditional method (assuming PAR of 70% of the theoretical cloud free radiation).

SML	^{18}O method			Traditional method
	P/R (α_r = 0.986)	P/R (α_r = 0.982)	P/R (α_r = 0.977)	VP/VR (=AGP/AR)
Hamilton Harbour	2.2 ±4.69; [42]			1.92 ±0.99; [19] **1.84 ±0.94; [21]**
Lake Ontario		0.63 ±0.74; [36]	0.75 ±0.68; [39]	2.06 ±1.36; [18]
Woods Bay	0.86 ±0.51; [2]	0.89 ±0.39; [2]	0.93 ±0.24; [2]	1.43 ±0.37; [2]
Georgian Bay	2.00 ±1.27; [2]	1.76 ±0.97; [2]	1.46 ±0.58; [2]	2.18 ±0.38; [2]

Note: bolded numbers indicate mean ± st. dev. for the traditional method using actually measured *in situ* PAR.

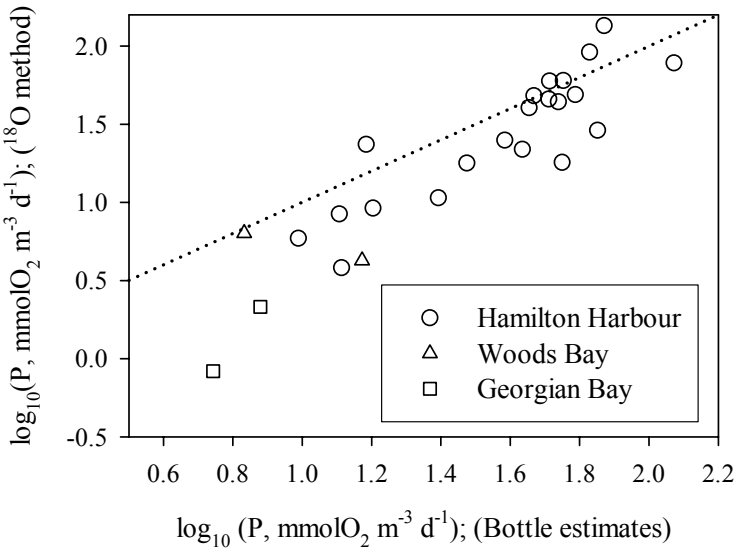

Fig. 4.11 Comparison of photosynthetic rates ($mmolO_2\ m^{-3}\ d^{-1}$) given by two methods, bottle estimates and ^{18}O method: Hamilton Harbour (circles), Woods Bay (triangles) and Georgian Bay (squares); dotted line is 1:1 line.

The largest disagreements between two methods, when ^{18}O-VR overestimated bottle-based respiration rates (8-Jul-2003, 22-Sep-2003, 6-Jul-2004, 23-Aug-2004 and 07-Oct-2004; see Fig. 4.8*c*, *d*), were caused by deepening of the thermocline and entrainment of low DO metalimnetic and hypolimnetic waters into the epilimnion. Two episodes in mid fall (22-Sep-2003 and 07-Oct-2004; Fig. 4.8*a*, *b*) were associated with the classical autumnal deepening of the seasonal thermocline into low oxygenized hypolimnion due to progressive cooling of the SML. Two other episodes (8-Jul-2003 and 23-Aug-2004; Fig. 4.8*c*, *d*) were associated with the deepening of the thermocline due to prevailing westerly winds blowing persistently over several days (Table 4.6) with Fig. 4.12*b* depicting this for 23-Aug-2004. The harbour has a triangular elongated shape oriented to the west so that its longest fetch is from the west to the east (particularly in the direction of west-south-west); it is openly exposed to the west and somewhat sheltered from the east and therefore the westerly winds

are more likely to cause larger scale motions (waves and circulations) than any other winds, and generate internal seiches and other turdulence. All these may result in thermocline deepening and its compression, as well as in the entrainment of low DO metalimnetic/hypolimnetic water into the SML. The last episode (6-Jul-2004) was different from others. The thermocline deepening was caused by an episodic western wind event rather than the prevalence of high persistent westerly winds (Table 4.6). The weather conditions proceeding 6-Jul-2004 were different from other episodes (Table 4.6). It was a hot day with the light easterly wind on 3-Jul-2004. The easterly wind began to intensify on 4-Jul-2004 and changed its direction to an opposing westerly wind at 7 pm. On 5-July-2004, in the morning (7 to 11 am) the wind became moderate (6 to 7 m s^{-1}, as measured at 3 m height), then started to slow down but intensified again and became a strong wind (8 to 10 m s^{-1}) from 2:00 pm to 10:30 pm. The data from the deployed temperature loggers indicated a production of turbulent energy at the bottom of the SML (4 and 5 m depth), in the metalimnion (6 and 7 m depth) and in the upper part of hypolimnion (8 m depth) as indicated by the large fluctuations of the temperature isotherms on Fig. 4.13*a*, *b*. As the result of the morning wind event on 05-Jul-2004, the thermocline downwelled by at least 1 m to a depth of 6.5 m (Fig. 4.12*a*) with a corresponding drop in average temperature of the SML (Fig. 4.13*a*). The second afternoon-and-evening wind event that was stronger that the first one resulted in further deepening of the thermocline to a depth of 7.5 m and T_w lowering. The deepening of the thermocline resulted in the drop of the average temperature of the SML by more than 2ºC (Fig. 4.13*a*). The wind stopped at midnight on 5-Jul-2004 but the thermocline remained suppressed until the late morning of 6-Jul-2004 when it finally relaxed and upwelled to its previous position at the depth of 5.5 m (Fig. 4.12*a*).

Table 4.6 24-h averaged values of meteorological conditions as recorded by Hamilton Harbour weather station in 3 m height: average wind speed (WS), peak wind speed (pkWS), vector average wind direction (WD), photosynthetically available radiation (PAR), and PAR as a percent of 100% cloud-free PAR (%PAR).

yyyy-mm-dd	year day	WS	pkWS	WD		PAR	%PAR
		$m\ s^{-1}$	$m\ s^{-1}$	degress	direction	$E\ m^{-2}\ d^{-1}$	% theoret.
2003-07-05	186	5.1	6.5	279	WNW	59.73	97.5
2003-07-06	187	3.7	4.5	242	WSW	20.42	33.4
2003-07-07	188	3.0	3.9	212	SW	52.30	85.6
2003-07-08	189	4.8	6.3	294	WNW	52.77	86.5
2004-07-03	185	2.5	3.3	74	ENE	54.04	88.1
2004-07-04	186	3.7	5.4	111	ESE	34.74	56.7
2004-07-05	187	6.5	8.6	280	WNW	24.98	40.8
2004-07-06	188	3.0	4.1	119	ESE	53.22	87.1
2004-08-20	233	3.5	4.5	285	WNW	17.11	33.1
2004-08-21	234	3.8	5.4	214	SW	42.57	82.8
2004-08-22	235	4.2	5.8	245	WSW	42.61	83.4
2004-08-23	236	5.0	6.4	252	WSW	30.34	59.8

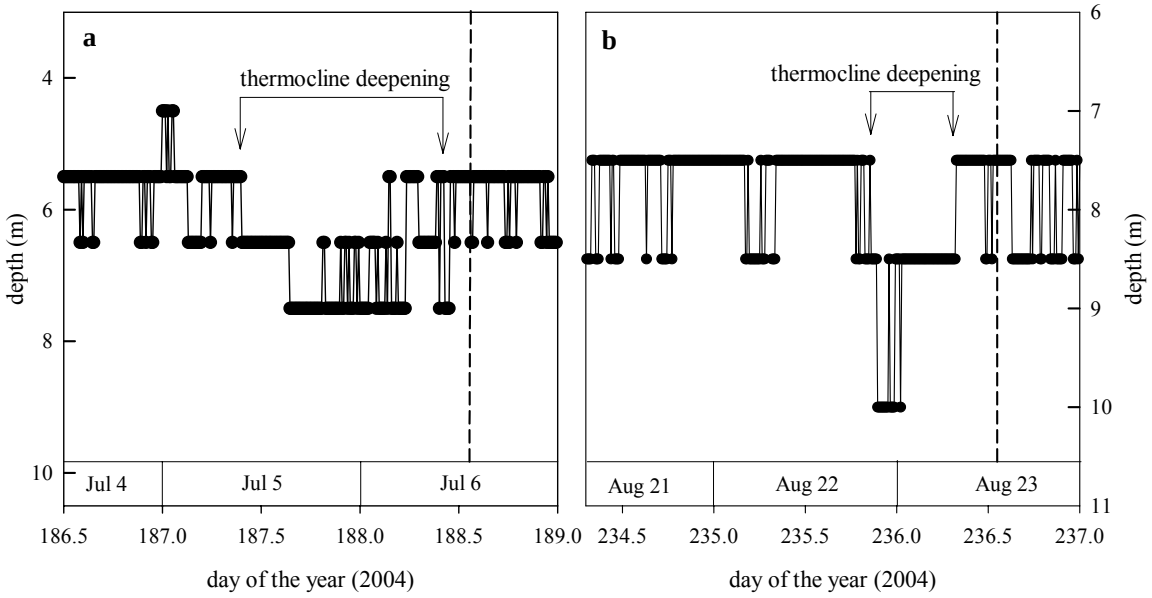

Fig. 4.12 The depth of the SML in Hamilton Harbour for the selected days determined from the thermister string. The vertical short-dashed line indicates the time of water sampling on July-6-2004 (a) and Aug-23-2004 (b) when ^{18}O-DO samples were collected.

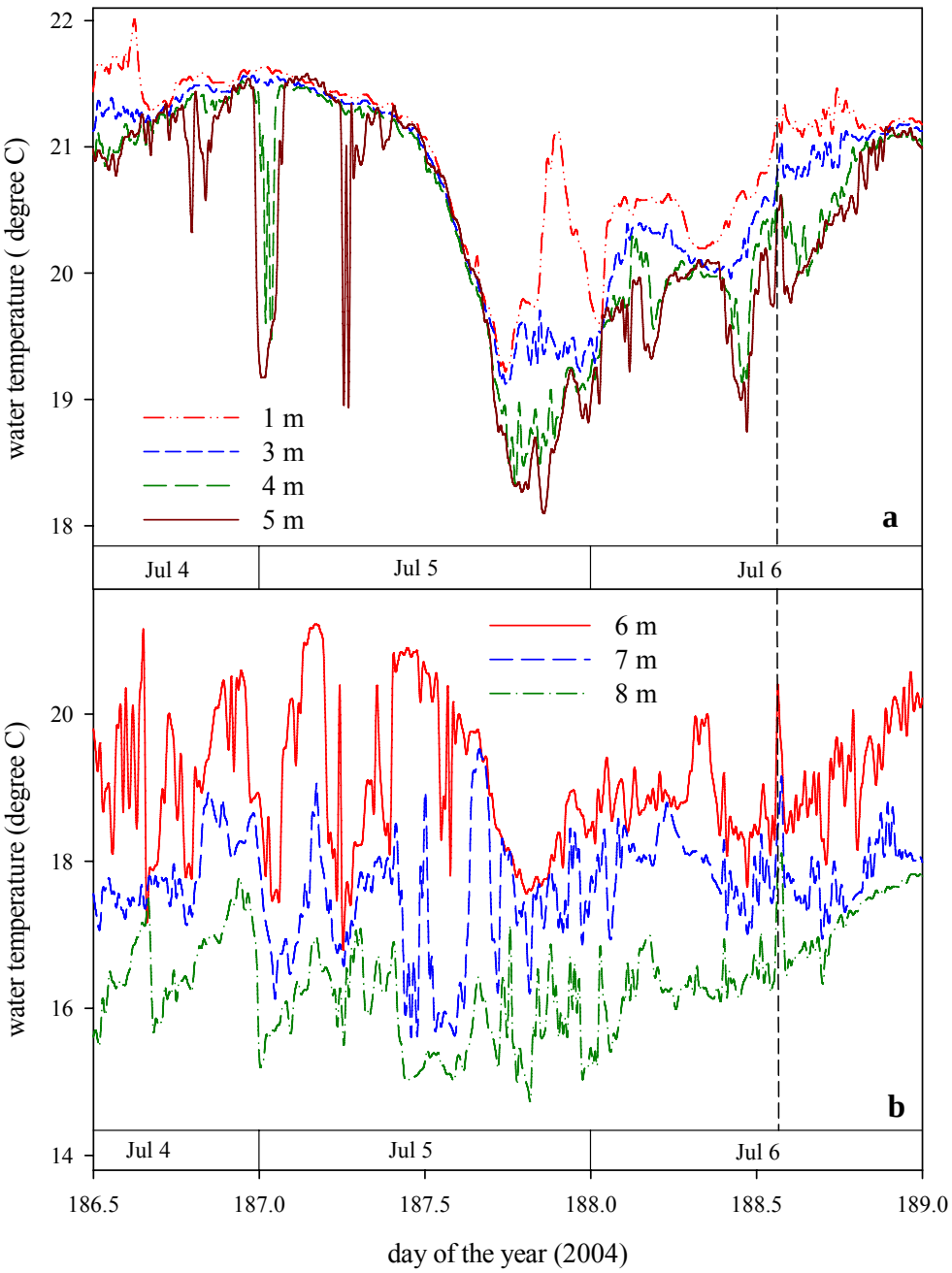

Fig. 4.13 Water temperatures measured at different depths in Hamilton Harbour: (a) shows those in the surface mixed layer (SML): 1 m (red dash-dot-dot line), 3 m (blue medium dash line), 4 m (green long dash line), 5 m (dark red solid line); (b) shows those in metalimnion and in the upper hypolimnion: 6 m (red solid line), 7 m (blue long dash line), 8 m (green medium dash-dot line).

The larger disagreements between two methods (^{18}O-VP vs. bottle incubations) in respect to the predictions of photosynthetic rates were observed on 08-Jul-2003, 3-Sep-2003, 6-Jul-2004 and

20-Jul-2005 (Fig. 4.8*a*, *b*). It was noticed that on the sunny, calm days with a shallow SML, ^{18}O method gave higher photosynthetic rates than the bottle estimates (e.g. 8-Jul-2003 and 6-Jul-2004; Fig. 4.8*a*, *b*), and lower rates (3-Sep-2003, 20-Jul-2005; Fig. 4.8*a*, *b*) on very foggy and hazy days.

Knowing that ^{18}O method gives rates of photosynthesis integrated over a certain time and to find out what the approximate integration time might be, the Fee model (bottle method) was also run with the PAR data averaged over two days: a day of sampling plus a proceeding day. It was noticed that on average (with some exceptions) the similarity of the results were dependent on Z_m. When Z_m was shallow, 1-day PAR data provided better fit with ^{18}O method; and when Z_m was deeper, the 2-day averaged PAR data gave closer results to those predicted by the oxygen stable isotope method.

4.5 Discussion

4.5.1 Variations in Chl-a concentrations

In Lake Ontario, the seasonal cycle of phytoplankton biomass, measured as Chl *a*, showed a typical pattern of the seasonal phytoplankton dynamics in an oligotrophic lake (Reynolds 1984) with two peaks in early and late summer with a midsummer minimum. In Hamilton Harbour, the average standing crop of phytoplankton was certainly much higher than that of Lake Ontario, but the annual cycle was characterized by abrupt fluctuations in total phytoplankton abundance indicating possibility of temporal decoupling of phytoplankton from their grazers or increased sedimentation losses trigged by the alterations in water column stability (Harris 1986) in the Hamilton Harbour. It was observed that the latter were co-occurring at the times of westerly winds and upwelling episodes in western Lake Ontario (Fig. 4.1*a*, *b*). Concentrations of Chl *a* in Woods Bay and Georgian Bay were typical for oligotrophic systems.

4.5.2 Variations in oxygen abundance and % saturation

A high correlation between epilimnetic DO and water temperature (T_w) in Lake Ontario suggests that the oxygen concentrations were mostly driven by physical processes such as movement and mixing of different water masses. The possible explanation of the persistence of DO% above saturation is either/and the slow warming up of the colder water rich in DO brought by upwellings and/or the prevalence of photosynthesis over respiration. The latter is somewhat supported by that fact that Chl *a* was positively correlated with DO% and, via multiple regression and apart from T_w, was a significant variable in predicting DO. Also, our bottle estimates have shown the prevailence of photosynthesis over respiration in the SML (see Chapter 3). Thus, even in large and clear oligotrophic lakes, photosynthesis may be a significant factor of DO over-saturation. In the study of another Laurentian Great Lake, namely oligotrophic east basin of Lake Erie, based on the high precision Winkler method performed on board, the SML was also found to be predominantly oversaturated in the stratified period (Wang 2005). The east basin of Lake Erie is shallow compared with Lake Ontario and therefore does not have a large volume hypolimnion with cold and DO rich water that can be brought to the surface by upwellings; therefore the observed over-saturation of the SML is likely due to biologically produced oxygen. However, the SML of Lake Superior that is even more clear and oligotrophic with very low DOC concentrations was found to be under-saturated with respect to DO (e.g. Russ et al. 2004) meaning that it differs from Lake Ontario and Lake Erie as it has deeper Z_m and its SML is probably light limited, and this is not surprising as every Great Lake represents its own unique ecosystem. Also, this follows a trophic gradient as anticipated (Wetzel 2001). In the SML of Hamilton Harbour, DO% and DO (via multiple regression) were also correlated positively with Chl *a*, suggesting the important contribution of biologically derived oxygen to its bulk concentration. In contrast to Lake Ontario, the low oxygen concentrations observed in the harbor hypolimnia suggest a much larger organic matter export potential from SML to hypolimnion as well as lower volumetric ratio of hypolimnia to epilimnion in Hamilton Harbour than that of Lake Ontario.

4.5.3 Variations in dissolved oxygen isotopic signatures

The temporal variations in δ^{18}O-DO had more or less similar trends for Hamilton Harbour and Lake Ontario (Fig. 4.5) with a clear photosynthetic signal (δ^{18}O-DO<24.2‰) during the stratified period. However, the signal in Lake Ontario is as not as pronounced as in Hamilton Harbour where Chl *a* concentrations are higher. Despite the fact that the pattern of δ^{18}O-DO changes in Lake Ontario generally mirrors the pattern of changes in phytoplankton biomass, the scale of changes is different, and therefore only a weak linear correlation is found between Chl *a* and δ^{18}O-DO. The biomass of autotrophs and heterotrophs is constrained by low nutrient and DOC concentrations, as well as relatively low temperatures, and was not sufficient to bring significant changes to δ^{18}O-DO. Also, the SML was highly variable and was frequently disturbed by upwelling and downwelling events. In contrast, the changes in δ^{18}O-DO in Hamilton Harbor well reflect changes in biomass and show a good correlation with Chl *a*.

4.5.4 Variations in both, oxygen abundance and its isotopic composition

The positions close to the equilibrium point with [DO%]= 1 and δ^{18}O-DO = 24.2‰ (Fig. 4.6) are expected for systems where gas exchange is the only process affecting DO concentrations (Ostrom et al. 2005). Temperate lakes are likely to reach those values in winter and early spring (Ostrom et al. 2005). Lake Ontario samples were also concentrated near that point meaning that the gas exchange between water and atmosphere was the dominant process prevailing over the biological fluxes. It can also mean that the rates of photosynthesis and respiration are small compared to gas exchange (re-aeration) and probably somewhat similar in magnitude with the photosynthetic rates slightly exceeding those of respiration.

Harbour samples did not pass through the equilibrium locus as the lake samples did (Fig. 4.6), and that may be expected. Hamilton Harbour has a high biomass and therefore has always enough photosynthetic oxygen to keep the DO signature below atmospheric equilibrium. There was also a clear trend in the harbour SML samples in both years from lower [DO%] and higher δ^{18}O-DO

towards higher [DO%] and lower δ^{18}O-DO (Fig. 4.6*a*, *b*) with the increase in biomass (as measured by Chl *a*) (not shown here) suggesting that photosynthesis as a powerful driving force in the SML.

It is also worth noticing that, overall, there was a clear trend in the harbour hypolimnetic samples (Fig. 4.6*a*) with a general slope being opposite to expected one for aerobic respiratory fractionation ($\alpha_r \leq 1$). Usually, we expect the degree of fractionation to increase as DO falls to very low values and the isotopic composition of the remaining DO to be very heavy. This is not what was observed in the harbour hypolimnion. The isotopic signature of DO is getting lighter as [DO%] is going down indicating clearly that we are observing an oxygen consuming process or a sum of several processes with an overall α_r being higher than unity (Fig. 4.6*a*). There are three possible explanations for the observed anomalous δ^{18}O-DO behaviour. One possibility is that the hypolimnetic data are not actually successive observations over time and the same water mass. The presented hypolimnetic data (Fig. 4.6*a*) are a result of pooling up the data from two seasons, 2003 and 2004, with different inter-seasonal dynamics (Fig. 4.5*c*, *d*). We do not see the classical seasonal progression of DO depletion through the summer (e.g. Fig. 4.1*c*) and steady seasonal increases in δ^{18}O-DO values (Fig. 4.5*c*, *d*), probably because both of them were affected by the intrusions of lake water into the harbour (e.g. Fig. 4.2*c*). The latter resulted in the layering of hypolimnetic water into two distinct layers, a DO richer and colder bottom layer and an overlaying and slowly upwelling hypoxic layer (e.g. Fig 4.2*c*). Therefore, we might have sampled different water masses. A second explanation is that we have observed more than one oxygen consuming processes having different oxygen isotope fractionations. For example, sediment respiration may fractionate very little ($\alpha_r \approx 1$) and may be more important as DO drops. It could also be that other unknown chemical, physical and biological oxygen consuming processes are responsible for the observed anomalous behavior of δ^{18}O-DO. The inverse isotope fractionations ($\alpha_r > 1$) and anomalous behavior of δ^{18}O-DO (^{18}O depletions) have also been observed and recently reported by Wassenaar and Hendry (2007) in their study of the vadose zone and groundwater environments, with a possible causal link to the sulfide oxidation and Fe-

oxyhydroxide processes (or some other unknown processes). The findings of the ^{18}O depletions were repeated and consistent over several years (Wassenaar and Hendry 2007), so they were real. Based on the ^{18}O anomalous behavior in the harbour hypolimnion (see Fig. 4.6*a*) we could hypothesize that the main process responsible for the oxygen depletion is a chemical oxidation process with $\alpha_r > 1$ (e.g. the sulfide-Fe^{2+} oxidation process with α_r of 1.01 to 1.03; Wassenaar and Hendry 2007) rather than aerobic microbial respiration. This means that under low DO, the chemical demand for oxygen is a prevailing process over aerobic microbial respiration with a resulting total $\alpha_r > 1$. The third explanation is that the observed inverse oxygen fractionation was due to the exchange with the lake water and dilution of the heavy hypolimnetic DO ($\delta^{18}O$-DO = 24.2‰) by the lighter lake DO ($\delta^{18}O$-DO ≈ 24.2‰), and, generally, the isotopic signatures of the hypolimnetic samples do not go below those of Lake Ontario. On the other hand, if the dilution is responsible for the hypolimnetic ^{18}O depletion, we should also see a corresponding increase in DO abundance as the DO signature gets lighter but we did not. Overall, the behavior of the isotopic signature of the hypolimnetic DO is very interesting and cannot be simply explained by the aerobic respiratory fractionation and therefore deserves further detailed investigation and research.

The ^{18}O anomalous behavior observed in the harbour hypolimnion should have some implications for the oxygen abundance and its isotopic composition in the SML if the later is mixed with the hypolimnetic water at certain times (e.g. during episodic strong wind events and a consequent deepening of the thermocline). Under moderate values of [DO%] (moderate depletion of DO) in the hypolimnion, the entrainment of hypolimnetic water into SML will greater affect the oxygen isotopic composition and only slightly its oxygen abundance. On the other hand, under very low oxygen concentrations in the hypolimnion, the entrainment of hypolimnetic water into the epilimnion will have greater effect on the SML DO concentrations with a much smaller effect on the oxygen isotopic composition.

4.5.5 Variations in isotopic signatures of water

In Lake Ontario and Hamilton Harbour, the seasonal changes in $\delta^{18}O\text{-}H_2O$ had similar trends in both years but Hamilton Harbour had steeper slopes than those of Lake Ontario. This means that the harbour is more susceptible to the progressive evaporative enrichment in $\delta^{18}O\text{-}H_2O$ because of its larger surface to volume ratio (e.g. surface to volume ratio for harbour is 44 while for Lake Ontario is only 11.6 km^2 km^{-3}) and a small volume (≈0.3 km^3). Lake Ontario has a volume of 1640 km^3 and this huge water storage capacity acts as a buffer to seasonal variations in isotopic composition of lake water. Also, despite Lake Ontario and Hamilton Harbour being two interconnected water bodies in the same watershed (e.g. receiving precipitation and snowmelt of the same isotopic composition), it is interesting to see that the $\delta^{18}O\text{-}H_2O$ values for the harbour are lower than those of Lake Ontario. The difference is the largest in the spring and almost diminishes in the fall. This fact could probably be explained that Lake Ontario circulates in the winter at 2-3°C without ice formation. Circulating in the winter when the ambient air temperatures are well below lake water temperature results in winter evaporative flux of lake water from the lake surface to the atmosphere. This allows a heavy isotope build-up in the wintertime. In contrast, Hamilton Harbour is frozen in the winter and cut off from the atmosphere by the ice cover. Thus, the evaporative flux from the water surface is greatly reduced and the evaporative enrichment in $^{18}O\text{-}H_2O$ is negligible. Also, Hamilton Harbour is more influenced by snowmelt than Lake Ontario (snowmelt is lighter in $^{18}O\text{-}H_2O$).

4.5.6 Ratios of P/R

According to the results of the steady state model and accepted value for α_r of 0.977, net heterotrophy was evident in Lake Ontario in the top of the SML (at 2 m depth) for the most of the time, except two brief episodes (4-Aug-2004 and 25-Aug-2004) of net autotrophic conditions observed at the depth of deep chlorophyll maximun (DCM) of about 10 m. However, the application of the ^{18}O method to Lake Ontario to estimate metabolic ratios yields questionable results as the same model predicts negative rates ^{18}O-VR and ^{18}O-VP that cannot be true. Also, there is indirect evidence that the SML

should be autotrophic rather than heterotrophic as the SML had DO% above 100% and δ^{18}O-DO values below 24.2 ‰. Bottle-derived estimates of photosynthesis and respiration rates also suggests autotrophic or balanced plankton metabolism in the SML.

In Hamilton Harbour, phytoplankton may be light limited as $Z_m \approx Z_{eu}$ and Chl *a* concentrations are elevated near surface. Therefore, one can expect that the P/R ratios measured in the top SML (2 m depth) should always exceed those measured at the deeper depths (3-5 m depth) where light climate is less favorable for growth. The results of ^{18}O method support this expectation (Fig. 4.7). This is interesting because one usually expects SML to be a well-mixed and homogenous system with similar parameters throughout the entire column of the SML. However, the SML is usually defined based on homogenous distribution of temperature or salinity while gradients of phytoplankton, DO and $^{18}O/^{16}O$ may exist resulting in the observed variations of P/R ratios at different depths (Fig. 4.7). Comparison of VP/VR between two methods, ^{18}O and bottle estimates, shows that on average they give similar mean values but the behavioral pattern of VP/VR dynamics may be different. On several occasions, when bottle estimates predict peaks, the ^{18}O methods gave minimum values (Fig. 4.10). This different behavior may be attributed to the methodological differences in measured rates of photosynthesis or respiration. Also, the ^{18}O method gives ratio of integrated *in situ* rates over longer time scales (of a few days probably), while classical method gives a ratio of the daily rates scaled from more or less instantaneous rates and limited depth integration. Bottle estimates integrate water column during sampling so no water column differentiation is allowed. The day-to-day variations in photosynthesis and respiration (within 2-3 days in a row) depend more on the light availability and mixing layer depth rather than on plankton biomass (as indexed by Chl *a*). Therefore there is no surprise that, in our data, ratios of instantaneous rates (bottle method) were positively correlated with the ratio of Z_{eu}/Z_m. Ratios of time-integrated rates of photosynthesis and respiration reflect those measured over a few days when the days maybe different in respect to both thermocline position and incoming solar radiation because of the day-to-day

variations in cloud cover. This may result that time integrated rates especially photosynthetic ones may not be dependent on one-day light measurements. Instead, they should be more dependent on biomass concentration. Our data support this assumption showing that ^{18}O-VP/VR ratios had a positive correlation with Chl *a* rather than with Z_{eu}/Z_m.

4.5.7 Absolute rates of P and R

The application of ^{18}O method to the productive waters of Hamilton Hamilton gives somewhat reasonable and expected rates of ^{18}O-VR and ^{18}O-VP. Generally, VP and ^{18}O-VP were well coupled (Fig. 4.8*a*, *b*) and highly correlated (Fig. 4.11) meaning a good match between bottle estimates (based on Fee model results) and those calculated based on fraction of oxygen saturation and natural abundance of ^{18}O. It is worth mentioning that two methods gave almost the same results when photosynthetic rates are high, and ^{18}O method slightly underestimated bottle estimates when photosynthetic rates were low (Fig. 4.11). The harbour data themselves do not depart significantly from 1:1 line (*t*-test: $t_{crit} = 1.223 < t_{tab} = 2.093$; $n = 21$) nor the harbour data plus two Woods Bay sites (*t*-test: $t_{crit} = 1.290 < t_{tab} = 2.080$; $n = 23$). However, the inclusion of two Georgian Bay sites has resulted in the significant deviation of the regression coefficient from unity. Georgian Bay is a low productivity system and such systems are going to lie close to atmospheric equilibrium and the productivity estimates will be very sensitive to measurement error. Therefore, there is a possibility that Georgian Bay points at the lower end of the productivity range (Fig. 4.11) happened to underestimates for more or less random reasons. Another possibility is that for Georgian Bay site we underestimated gas exchange as we did not have measured estimates of the wind speed.

It was observed that the ^{18}O method slightly overestimated photosynthetic rates predicted by bottle incubations when the SML was shallow and the days were calm with low cloud cover (e.g. early July 2003 and 2004) and underestimated VP when the SML was getting deeper and the days were foggy and hazy (e.g. late July 2004). Thus, occasionally, ^{18}O-VP rates in SML predicted by ^{18}O may be affected by the over-warming of the shallow SML and/or vertical mixing with hypolimnetic

waters and low amount of incoming solar radiation, but overall, these rates are well predicted by the stable isotope method.

In Hamilton Harbour, the rates of ^{18}O-VR predicted by ^{18}O were not correlated with those predicted by bottle method but were are somewhat within its range (Fig. 4.8*c*, *d*) except times of wind-driven mixing events and thermocline deepening (e.g. early July 2003; early July and late August 2004) as well as autumnal thermocline deepening (e.g. late September 2003 or early October 2004; Fig. 4.8*c*, *d*). Thus, ^{18}O-VR rates reflect not only plankton respiration (e.g. dark oxygen consumption) and possibly littoral respiration but also a degree of mixing with metalimnetic/hypolimnetic water. However, the magnitude in respiration and photosynthetic rates predicted by ^{18}O seems to be real. For example, the model predicts that ^{18}O-VR exceeded ^{18}O-VP on a few occasions (Fig. 4.9; see also Fig. 4.10): early July 2003, early July and late August 2004. Contrary, the bottle estimates (Fig. 4.10) showed that the VP/VR ratios were above unity on those dates. However, according to the field observations, the SML in the harbour did have DO concentrations below saturation on those three occasions. For example, the very low DO% (= 54%) and DO (= 4.6 mg L^{-1}) concentrations in the SML at 2 m depth were observed on July-8-2003 a possibly as a result of upwelling of hypolimnetic water (into the SML) being pushed up by the intrusion of cold and dense lake water into the harbour hypolimnia (Fig. 4.2*c*). The SML was very shallow (Z_m = 2.6 m) because of the formation of the diurnal thermocline in addition to the existing seasonal thermocline, and there was a steep gradient in DO determined by Winkler method (mg L^{-1}) on that day: 4.6 at 2 m, 2.4 at 3 m, 0.6 at 4 m, and 4.2 at 12 m. The ^{18}O method predicts on this day a noticeable spike in the respiration rates and heterotrophic conditions in the SML. On two other dates, average DO% of the SML was 90% on 6-Jul-2004 and 94% on 23-Aug-2004. The estimates of the bottle method are based on measurements of more or less instantaneous metabolic rates over a few hours in plankton communities and therefore are unable to capture or integrate in its assessment the most recent history of lake metabolism. The events driving DO concentrations below saturation were

the wind-driven thermocline deepening and entrainments of low DO hypolimnetic water into the epilimnion. The observed under-saturation could also be caused in part by low biomass concentrations. Under high persistent westerly winds, phytoplankton could simply be flushed out with the epilimnetic water into the lake. If we apply usual rates of mean mass exchange in each direction (bi-flow) through the Burlington Canal that connects harbour with the lake (110 m^3 s^{-1}, Palmer and Poulton 1976) and assume the average depth of the SML to be 5 m, then 7-8 days are needed to reduce average epilimnetic Chl *a* concentrations in the harbour from 12 (e.g. mean summer Chl *a* = 10.9 mg m^{-3}) to about 6 mg m^{-3} (observed Chl *a* minimums). However, under prevalent westerly winds the epilimnetic water will be pushed out of the harbour to the lake, then, if we assume the same water velocity in the Canal (e.g. Palmer and Poulton 1976) but consider uni-flow conditions, then only 4 days are needed to reduce concentration of biomass by a factor of two. High persistent westerly winds blowing for 4 days are not uncommon in the harbour (e.g. Table 4.6; Fig. 4.3). All this might explain why we observed minimums in Chl *a* at times of prevalent westerly winds and consequent upwellings in western Lake Ontario.

If we apply steady state model with the value of α_r measured for Lake Kinneret (Luz et al. 2002) to Lake Ontario without paying attention to the validity of absolute rates of photosynthesis and respiration, our calculated P/R ratios are similar to those reported for the oligotrophic Lake Superior by Russ et al. (2004). Lake Superior is somewhat similar to Lake Ontario because of its size, low concentrations of phosphorus (Baehr and McManus 2003), phytoplankton biomass (Barbiero and Touchman 2001) as well as low DOC, and therefore one can expect some similarities between these two lakes. However, the ^{18}O method and its assumption do not work for Lake Ontario as it yilds negative metabolic rates. Continuous over-saturation of the SML and resulting oxygen flux from the lake to atmosphere of almost the same or even higher magnitude as the biological fluxes of oxygen, and the fact that water column was frequently perturbed by upwelling and downwelling episodes, do not fit the assumptions of a steady state model. Also, very low biomass and consequently low

respiration and photosynthetic rates relative to gas exchange are not conducive to the successful application of the ^{18}O method. Contrary to Lake Ontario, Hamilton Harbour is a stably stratified water body without any disruptions in the thermocline once it has been set up. Also, the oxygen fluxes through respiration and photosynthesis are much higher and very significant with the volumetric rates of almost 5-fold of those measured in Lake Ontario. This makes the application of a steady state model more likely to be successful. The ^{18}O method also showed reasonable results when applied to Georgian Bay and Woods Bay sites, but those stations were quite shallow and completely mixed.

4.6 Conclusions

Lake Ontario, similar to some other LGL studies (e.g. Russ et al. 2004, Ostrom et al. 2005), was found to be predominantly net heterotrophic based on the results of ^{18}O method under the assumption that α_r is low and similar to the annual value obtained for the sub-tropical Lake Kinneret (Luz et al. 2002). However, the results for Lake Ontario are questionable as (i) the same model predicts negative rates of photosynthesis and respiration, and (ii) the applied value for α_r was assumed from the literature and not the calculated one. The problem may be in the degree of over-saturation, and low productivity and biological fluxes as well as significant perturbations in the SML caused by upwelling and downwelling episodes. The latter is probably the most important factor as the previous studies indicated that even in small oligotrophic lakes the biomass was still sufficient to produce a well defined and nicely shaped diel oxygen curve (e.g. Cole et al. 2000). However, the ^{18}O method applied to a more productive and firmly stratified system, Hamilton Harbour, was a success. The ^{18}O model also worked for shallow and well-mixed stations in Georgian Bay and Woods Bay.

The interpretation of the results of the ^{18}O method for Hamilton Harbour led to a significant understanding of temporal variability of P/R ratios under real, *in situ* conditions, that would be otherwise have been difficult to measure. The behavior of P/R is different and more dynamic from those predicted by the traditional method that is based on *in vitro* bottle incubations; however, on

average, P/R are similar and within the range of values given by the bottle method. The P/R ratios calculated by two methods are not correlated, probably because ^{18}O and bottle methods measure ratio of different rates, time-averaged and more or less instantaneous ones. The method predicts volumetric photosynthesis well but may overestimate the respiration rates at times due to mixing events. This method also supports the classical hypothesis about variations of time-integrated P/R ratios depending on the trophic status (as indexed by Chl *a*).

The insight into the Hamilton Harbour hypolimnetic oxygen abundance vs. oxygen isotopic composition data has suggested that ^{18}O dynamics cannot be entirely explained based on the traditional knowledge of the aerobic respiratory fractionation, and suggest that other fractionation processes maybe important or some other processes may be involved (e.g. dilution with Lake Ontario water). The anomalous behavior of ^{18}O deserves further detailed investigation and research. The finding that non-respiratory oxygen consuming processes are mainly responsible for the hypolimnetic DO depletion may have some important implications for the Hamilton Harbour water management strategy.

As with any other method, ^{18}O method has its own drawbacks and advantages. It does not work in low productivity system such as Lake Ontario that is subject to major water column perturbations. It does not measure a pure plankton metabolism and its results can be influenced by a degree of mixing with the deeper water. It integrates rates over a time that is somewhat unknown depending on many involved factors such the intensity of biological fluxes, Z_m, water-atmosphere gas exchange and mixing. Also, the necessity to measure the fractionation factor associated with respiration (α_r) from incubation experiments may put some limitations on the applicability of this method. The values of α_r obtained from hypolimnion may not be applied to the SML as they are probably a product of several fractionation processes or some other physical processes that are not specific to the SML. One of the main advantages of the ^{18}O method over the bottle method is that it does not need incubations (except for α_r) and the samples can be easily collected over broad interval

in space, depth and time allowing better estimates of temporal and spatial dynamics in metabolic balance (P/R ratios).

Overall, the new ^{18}O method seems to give reasonable and explainable results for eutrophic systems, and is likely to provide a major step forward for understanding cycling of matter and energy within these aquatic ecosystems.

Chapter 5: Overall Summary and Conclusions

5.1 General Comments

The preceding chapters have described my research on plankton metabolic balance and its controlling factors at the nearshore zones of the LGL. Each chapter attempts to address a specific objective(s). In this chapter, I summarize the objectives and major conclusions of each of the preceding data chapters (Chapters 2-4) as well as give some recommendations and directions for the future research.

5.2 Chapter 2 Summary

Chapter two describes the PMB as mainly a product of two ratios, P_{max}/R and Z_{eu}/Z_m, and suggests analyzing them separately to understand the way environmental variables affect plankton metabolic balance; and it deals primarily with the analysis of P_{max}/R that is a metabolic balance without the confounding influences of physical structure (Z_{eu}/Z_m) that affects PMB_m. Chapter two introduces two studied systems and four sampling sites (Hamilton Harbour vs. Lake Ontario and Georgian Bay vs. Woods Bay) and provides some information on their physical structure and underwater light environment, concentrations of TP, Chl *a* and DOC. It reports the volumetric rates of light saturated photosynthesis and community respiration derived from the light-and-dark oxygen bottle method. In addition to regression and correlation analyses, a principal component analysis is introduced to show the difference between our sampling sites (e.g. eutrophic vs. oligotrophic) and visualize the relationship amongst key water quality parameters: volumetric metabolic rates and their ratios, TP, Chl *a*, light attenuation coefficient (as a surrogate for the DOC) and phytoplankton size structure (proportions of pico- , nano- and microplankton). The specific objectives of this chapter were (i) to determine the environmental correlates of P_{max}/R for both within and between systems without the confounding influences of physical structure, Z_{eu}/Z_m, and (ii) to test the idea that allochthonous organic inputs, as indexed by DOC, control PMB_m through P_{max}/R. The main conclusions of this Chapter are as follows:

1. Individual P_{max}/R were higher at more eutrophic but also higher DOC sites. This was explained by the different structure of the phytoplankton community and the lower biomass of heterotrophic to autotrophic organisms (e.g. Biddanda et al. 2001).

2. Strong and significantly different relationships were observed between individual P_{max} and Chl *a* and between R and Chl *a* meaning that P_{max}/R is an increasing function of Chl *a*. The dependence of P_{max}/R on Chl *a* may suggest a looser coupling between production and consumption on the scale of individual observations.

3. P_{max}/R increased as the proportion of microplankton Chl *a* increased. However, trophic status effects were stronger than cell size effects.

4. There was a strong relationship between P_{max} and R suggesting a close coupling between heterotrophic consumption and autotrophic production.

5. With additional data from the literature, it was found that total variation of P_{max}/R (including within-system and between system variations) was best explained by a regression model that increased with Chl *a* concentration but decreased with TP and Z_{eu}/Z_m. This is consistent with the previous suggestions that phosphorus may stimulate bacterial respiration (e.g. Roberts and Howarth 2006) and increase degradability of DOC (e.g. Schindler et al. 1992), and that Z_{eu}/Z_m may select for phytoplankton with different P_{max}/R efficiencies (e.g. Harris 1978).

6. However, season average behaviour of P_{max}/R was only predicted by Z_{eu}/Z_m (negative relationship), suggesting that on the larger scale (seasonal), the succession of phytoplankton and therefore, algal taxonomic properties seem to be more powerful than the lake trophic effect in determining P_{max}/R.

7. Over the range of conditions covered in this study (DOC = 2.1 to 6.6 mg L^{-1}), there was no evidence that DOC was correlated with P_{max}, R or their ratio.

8. Based on the results of this study, P_{max}/R seems to be under mainly physical control on the seasonal time scale. Therefore, a climate change affecting the physical environment is likely to bring systematic changes to the autotrophic-heterotrophic potential.

5.3 Chapter 3 Summary

Chapter three introduces the ^{14}C method and makes use of some previously reported results from the light-and-dark oxygen method (Chapter two). It reports the areal rates of gross photosynthesis and community respiration as well as their ratios. Apart from regression and correlation analyses, the principal component analysis of our own season averaged data plus those gathered from the literature was used to visualize the relationship amongst AGP, AR, DOC, TP and Chl *a*. The specific objectives of this chapter were: (i) to test the expectation that PMB_m will be dependent on both P_{max}/R and Z_{eu}/Z_m; (ii) to determine the environmental controls of PMB_m (iii) to ascertain the potential mechanism through which DOC affects plankton metabolic balance; and, (iv) to test if ^{14}C method with short 1-hour incubations is able to give estimates of gross photosynthesis. Overall, the main conclusions of Chapter three were as follows:

9. Contrary to the emergent idea about the prevalence of heterotrophic conditions in the SML of lakes, it was observed that PMB was net autotrophic in most of the cases (73% of the observations) suggesting that autotrophy in lakes is predominant in larger systems during stratification.

10. Strong relationships have been found between AR and AGP for both individual and site-averaged data for sites with low to moderate DOC concentrations suggesting mostly autochthonous based plankton metabolism; however AR seems to be uncoupled from AGP at higher DOC concentrations (>7-8 mg L^{-1}). As literature data are lacking information on respiration measurements, the observed relationships between AR and AGP at low to moderate DOC can be used to obtain respiration data from the great bulk of the accumulated production data.

11. Again, an observed strong relationship between AR and AGP suggests a balanced plankton metabolism at DOC < 7-8 mg L^{-1} with some export potential to support other trophic levels.

12. It was confirmed that within- and inter-system variations in PMB_m were heavily dependent on both ratios, P_{max}/R and Z_{eu}/Z_m as it was postulated in Chapter two.

13. Short-term within-system variations in PMB_m were driven by the interplay of Chl *a*, TP and Z_{eu}/Z_m; with Chl *a* and Z_{eu}/Z_m having a positive effect and TP having a negative effect.

14. PMB_m determined as average ratio of AGP/AR was dependent only on DOC or single physical parameters such as Z_{eu} or Z_m, while PMB_m determined as the ratio between averages AGP and AR was controlled by the joint effect of DOC, TP and Chl *a* with DOC and TP having negative effects and Chl *a* having a positive effect

15. It was found that DOC affected average AGP/AR ratios primarily via its control over fluctuations of the physical environment and had a depressing effect on AGP rates but did control rates of AR.

16. It was observed that short incubation ^{14}C method performed with an acidification technique gave estimates lower than expected for the gross photosynthesis estimated as oxygen evolution. However, its estimates are close to gross photosynthesis as, on average, it was able to provide an apparent photosynthetic quotient in the physiological range expected for the nitrate assimilation growth.

5.4 Chapter 4 Summary

Chapter four describes the application of the ^{18}O method as a steady state isotope model adjusted for the wind-driven gas exchange. The absolute rates of volumetric P and R, and their ratios derived from this method are compared against bottle estimates. The main objective of this Chapter was to validate the results and meanings of the stable isotope method by the direct comparison with the traditional bottle incubation methods. The major outcomes were as follows:

17. The application of the ^{18}O method to Lake Ontario gave internally inconsistent results (e.g. negative absolute rates of P and R) and poor agreement with independent estimates of P, R and P/R despite superficially plausible estimates for P/R. This was explained by the low productivity and strong physical disturbance in Lake Ontario that masked the biological signals in DO and the isotope signature invalidating the steady-state isotope model assumptions.

18. The ^{18}O method results are very sensitive to the values of α_r used in calculations P/R ratios. Therefore, the ^{18}O method applied to Lake Superior (Russ et al. 2004) may not yield the same results as they were reported if the measured α_r is used instead of the literature value for Lake Kinneret ($\alpha_r = 0.977$).

19. The hypolimnion of Hamilton Harbour presented another type of paradoxical behaviour, as the seasonal development of DO depletion was not accompanied by the progressive isotope enrichment expected from respiratory fractionation. The observed inverse oxygen fractionation was explained by one of the following: (i) the hypolimnetic data were not actually successive observations over time and the same water mass; (ii) there were more than one oxygen consuming processes with different oxygen isotope fractionations; and (iii) the exchange with the Lake Ontario water resulted in the dilution of the heavy isotopes.

20. However, the application of the ^{18}O method to the surface mixed layer of Hamilton Harbour and some other relatively sheltered sites that were sampled occasionally gave reasonable and explainable results. The absolute rates of P from the isotope model correlated well with the bottle estimates. The estimates for R and P/R were not well correlated with the bottle estimates but were of comparable magnitude on average, and differences were explicable in terms of physical forces and the different time scales of response for the two methods.

21. Overall, the new ^{18}O method seems to give reasonable and explainable results for eutrophic systems. The main advantage of this method over the bottle method is that it does not need incubations and the samples can be easily collected over broad interval in space, depth and time allowing better estimates of temporal and spatial dynamics in metabolic rates and their balance. This method is likely to provide a major step forward for understanding cycling of matter and energy in the eutrophic aquatic ecosystems.

5.5 Recommendations and Directions for the future research

Based on the research work presented here and some others in the literature, I suggest that the following six questions would prove fruitful for future research:

1. Most of the current research on PMB_m is being focused on between-systems comparisons with very limited measurements in any given lake (e.g. del Giorgio and Peters 1994; Hanson et al. 2003). While this is very important in increasing our understanding of plankton metabolism, it seems that, based on the results of this study, between-systems and within-systems variations are driven by different factors. Therefore more research and insights on the seasonal dynamics of PMB_m and its controlling factors are needed.

2. Again, the foundation of our present knowledge of PMB_m has being mainly built on small lakes that are easy to sample. However, Great Lakes may be different from the small lakes, and definitely, they are in many parameters. Despite the fact that many small lakes might be heterotrophic, the possibility of the summer-time autotrophy in the SML of the Great Lakes observed in this study cannot be easily ruled out, and needs further attention and research.

3. As it has been shown in this study, the PMB_m calculated as the average ratio or ratio between averages are driven by different factors. Therefore, the studies on PMB_m and its controlling factors should clearly state what type of PMB_m they consider.

4. The relative importance of phytoplankton cell size effect vs. trophic status effect on plankton metabolism is very interesting and deserves further investigation. It may happen that our conclusions towards more important role of the trophic status were influenced by a limited sample size and inability to fully separate the cell size effect from the trophic status effect.

5 In our site-averaged data, we observed that P_{max}, R and P_{max}/R were positively related to the proportion of microplankton in the total plankton and relationships were statistically significant despite the small sample size ($n = 6$). We lack enough data to test this at the season average, inter-system scale with the larger sample size. It would be interesting to extend a similar study to other systems to test the importance of microplankton fraction in determining a season average behaviour of metabolic rates and their ratio.

6. The inverse oxygen fractionation observed in the Hamilton Harbour hypolimnion is a very interesting phenomenon and is worth further studies on which oxygen consuming process prevails over others. It is clear that oxygen depletion in the hypolimnion cannot be explained by our knowledge of the aerobic microbial respiration and therefore, some other fractionation processes might be involved as well. If any of the chemical oxidation processes are involved and dominate over others, then it might have some very important implications for Hamilton Harbour water management authorities.

References

Alpine, A. E., and J. E. Cloern. 1988. Phytoplankton growth rates in a light-limited environment, San Francisco Bay. Mar. Ecol. Prog. Ser., 44: 167-173.

Bachmann, R. W., M. V. Hoyer, and D. E. Canfield. 2000. Internal heterotrophy following the switch from macrophytes to algae in lake Apopka, Florida. Hydrobiol., 418: 217-227.

Baehr, M. M., and J. McManus. 2003. The measurement of phosphorus and its spatial and temporal variability in the western arm of Lake Superior. J. Great Lakes Res., 29(3): 479-487.

Bannister, T. T. 1974. Production equation in terms of chlorophyll concentration, quantum yield, and upper limit to production. Limnol. Oceanogr., 19: 1-12.

Barbiero, R. P., and M. L. Tuchman. 2001. Results from the U.S. EPA's Biological Open Water Surveillance Program of the Laurentian Great Lakes: I. Introduction and phytoplankton results. J. Great Lakes Res., 27(2): 134-154.

Barica, J. 1989. Unique Limnological Phenomena Affecting Water Quality of Hamilton Harbour, Lake Ontario. J. Great Lakes Res., 15(3): 519-530.

Bell, R. T., and J. Kuparinen. 1984. Assessing phytoplankton and bacterioplankton production during early spring in Lake Erken, Sweden. Appl. Environ. Microbiol. 48: 1221-1230.

Bender, M., J. Orchardo, M.-L. Dickson, R. Barber, and S. Lindley. 1999. In vitro O_2 fluxes compared with ^{14}C production and other rate terms during the JGOFS Equatorial Pacific experiment. Deep-Sea Res., I 46**:** 637–654.

Benson, B. B., and D. Krause. 1984. The concentration and isotopic fractionation of oxygen dissolved in fresh water and seawater in equilibrium with the atmosphere. Limnol. Oceanogr., 29: 620-632.

Berman, T., L. Stone, Y. Z. Yacobi, B. Kaplan, M. Schlichter, A. Nishri, and U. Pollingher. 1995. Primary Production and Phytoplankton in Lake Kinneret: A Long-Term Record (1972-1993). Limnol. Oceanogr., 40(6): 1064-1076.

Blanton, J. O. 1975. Nearshore lakes currents measured during upwelling and downwelling of the thermocline in Lake Ontario. J. Phys. Oceanogr., 5(1): 111-124.

Blight, S. P., T. L. Bentley, D. Lefevre, C. Robinson, R. Rodrigues, J. Rowlands, and P. J. le B. Williams. 1995. Phasing of autotrophic and heterotrophic plankton metabolism in a temperate coastal ecosystem. Mar. Ecol. Prog. Ser., 128: 61-75.

Biddanda, B., S. Opsahl, and R. Benner. 1994. Plankton respiration and carbon flux through bacterioplankton on the Louisiana shelf. Limnol. Oceanogr., 39(6), 1994, 1259-1275.

Biddanda, B., M. Ogdahl, and J. Cotner. 2001. Dominance of bacterial metabolism in oligothropic relative to euthropic waters. Limnol. Oceanogr., 46(3): 730-739.

Biddanda, B. and Cotner, J. 2002. Love Handles in Aquatic Ecosystems: The role of dissolved organic carbon drawdown, resuspended sediments, and terriginous inputs in the carbon balance of Lake Michigan. Ecosystems, 5: 431-445.

Boyce, F. M. 1974. Some aspects of Great Lakes physics of importance to biological and chemical processes. J. Fish. Res. Board Can., 31: 689–730.

Boyce, F. M. 1977. Response of the coastal boundary layer on the north shore of Lake Ontario to a fall storm. J. Phys. Oceanogr., **7**(5): 719-732.

Broecker, W. S., and V. M. Oversby. 1971. Chemical equilibrium in the Earth. McGraw-Hill.

Bukaveckas, P. A., J .J. Williams, and S. P. Hendricks. 2002. Factors regulating autotrophy and heterotrophy in the main channel and the embayment of a large river impoundment. Aquatic Ecology, 36: 355-369.

Calado, A. J., S. C. Craveiro, and O. Moestrup. 1998. Taxonomy and ultrastructure of a freshwater, heterotrophic *Amphidinium* (Dinophyceae) that feeds on unicellular protists. J. Phycol., 34: 536–554.

Carignan, R., A.-M. Blais, and C. Vis. 1998. Measurements of primary production and community respiration in oligotrophic lakes using the Winkler method. Can. J. Fish. Aquat. Sci., 55: 1078-1084.

Carignan, R., D. Planas, and C. Vis. 2000. Planktonic production and respiration in oligotrophic Shield lakes. Limnol. Oceanogr., 45(1): 189-199.

Caron, D. A., E. L. Lin, R. W. Sanders, M. R. Dennett M. R., and U. G. Berneger. 2000. Response of bacterioplankton to organic carbon and inorganic nutrients additions in contrasting oceanic ecosystems. Aquat. Microb. Ecol., 22: 175-184.

Carpenter, S. R., J. J Cole, J. F. Kitchell, and M. L. Pace. 1998. Impact of dissolved organic carbon, phosphorus, and grazing on phytoplankton biomass and production in experimental lakes. Limnol. Oceanogr., 43: 73–80.

Carter, J. C. H., W. D. Taylor, and C. Tudorancea. 1995. A horizontal gradient in zooplankton community structure, and its implications for the relationships among mesozooplankton, microzooplankton, and phytoplankton. Arch. Hydrobiol., 133: 197-222.

Charlton, M. N., and R. Le Sage. 1996. Water quality trends in Hamilton Harbour: 1987 to 1995. Water Qual. Res. J. Canada, 31(3): 473-484.

Chisholm, S. W. 1992 Phytoplankton size, p 213-237. *In* P. G. Falkowski. and A. D. Woodhead [eds.], Primary Productivity and Biogeochemical Cycles in the Sea. Plenum Press.

Christensen, D. L., S. R. Carpenter, K. L. Cottingham, S. E. Knight, J. P. LeBouton, D. E. Schindler, N. Voichick, J. J. Cole, and M. L. Pace. 1996. Pelagic responses to changes in dissolved organic carbon following division of a seepage lake. Limnol. Oceanogr., 41(3): 553-559.

Cimbleris, A. C. P., and J. Kalff. 1998. Planktonic bacterial respiration as a function of C:N:P ratios across temperature lakes. Hydrobiol., 384: 89-100.

Cole, J. J., and N. F. Caraco. 1993. The pelagic microbial food web of oligotrophic lakes, p. 101-111. *In* T.E. Ford [ed.], Aquatic microbiology. Blackwell Scientific Press.

Cole J. J., S. R. Carpenter, and J. F. Kitchell. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. Limnol. Oceanogr., 45: 1718–1730.

Cole J. J., M. L. Pace, S. R. Carpenter, and J. F. Kitchell. 2000*a*. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. Limnol. Oceanogr., 45(8): 1718-1730.

Cole, J. J., S. R. Carpenter, J. F. Kitchell, and M. L. Pace. 2002. Pathways of organic carbon utilization in small lakes: Results from a whole-lake ^{13}C addition and coupled model. Limnol. Oceanogr., 47(6): 1664-1675.

Cotner J.B., and B. A. Biddanda. 2002. Small player, large role: microbial influence on biogeochemical processes in pelagic aquatic ecosystems. Ecosystems, 5: 105-121.

Crusius, J, and R. Wanninkhof. 2003. Gas transfer velocities measured at low wind speed over a lake. Limnol. Oceanogr., 48(3): 1010–1017.

Cushing, D. H. 1989. A difference in structure between ecosystems in strongly stratified waters and in those that are only weakly stratified. Review. J. Plankton Res., 11(1): 1-13.

DeBruyn, J. M., J. A. Leigh-Bell, R. M. L. McKay, R. A. Bourbonniere, and S. W. Wilhelm. 2004. Microbial distributions and the impact of phosphorus on bacterial activity in Lake Erie. J. Great Lakes Res., 30(1): 166–183.

del Giorgio, P. A., and R. H. Peters. 1994. Patterns in planktonic P:R ratios in lakes: Influence of lake trophy and dissolved organic carbon. Limnol. Oceanogr., 39(4): 772-787.

del Giorgio P. A., J. J. Cole, and A. Cimbleris. 1997. Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. Nature, 385: 148 – 151.

Depew, D. C., S. J. Guildford, and R. E. H. Smith. 2006*a*. Nearshore-offshore comparison of chlorophyll-*a* and phytoplankton production in the dreissenid-colonized eastern basin of Lake Erie. Can. J. Fish. Aquat. Sci., 63: 1115-1129.

Depew D. C., R. E. H. Smith, and S. J. Guildford. 2006*b*. Production and respiration in lake Erie plankton communities. J. Great Lakes Res., 32: 817-831.

Dickson, M.-L., J. Orchardo, R. T. Barber, J. Marra, J. J.McCarthy, and R. N. Sambrotto. 2001. Production and respiration rates in the Arabian Sea during the 1995 Northeast and Southwest Monsoons. Deep-Sea Res. II 48: 1199–1230.

Dring, M. J., and D. H. Jewson. 1982. What does ^{14}C uptake by phytoplankton really measure? A theoretical modelling approach. Proc. R. Soc. Lond., B 214: 351-368.

Elliott, W. P. 1958. The growth of the atmospheric internal boundary layer. Trans. Amer. Geophys. Un., 39: 1048-1054.

Emerson, S. 1975. Gas exchange rates in small Canadian Shield lakes. Limnol. Oceanogr., 20 (5): 754-761.

Emerson, S., P. Quay, C. Stump, D. Wilbur, and M. Knox. 1991. O_2, Ar, N_2, and ^{222}Rn in waters of the sub-arctic ocean: Net biological O_2 production. Global Biogeochem. Cycles, 5: 49-69.

Emerson, S., C. Stump, D. Wilbur, and P. Quay. 1999. Accurate measurements of O_2, N_2, and Ar gases in water and solubility of N_2. Mar. Chem., 64:337-347.

Epstein, S., and T. K. Mayeda. 1953. Variations of the $^{18}O/^{16}O$ ratio in natural waters. Geochimica et Cosmochimica Acta, 4(5): 213-224.

Fagerbakke, K. M., M. Heldal, and S. Norland. 1996. Content of carbon, nitrogen, oxygen, sulfur and phosphorus in native aquatic and cultured bacteria. Aquat. Microb. Ecol., 10: 15-27

Fahnenstiel, G. L., T. B. Bridgeman, G. A. Lang, M. J. McCormick, and T. F. Nalepa. 1995. Phytoplankton productivity in Saginaw Bay, Lake Huron: effects of zebra mussel (Dreissena polymorpha). J. Great Lakes Res., 21(4): 465-475.

Fahnenstiel, G. L., and H. J. Carrick. 1988. Primary production in lakes Huron and Michigan: in vitro and in situ comparisons. J. Plankton Res., 10(6): 1273-1283.

Fahnenstiel, G. L., and D. Scavia. 1987. Dynamics of Lake Michigan phytoplankton: primary production and growth. Can. J. Fish. Aquat. Sci., 44: 499-508.

Falkowski, P. G., and J. A. Raven. 1997. Aquatic photosynthesis. Capital City Press.

Fang, X., and H. G. Stefan. 1994. Temperature and dissolved oxygen simulations in a lake with ice cover. Project Report 356, St. Anthony Falls Hydraulic Laboratory, University of Minnesota.

Farjalla, V. F., A. Enrich-Prast, F. A. Esteves, and A. Cimbleris. 2006. Bacterial growth and DOC consumption in a tropical coastal lagoon. Braz. J. Biol., 66(2A): 383-392.

Fee, E. J. 1990. Computer programs for calculating in-situ phytoplankton photosynthesis. Can. Tech. Rep. Fish. Aquat. Sci., No. 1740.

Fee, E. J., R. E. Hecky, and H. A. Welch. 1987. Phytoplankton photosynthesis parameters in central Canadian lakes. J. Plankton Res., 9(2): 305-316.

Fee, E. J., A. Shearer, E. R. DeBruyn, and E. U. Schindler. 1992. Effects of lake size on phytoplankton photosynthesis. Can. J. Fish. Aquat. Sci., 49: 2445–2459.

Fee, E. J., R. E. Hecky, S. E. M. Kasian, and D. R. Cruikshank. 1996. Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. Limnol. Oceanogr., 41(5): 912-920.

Fitzwater, S. E., G. A. Knauer, and J. H. Martin. 1982. Metal contamination and its effect on primary production measurements. Limnol. Oceanogr., 27: 544-551.

Ford, D.E. and H. G. Stefan. Thermal predictions using integral energy model. J. Hydraul. Divis. ASCE, 106 (HY1): 39-55.

Fritz, P., S. K. Frape, R. J. Drimmie, and A. R. Heemskerk. 1986. Reply to comments by Grabczak et al. on "Water-rock interaction and chemistry of groundwaters from the Canadian Shield. Geochimica et Cosmochimica Acta, 50: 1561-1563.

Fry, B. 2006. Stable Isotope Ecology. Springer, 308 pp.

Geider, R. J., and B. A. Osborne. 1989. Respiration and microalgal growth: a review of the quantitative relationship between dark respiration and growth. New Phytol., 112: 327-341.

Geider, R. J. 1992. Respiration: taxation without representation?, p. 333-360. *In* P. G. Falkowski and A. D. Woodhead [eds.], Primary productivity and biogeochemical cycles in the sea. Plenum, New York.

Glooshenko, W. A., J. E. Moore, M. Munawar, and R.A. Vollenweider. 1974. Primary production in Lakes Ontario and Erie: a comparative study. J. Fish. Res. Board Can., 31: 253-263.

González, N., R. Anadón, and E. Marañón. 2002. Large-scale variability of planktonic community metabolism in the Atlantic Ocean: importance of temporal changes in oligotrophic subtropical waters. Mar. Ecol. Prog. Ser., 233: 21-30.

Gouvêa, S. P., C. Melendez, M. J. Carberry, G. S. Bullerjahn, S. W. Wilhelm, T. A. Langen, and M. R. Twiss. 2006. Assessment of phosphorus-microbe interactions in Lake Ontario by multiple techniques. J. Great Lakes Res., 32: 455–470.

Grobbelaar, J. U. 1981. Deterministic production model for describing algal growth in large outdoor mass algal cultures, p. 173-181. *In* J. U. Grobbelaar, C. J. Soeder and D. F. Toerien [eds.], Wastewater for Agriculture, UOFS Publ., Series C, No.3.

Grobbelaar, J. U. 1985. Phytoplankton productivity in turbid waters. J. Plankton Res., 7(5): 653-663.

Grobbelaar, J. U., C. J. Soeder, and E. Stengel. 1984. Modelling algal productivity and oxygen production in large outdoor cultures. Jül-Spez-282, Jülich FRG.

Guy, R.D., M. L. Fogel, and J.A. Berry. 1993. Photosynthetic fractionation of the stable isotopes of oxygen and carbon. Plant Physiol., 101: 37-47.

Hadas, O., and R. Pinkas. 1995. Sulfate reduction processes in sediments at different sites in Lake Kinneret, Israel. Microbial Ecology, 30(1): 55-66.

Hambright, K. D., M. Gophen, and S. Serruya. 1994. Influence of Long-Term Climatic Changes on the Stratification of a Subtropical, Warm Monomictic Lake. Limnol. Oceanogr., 39(5): 1233-1242.

Hanson, P. C., D. L. Bade, S. R. Carpenter, and T. K. Kratz. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. Limnol. Oceanogr., 48(3): 1112–1119.

Harris, G. P. 1978. Photosynthesis, productivity and growth: The physiological ecology of phytoplankton. Arch. Hydrobiol. Beih. Ergeb. Limnol., 10: 1-171.

Harris, G. P. 1986. Phytoplankton ecology: structure, function, and fluctuation. Chapman and Hall.

Harris, G. P., and B. B. Piccinin. 1977. Photosynthesis by natural phytoplankton populations. Arch. Hydrobiol., 80: 405-457.

Harris, G. P., and B. B. Piccinin. 1980. Physical variability and phytoplankton communities. IV. Temporal changes in the phytoplankton community of a physically variable lake. Arch. Hydrobiol., 89: 447-473.

Hart, D. R., L. Stone, and T. Berman. 2000. Seasonal Dynamics of the Lake Kinneret Food Web: The Importance of the Microbial Loop. Limnol. Oceanogr., 45(2): 350-361.

Hecky, R. E., and S. J. Guildford. 1984. Primary Productivity of Southern Indian Lake before, during, and after Impoundment and Churchill River Diversion. Can. J. Fish. Aquat. Sci., 41(4): 591-604.

Hiriart, V. P., B. M. Greenberg, S. J. Guildford, and R. E. H. Smith. 2002. Effects of ultraviolet radiation on rates and size-distribution of primary production by Lake Erie phytoplankton. Can. J. Fish. Aquat. Sci., 59: 317-328.

Horn, H., and L. Paul. 1984. Interactions between light situation, depth of mixing and phytoplankton growth during the spring period of full circulation. Int. revue ges. Hydrobiol., 69: 507-519.

Houser, J. N. 2006. Water color affects the stratification, surface temperature, heat content, and mean epilimnetic irradiance of small lakes. Can. J. Fish. Aquat. Sci., 63: 2447-2455, [doi: 10.1139/F06-131].

Howarth, R. W., and A. F. Michaels 2000. The Measurement of primary production in aquatic ecosystems, p. 72-85. *In* O. E. Sala, R. B. Jackson, H. A. Mooney and R. W Howarth [eds.]. Methods in Ecosystem Science. Springler-Verlag Inc.

Jackson, T. A., and R. E. Hecky. 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. Can. J. Fish. Aquat. Sci., 37: 2300-2317.

Jassby A. D., and T. Platt. 1976. Mathematical formulation of the relationship between photosynthesis and light for phytoplankton. Limnol. Oceanogr., 21(4): 540-547.

Jones, R. I. 1992. The influence of humic substances on locustrine planktonic food chains. Hydrobiol., 229: 73-91.

Kalff, J. 2002. Limnoecology. Inland Water Ecosystems. Prentice Hall.

Kiddon J., M. L. Bender, J. Orchardo., D. A. Caron., J. C. Goldman, and M. Dennet. 1993. Isotopic fractionation of oxygen by respiring marine organisms. Global Biogeochem. Cycles, 7: 679-694.

Kiddon, J., M. L. Bender, and J. Marra. 1995. Production and respiration in the 1989 North Atlantic spring bloom: An analysis of the irradiance-dependent changes. Deep-Sea Res., 42: 553–576.

Kirk, J. T. O. 1994. Light and photosynthesis in aquatic ecosystems, 2nd ed. Cambridge University Press.

Knox, M., P. D. Quay, D. Wilbur. 1992. Kinetic isotopic fractionation during air-water gas transfer of O_2, N_2, CH_4, and H_2. J. Geophys. Res., 97: 20335-20343.

Kohler, M. A., and L. H. Parmele. 1967. Generalized estimates of free-water evaporation. Water Resour. Res., 3: 997-1005.

Kraus, E. B. 1972. Atmosphere – ocean interaction. Oxford University Press.

Krause-Jensen, D., and K. Sand-Jensen. 1998. Light attenuation and photosynthesis of aquatic plant communities. Limnol. Oceanogr., 43(3): 396-407.

Kritzberg, E. S., J. J. Cole, M. L. Pace, W. Graneli, and D. L. Bade. 2004. Autochthonous versus allochthonous carbon sources of bacteria: Results from whole-lake ^{13}C addition experiments. Limnol. Oceanogr., 49: 588-596.

Lampert, W., and U. Sommer. 1997. Limnoecology: The Ecology of lakes and streams. Oxford University Press.

Langdon, C. 1992. The significance of respiration in production measurements based on oxygen, p. 69-78. *In* Measurement of primary production from the molecular to the global scale. Proceedings of an ICES marine science symposium. 21-24 April 1992, La Rochelle, France, Vol. 197.

Laws, E. A., M. R. Landry, R. T. Barber, L. Campbell, M.-L. Dickson, and J. Marra. 2000. Carbon cycling in primary production bottle incubations: Inferences from grazing experiments and photosynthetic studies using ^{14}C and ^{18}O in the Arabian Sea. Deep-Sea Res. II, 47: 1339–1352.

Leggett M. F., M. R. Servos, R. Hesslein, O. Jahannsson, E. S. Millard, and D. G. Dixon. 1999. Biogeochemical influences on the carbon isotope signatures of Lake Ontario biota. Can. J. Fish. Aquat. Sci., 56: 2211-2218.

Luz, B., E. Barkan, Y. Sagi, and Y. Z. Yacobi. 2002. Evaluation of community respiratory mechanisms with oxygen isotopes: A case study in Lake Kinneret. Limnol. Oceanogr., 47(1): 33-42.

MacIntyre, S., R. Wanninkhof, and J. P. Chanton. 1995. Trace gas exchange across the air-water interface in freshwaters and coastal marine environments, p. 52–97. *In* P. A. Matson and R. C. Harris [eds.], Biogenic trace gases: Measuring emissions from soil and water. Blackwell Scientific, Oxford.

Malone, T.C., 1980. Size-fractionated primary productivity of marine phytoplankton, p. 301-319. *In* P. G. Falkowski [ed.], Primary productivity in the sea. Plenum Press.

Markarger, S., and K. Sand-Jensen. 1989. Pattern of night-time respiration on a dense phytoplankton community under a natural light regime. J. Ecol., 77: 49-61.

Markarger, S., and W. F. Vincent. 2001. Light absorption by phytoplankton: development of matching parameter for algal photosynthesis under different spectral regimes. J. Plankton Res., 23: 1373-1384.

Marra, J. 2002. Approaches to the measurement of plankton production, p. 78-108. *In* P. J. L. Williams, D. N. Thomas and C. S. Reynolds [eds.], Phytoplankton productivity: Carbon assimilation in marine and freshwater ecosystems. Blackwell Scientific, Oxford.

Megard, R. O., T. Berman, P. J. Curtis, and P. W. Vaughan. 1985. Dependence of phytoplankton assimilation quotients on light and nitrogen source: implications for oceanic primary productivity. J. Plankton Res., 7: 691-702.

Millard, E. S., D. D. Myles, O. E. Johannsson, and K. M. Ralph. 1996. Phytoplankton photosynthesis at two index stations in Lake Ontario 1987-1992: assessment of the long-term response to phosphorus control. Can. J. Fish. Aquat. Sci., 53: 1092-1111.

Millard, E. S., E. J. Fee, D. D. Myles, and J. A. Dahl. 1999. Comparison of phytoplankton photosynthesis methodology in Lakes Erie, Ontario, the Bay of Quinty and the Northwest Ontario Lake Size Series, p. 441-468. *In* M. Munawar, T. Edsall and I. F. Munawar [eds.], State of Lake Erie (SOLE) – past, present and future, pp. 441-468. Ecovision World Monograph Series, Backhuys Publisher.

Millard, E. S., O. E. Johannsson, M. A. Neilson, and A. H. El-Shaarawi. 2003. State of lake Ontario (SOLO) – Past, Present and Future (Munawar M. [ed.]). Ecovision World Monograph Series, Aquatic Ecosystem health and Management Society.

Murphy, T. P., K. Irvine, J. Guo, J. Davies, H. Murkin, M. Charlton, and S. B. Watson. 2003. New Microcystin Concerns in the Lower Great Lakes. Water Qual. Res. J. Canada, 38 (1): 127-140.

Neilson, M. A., D. S. Painter, G. Warren, R. A. Hites, I. Basu, D. V. Weseloh, D. M. Whittle, G. Christie, R. P. Barbeiro, M. L. Tuchman, O. E. Johansson, T. F. Nalepa, T. A. Edsall, G. Fleischer, C. Bronte, S. B. Smith, and P. C. Baumann. 2003. Ecological monitoring for assessing the state of nearshore and offshore waters of the great lakes. Ecol. Mon. Assess., 88: 103–117.

Nicholls, K. H., G. J. Hopkins, S. J. Standke, and L. Nakamoto. 2001. Trends in Total Phosphorus in Canadian Near-Shore Waters of the Laurentian Great Lakes: 1976-1999. J. Great Lakes Res., 27(4): 402-422.

Odum, H. T. 1956. Primary production in flowing waters. Limnol. Oceanogr., 1: 102-117.

Ostrom, N. E., H. J. Carrick, M. R. Twiss, and L. Piwinski. 2005. Evaluation of primary production in Lake Erie by multiple proxies. Oecologia, 144(1): 115-124.

Pace, M. L., J. J. Cole, S. R. Carpenter, J. F. Kitchell, J. R. Hodgson, M. C. Van de Bogert, D. L. Bade, E. S. Kritzberg, and D. Bastviken. 2004. Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs. Nature, 427: 240-243.

Pace, M. L. and Y. T. Prairie. 2005. Respiration in lakes, p. 103-121. *In* P. A. del Giorgio and P. J. le B Williams [eds.], Respiration in Aquatic Ecosystems. Oxford University Press.

Palmer, M. D., and D. J. Poulton. 1976. Hamilton Harbor: Periodicities of the Physicochemical Process. Limnol. Oceanogr., 21(1): 118-127.

Platt, T. 1986. Primary production in the ocean water column as a function of surface light intensity: Algorithms for remote sensing. Deep See Res., 33: 149-163.

Polis, G. A., R. D. Holt, B. A. Menge, and K. O. Winemiller. 1996. Time, space and life history: Influences on food webs, p. 435-460. *In* G. A. Polis and K. O. Winemiller [eds.], Food webs: Integration of patterns and dynamics. Chapman and Hall, New York.

Prairie, Y. T., D. F. Bird, and J. J. Cole. 2002. The summer metabolic balance in the epilimnion of southern Quebec lakes. Limnol. Oceanogr., 47(1): 316-321.

Quay, P. D., S. Emerson, D. O. Wilbur, C. Stump, and M. Knox. 1993. The $\delta^{18}O$ of Dissolved O_2 in the Surface Waters of the Subarctic Pacific: A Tracer of Biological Productivity. J. Geophys. Res., 98 (C5): 8447-8458.

Quay, P.D., D.O. Wilbur, J. E. Richey, A. H. Devol, R. Benner, and B. R. Forsberg. 1995. The ^{18}O:^{16}O of dissolved oxygen in rivers and lakes in the Amazon Basin: Determining the ratio of respiration to photosynthesis rates in freshwaters. Limnol. Oceonogr., 40(4): 718-729.

Rao, Y. R., and C. R. Murthy. 2001*a*. Coastal boundary layer characteristics during summer stratification in Lake Ontario. J. Phys. Oceanogr., 31: 1088-1104.

Rao, Y. R. and C. R. Murthy, 2001*b*. Nearshore currents and turbulent exchange characteristics during upwelling and downwelling events in Lake Ontario. J. Geophys. Res., 106, C2: 2667-2678.

Raven, J.A. 1997. The vacuole: a cost-benefit analysis. Adv. Bot. Res., 25: 59-86.

Reynolds, C. S. 1984. The ecology of freshwater phytoplankton. Freshwater Biological Association. Cambridge University Press.

Riley, J. P., and G. Skirrow. 1974. Chemical Oceanography. Academic Press, London.

Roberts, B. J. and R. W. Howarth. 2006. Nutrient and light availability regulate the relative contribution of autotrophs and heterotrophs to respiration in freshwater pelagic ecosystems. Limnol. Oceanogr., 51(1): 288-298.

Russ, M. E., N. E. Ostrom, H. Gandhi, P. H. Ostrom, and N. R. Urban. 2004. Temporal and spatial variations in R:P ratios in Lake Superior, an oligotrophic freshwater environment. J. Geophys. Res., 109 (C5): 8447-8458.

Sakshaug, E., A. Bricaud, Y. Dandonneau, P. G. Falkowski, D. A. Kiefer, L. Legendre, A. Morel, J. Parslow, and M. Takahashi. 1997. Parameters of photosynthesis: definitions, theory and interpretation of results. J. Plankton Res., 19: 1637-1670.

Scavia, D., and G. A. Laird. 1987. Bacterioplankton in Lake Michigan: Dynamics, controls, and significance to carbon flux. Limnol. Oceanogr., 32(5): 1017-1033.

Scavia, D., and G. L. Fahnenstiel. 1987. Dynamics of Lake Michigan phytoplankton: mechanisms controlling epilimnetic communities. J. Great Lakes Res., 13(2): 103-120.

Schelske, C. L., and D. A. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnol. Oceanogr., 40: 918–929.

Schelske, C. L., F. J. Aldridge, H. J. Carrick, and M. F. Coveney. 2003. Phytoplankton community photosynthesis and primary production in a hypereutrophic lake, Lake Apopka, Florida. Archiv. Hydrobiol., 157: 145–172.

Schindler, D. W., S. E. Bayley, P. J. Curtis, B. R. Parker, M. P. Stainton, and C. A. Kelley. 1992. Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. Hydrobiol., 229: 1-21.

Scully, N. M., and D. R. S. Lean. 1994. The attenuation of ultraviolet radiation in temperate lakes. Arch. Hydrobiol. Beih., 43: 135-144.

Scully, N. M., D. J. McQueen, D. R. S. Lean, and W. J. Cooper. 1996. Hydrogen peroxide formation: The interactions of ultraviolet radiation and dissolved organic carbon in lake waters along a 43-75ºN gradient. Limnol. Oceanogr., 41(3): 540-548.

Senft, W. H. 1978. Dependence of light-saturated rates of algal photosynthesis on intracellular concentrations of phosphorus. Limnol. Oceanogr., 23(4): 709-718.

Silsbe, G. M. 2004. Phytoplankton production in the Lake Victoria, East Africa. M.Sc. thesis. Univ. of Waterloo.

Smith, E. M., and W. M. Kemp. 2001. Size structure and the production/respiration balance in a coastal plankton community. Limnol. Oceanogr., 46(3): 473-485.

Smith, R. E. H., C. D. Allen, and M. N. Charlton. 2004. Dissolved organic matter and ultraviolet radiation penetration in the Laurentian Great Lakes and tributary waters. J. Great Lakes Res., 30(3): 367-380.

Smith, R. E. H., V. P. Hiriart-Baer, S. N. Higgins, S. J. Guildford, and M. N. Charlton. 2005. Planktonic primary production in the offshore waters of Dreissenid-infested Lake Erie in 1997. J. Great Lakes Res., 31(Suppl. 2): 50-62.

Staehr, P. A., and K. Sand-Jensen. 2007. Temporal dynamics and regulation of lake metabolism. Limnol. Oceanogr., 52(1): 108-120.

Stolte, W., and R. Riegman. 1995. Effect of phytoplankton cell size on transient-state nitrate and ammonium uptake kinetics. Microbiology, 141(5): 1221–1229.

Strickland, J. D. H. 1960. Measuring the production of marine phytoplankton. Bull. Fish. Res. Bd. Canada, 122, 172 p.

Strom, S. 2002. Novel interactions between phytoplankton and microzooplankton: their influence on the coupling between growth and grazing rates in the sea. Hydrobiol., 480: 41–54.

Sverdrup, H.U., and W.E. Allen. 1939. Distribution of diatoms in relation to the character of water masses and currents off southern California in 1938. J. Mar. Res., 2: 131-144.

Talling, J. F. 1957*a*. Photosynthetic characteristics of some freshwater plankton diatoms in relation to underwater radiation. New Phytol., 56: 29-50.

Talling, J. F. 1957*b*. The phytoplankton population as a compound photosynthetic system. New Phytol., 56: 133-149.

Tobias, C. R., J. K. Böhlke, and J. W. Harvey. 2007. The oxygen-18 isotope approach for measuring aquatic metabolism in high productivity waters. Limnol. Oceanogr., 52(4): 1439-1453.

Tremblay, J.-E., and L. Legendre. 1994. A model for the size-fractionated biomass and production of marine phytoplankton. Limnol. Oceanogr., 39(8): 2004-2014.

Urban, N. R., D. S. Apul, and M. T. Auer. 2005.Community respiration rates in lake Superior. J. Great Lakes Res., 30 (Suppl. 1): 230-244.

Wang, X. 2005. Determining the ratio of photosynthesis to respiration rates in Lake Erie (East Basin) using the ^{18}O:^{16}O of dissolved oxygen. M.Sc. thesis. Univ. of Waterloo.

Wang, X., and J. Veizer. 2000. Respiration-photosynthesis balance of terristrial aquatic ecosystems, Ottawa area, Canada. Geochimica et Cosmochimica Acta, 64(22): 3775-3786.

Wanninkhof, R. 1992. Relationship between windspeed and gas exchange over the ocean. J. Geophys. Res., 97(C5): 7373–7382.

Wassenaar, L. I., and G. Koehler. 1999. An on-line tchnique for the determination of the $\delta^{18}O$ and $\delta^{17}O$ of gaseous and dissolved oxygen. Anal. Chem., 71 (21): 4965 –4968.

Wassenaar, L. I., and M. J. Hendry. 2007. Dynamics and stable isotope composition of gaseous and dissolved oxygen. Ground Water, 45(4): 447-460.

Watson, N. H. F., L. R. Culp, and H. F. Nicholson. 1975. Technical Report No. 600. Chlorophyll-a and primary production in Georgian Bay, North Channel and Lake Huron, April to December, 1974. The fourteenth Technical Report from the Research and Development Directorate. Great Lakes Biolimnology Laboratory, Canada Center for Inland Waters, Burlington, Ontario.

Welch, H. E. 1985. Introduction to limnlogical research at Saqvaqjuac, northern Hudson Bay. Can. J. Fish. Aquat. Sci., 42: 494-505.

Wetzel, R. G. 1992. Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiol., 229: 181-198.

Wetzel, R. G. 2001. Limnology. Lake and River Ecosystems. 3rd ed. Academic Pres.

Wetzel, R. G., and G. E. Likens. 2000. Limnological Analyses, 3rd ed. Springer.

Williams, P. J, Le B., R. C. T. Raine, and J. R. Bryan. 1979. Agreement between the ^{I4}C and oxygen methods of measuring phytoplankton production: reassessment of the photosynthetic quotient. Oceanol. Acta, 2: 411-416.

Williams, P. J. le B. 1981. Microbial contribution to overall marine plankton metabolism: direct measurements of respiration. Oceanol. Acta, 4: 359-364.

Wu, J., I. K. Tsanis, and F. Chiocchio. 1996. Observed currents and water levels in Hamilton Harbour. J. Great Lakes Res., 22(2): 224-240.

Yacobi, Y. Z., N. Perel, E. Barkan, and B. Luz. 2007. Unexpected underestimation of primary productivity by ^{18}O and ^{14}C methods in a lake: Implications for slow diffusion of isotope in and out of cells. Limnol. Oceanogr., 52(1): 329-337.

Yentsch, C. S. 1962. Marine plankton, p. 771-797. *In* R. A. Lewin [ed.], Physiology and Biochemistry of Algae. Academic Press.

Appendix A1: Appendices of "pooled" data

A1.1 Pooled 1 dataset (site average data)

Table A1.1 Pooled 1 dataset (site average data, n = 19).

Study[1]	Lake	Z_{mix}	Z_{eu}	Z_{eu}/Z_m	Chl a	TP	DOC	P_{max}	R	P_{max}/R	AGP	AR	AGP/AR	AGP/AR
						mmol		$mmolO_2$	$mmolO_2$		$mmolO_2$	$mmolO_2$	mean	ratio of
		m	m		mg m^{-3}	m^{-3}	mg L^{-1}	m^{-3} h^{-1}	m^{-3} h^{-1}		m^{-2} d^{-1}	m^{-2} d^{-1}	ratio	averages
c. study	Ham. Hbr.'03	8.68	5.73	1.08	12.03	1.098	4.22	8.172	1.210	7.702	301.04	234.67	1.89	1.28
c. study	Ham. Hbr.'04	8.62	6.51	0.95	9.88	0.835	4.22	6.720	0.908	7.535	274.45	173.21	1.94	1.58
c. study	L.Ontario'03	11.60	23.14	3.80	2.16	0.347	2.60	0.975	0.252	3.934	118.16	62.72	1.79	1.88
c. study	L. Ontario'04	13.22	19.70	1.83	1.79	0.265	2.60	0.903	0.196	5.576	105.59	62.11	2.34	1.70
c. study	Woods Bay	6.00	5.35	0.89	3.30	0.240	4.90	1.497	0.304	4.730	65.03	43.77	1.43	1.49
c. study	Georgian Bay	6.00	11.32	1.89	0.90	0.127	2.93	0.533	0.129	4.260	39.31	18.63	2.18	2.11
Depew	Lake Erie	13.00	14.72	1.13	2.13	0.288	3.49	0.686	0.156	6.665	51.75	44.15	1.78	1.17
Carignan	Achigan	6.19	8.47	1.48	2.09	0.130	3.35	0.802	0.169	5.301	39.32	21.78	1.76	1.81
Carignan	A l'Ours	3.25	3.46	1.37	7.28	0.454	6.64	2.137	0.362	6.425	42.66	23.06	1.89	1.85
Carignan	Bélair	4.06	7.11	1.95	1.63	0.202	3.35	0.827	0.208	5.369	28.73	16.20	2.03	1.77
Carignan	Chertsey	7.69	16.60	2.37	0.79	0.110	2.33	0.410	0.085	7.173	29.63	12.49	2.94	2.37
Carignan	Croche	3.07	8.24	2.74	1.39	0.124	3.50	0.482	0.148	3.697	16.91	10.42	1.67	1.62
Carignan	Cromwell	2.55	4.94	2.32	3.68	0.309	5.17	1.372	0.401	3.577	31.14	23.27	1.38	1.34
Carignan	En Coeur	4.31	8.22	2.33	3.58	0.230	3.53	1.016	0.268	4.140	41.91	26.01	1.59	1.61
Carignan	Masson	5.19	8.01	1.77	1.61	0.131	4.33	0.573	0.132	5.641	24.10	12.97	1.91	1.86
Carignan	Mont-Naire	6.38	14.46	3.16	1.77	0.173	2.07	0.670	0.157	4.887	43.78	21.01	2.07	2.08
Carignan	Pin Rouge	3.44	4.50	1.57	3.74	0.305	6.06	1.022	0.228	6.299	21.64	15.18	1.49	1.43
Carignan	Raymond	4.75	4.13	1.26	3.40	0.464	3.86	1.683	0.462	5.721	41.41	43.07	1.31	0.96
Carignan	Violon	4.75	8.53	2.13	1.42	0.123	2.92	0.494	0.131	4.449	23.30	12.74	1.84	1.83

[1] the following abbreviations were used: "c. study" means current study; "Depew" means Depew et al. 2007*b*; and "Carignan" means Carignan et al. 2000.

A1.2 Pooled 2 dataset (site average data)

The dataset consists of del Giorgio and Peters 1994 and Hanson et al. 2003 datasets (Table A.1.2) in addition to pooled 1 dataset (not shown, see Table A1.1). In Table A1.2, "del Giorgio" means del Giorgio and Peters 1994, and "Hanson" means Hanson et al. 2003.

Table A1.2 Pooled 2 dataset (site average data, n = 64; see also pooled 1 dataset, Table A1.1)

Study	Lake	Z_m	Chl *a*	TP	DOC	AGP	AR	AGP/AR	AGP/AR
			mg	mmol	mg	$mmolO_2$	mmolO2	mean	ratio of
		m	m^{-3}	m^{-3}	L^{-1}	m^{-2} d^{-1}	m^{-2} d^{-1}	ratio	averages
del Giorgio	Nicolet	7.5	0.70	0.158	3.30	15.63	41.32	n/a	0.38
del Giorgio	Bowker	7.0	1.00	0.174	2.70	17.27	52.23	n/a	0.33
del Giorgio	Lyster	7.5	1.10	0.184	3.60	25.88	43.16	n/a	0.60
del Giorgio	Orford	6.2	1.10	0.226	3.30	24.90	42.61	n/a	0.58
del Giorgio	Baldwin	4.0	1.70	0.271	3.80	21.47	26.20	n/a	0.82
del Giorgio	Truite	4.5	3.10	0.277	5.10	34.35	33.71	n/a	1.02
del Giorgio	Brompton	7.3	2.30	0.332	5.50	23.73	49.17	n/a	0.48
del Giorgio	Massawippi	7.2	3.10	0.352	4.20	52.92	76.31	n/a	0.69
del Giorgio	Stukely	6.7	2.30	0.361	4.50	24.79	42.89	n/a	0.58
del Giorgio	Petite Bromp	5.2	1.30	0.390	5.10	16.99	37.67	n/a	0.45
del Giorgio	D'Argent	4.2	2.50	0.397	5.30	21.14	35.54	n/a	0.59
del Giorgio	St. Francois	8.0	1.90	0.413	7.20	11.20	64.78	n/a	0.17
del Giorgio	Aylmer	8.0	2.40	0.416	7.30	11.33	74.43	n/a	0.15
del Giorgio	Coulombe	4.0	3.40	0.448	7.50	19.07	43.96	n/a	0.43
del Giorgio	Lovering	6.5	4.40	0.458	5.90	35.21	54.87	n/a	0.64
del Giorgio	Central	8.5	3.40	0.523	4.30	58.23	104.50	n/a	0.56
del Giorgio	Brome	5.0	6.90	0.616	4.10	91.33	49.61	n/a	1.84
del Giorgio	Magog	7.0	6.90	0.852	4.50	93.80	114.95	n/a	0.82
del Giorgio	Yamaska	5.0	10.40	0.932	5.20	106.00	99.07	n/a	1.07
del Giorgio	Waterloo	4.0	37.2	1.474	5.40	251.533	109.647	n/a	2.29
Hanson	Allequash	5.8	9.6	1.284	3.70	198.36	229.68	n/a	0.86
Hanson	Big Muskellunge	10.0	4.5	0.303	4.50	118	200	n/a	0.59
Hanson	Bog Pot	1.5	37.5	1.339	13.50	112.35	143.55	n/a	0.78
Hanson	Brown	2.5	13.2	1.803	9.10	92.25	97.5	n/a	0.95
Hanson	Crampton	5.3	4.1	0.426	4.00	20.14	73.14	n/a	0.28
Hanson	Cranberry Bog	1.8	22.6	0.577	11.50	61.92	88.92	n/a	0.70
Hanson	Crystal	7.5	2.7	0.142	1.60	45.75	42	n/a	1.09
Hanson	Diamond	7.8	2.5	0.229	1.90	78	100.62	n/a	0.78
Hanson	East Long	2.5	14.7	0.748	12.40	63.75	114.75	n/a	0.56

Table A1.2 Continued.

Study	Lake	Z_m	Chl *a*	TP	DOC	AGP	AR	AGP/AR	AGP/AR
		m	mg m^{-3}	mmol m^{-3}	mg L^{-1}	mmolO_2 m^{-2} d^{-1}	mmolO2 m^{-2} d^{-1}	mean ratio	ratio of averages
Hanson	Helmet	1.5	3.5	0.642	20.30	11.7	76.5	n/a	0.15
Hanson	Hiawatha	3.5	13.6	0.652	17.50	46.55	96.25	n/a	0.48
Hanson	Hummingbird	1.5	19.8	1.106	20.30	22.5	218.7	n/a	0.10
Hanson	Kickapoo	1.0	14.3	1.126	14.20	77.9	121	n/a	0.64
Hanson	Little Arbor Vitae	5.0	56.9	3.397	3.20	721.5	560.5	n/a	1.29
Hanson	Mary	2.0	25.1	0.600	21.70	70	94.6	n/a	0.74
Hanson	Muskellunge	4.0	18.4	2.526	5.00	191.6	166.4	n/a	1.15
Hanson	Northgate Bog	1.5	2.7	0.494	24.60	10.65	116.4	n/a	0.09
Hanson	Peter	3.5	30.2	0.687	6.40	212.8	161.35	n/a	1.32
Hanson	Plum	7.0	10.3	0.903	4.70	198.1	292.6	n/a	0.68
Hanson	Redington Bog	1.5	17.6	1.097	23.10	19.95	165	n/a	0.12
Hanson	Tenderfoot	5.0	17.3	1.371	7.80	152.5	197	n/a	0.77
Hanson	Trout Bog	1.5	38.8	0.945	17.00	73.65	52.8	n/a	1.39
Hanson	Trout Lake	11.0	3	0.813	2.20	80.3	81.4	n/a	0.99
Hanson	Ward	3.0	5.8	0.906	7.00	96.3	106.2	n/a	0.91
Hanson	West Long	3.5	7.6	0.445	6.60	103.95	137.55	n/a	0.76

Appendix A2: Pearson correlation matrices for all datasets

Table A2.1 Pearson correlation matrix of some selected parameters for our own data (individual data, $n = 41$):

	Z_m	Z_{eu}	Z_{eu}/Z_m	Chl-*a*	TP	P_{max}	R	P_{max}/R	AR	AGP	AGP/AR	pico-	nano-
Z_m	1.000												
Z_{eu}	0.325	1.000											
Z_{eu}/Z_m	-0.629	0.531	1.000										
Chl-*a*	-0.327	-0.820	-0.381	1.000									
TP	-0.111	-0.685	-0.463	0.832	1.000								
P_{max}	-0.240	-0.845	-0.479	0.948	0.837	1.000							
R	-0.298	-0.786	-0.379	0.900	0.815	0.897	1.000						
P_{max}/R	-0.026	-0.527	-0.409	0.558	0.460	0.677	0.281	1.000					
AR	0.436	-0.508	-0.808	0.614	0.688	0.673	0.729	0.247	1.000				
AGP	0.199	-0.532	-0.616	0.736	0.689	0.840	0.697	0.663	0.800	1.000			
AGP/AR	-0.417	0.037	0.404	0.092	-0.099	0.151	-0.155	0.585	-0.445	0.182	1.000		
pico-	0.150	0.509	0.284	-0.465	-0.424	-0.492	-0.440	-0.334	-0.307	-0.373	-0.054	1.000	
nano-	0.148	0.128	-0.028	-0.209	-0.270	-0.189	-0.351	0.174	-0.225	-0.092	0.231	-0.264	1.000
micro-	-0.346	-0.632	-0.209	0.556	0.555	0.613	0.620	0.298	0.336	0.353	-0.024	-0.668	-0.408

Table A2.2 Pearson correlation matrix of some selected parameters for pooled 1 dataset (individual data, n = 126):

	Z_m	Z_{eu}	Z_{eu}/Z_m	Chl-*a*	TP	P_{max}	R	P_{max}/R	AR	AGP
Z_m	1.000									
Z_{eu}	0.538	1.000								
Z_{eu}/Z_m	-0.679	0.254	1.000							
Chl-*a*	-0.070	-0.584	-0.428	1.000						
TP	0.131	-0.327	-0.436	0.727	1.000					
P_{max}	-0.059	-0.530	-0.394	0.911	0.761	1.000				
R	-0.227	-0.446	-0.127	0.686	0.676	0.815	1.000			
P_{max}/R	0.256	-0.202	-0.470	0.473	0.234	0.423	-0.180	1.000		
AR	0.500	-0.019	-0.590	0.561	0.693	0.684	0.729	0.019	1.000	
AGP	0.420	-0.004	-0.486	0.684	0.663	0.807	0.605	0.425	0.833	1.000
AGP/AR	-0.187	0.026	0.237	0.145	-0.125	0.132	-0.287	0.674	-0.386	0.189

Table A2.3 Pearson correlation matrix for some selected parameters for pooled 1 dataset (site average data, n = 19):

	Z_m	Z_{eu}	Z_{eu}/Z_m	Chl-*a*	TP	DOC	P_{max}	R	P_{max}/R	AR	AGP
Z_m	1.000										
Z_{eu}	0.704	1.000									
Z_{eu}/Z_m	-0.090	0.590	1.000								
Chl-*a*	-0.054	-0.610	-0.599	1.000							
TP	0.200	-0.388	-0.523	0.906	1.000						
DOC	-0.526	-0.858	-0.590	0.656	0.456	1.000					
P_{max}	0.114	-0.496	-0.645	0.940	0.936	0.493	1.000				
R	0.013	-0.539	-0.564	0.932	0.936	0.507	0.975	1.000			
P_{max}/R	0.390	-0.144	-0.612	0.400	0.469	0.182	0.469	0.313	1.000		
AR	0.593	-0.008	-0.498	0.707	0.855	0.093	0.842	0.808	0.425	1.000	
AGP	0.659	0.124	-0.408	0.623	0.768	-0.030	0.786	0.720	0.422	0.969	1.000
AGP/AR	0.466	0.616	0.236	-0.422	-0.287	-0.594	-0.252	-0.405	0.358	-0.067	0.129

Table A2.4 Pearson correlation matrix for some selected parameters for pooled 2 dataset (site average data, $n = 64$):

	Z_m	Chl-*a*	TP	DOC	AR	AGP
Z_m	1.000					
Chl-*a*	-0.523	1.000				
TP	-0.377	0.857	1.000			
DOC	-0.803	0.571	0.508	1.000		
AR	-0.119	0.710	0.816	0.363	1.000	
AGP	0.126	0.653	0.598	-0.129	0.625	1.000
AGP/AR	0.283	-0.014	-0.198	-0.558	-0.371	0.493

Appendix A3: Input data for calculation of oxygen transfer velocities

A3.1 Hamilton Harbour site

Table A3.1 Input data for calculation oxygen transfer velocities (k_{O2}, m d^{-1}) for sampling days in Hamilton Harbour.

date	Julian day	wind speed* at 3 m	wind speed* at 10 m	peak wind speed* at 3 m	surface water temp*	salinity	Schmidt number Sc (O_2)	fetch	oxygen transfer velocity
dd/mm/yy		m s^{-1}	m s^{-1}	m s^{-1}	degree C	ppt	none	m	m d^{-1}
13/05/2003	133	7.67	9.19	10.47	11.16	0.4	866.40	3000	8.03
26/05/2003	146	2.66	3.18	3.65	13.57	0.4	749.17	3000	1.04
09/06/2003	160	4.01	4.80	5.33	16.57	0.4	633.11	3000	2.57
23/06/2003	174	3.42	4.10	4.71	21.49	0.4	494.29	3000	2.11
08/07/2003	189	3.76	4.51	4.81	27.06	0.4	377.13	3000	2.93
22/07/2003	203	3.25	3.89	4.34	23.61	0.4	447.23	3500	2.03
05/08/2003	217	2.24	2.68	3.22	23.52	0.4	448.98	3000	0.95
18/08/2003	230	3.79	4.54	5.21	27.26	0.4	373.11	3000	2.99
03/09/2003	246	2.57	3.07	3.74	24.10	0.4	436.91	3000	1.27
22/09/2003	265	4.22	5.05	5.58	21.06	0.4	504.51	3000	3.18
10/05/2004	131	2.86	3.43	4.14	10.91	0.4	879.70	6000	1.16
18/05/2004	138	3.66	4.39	4.90	14.86	0.4	695.49	3500	2.07
01/06/2004	153	3.55	4.25	5.12	15.53	0.4	670.18	3000	1.95
15/06/2004	167	3.74	4.48	5.07	18.40	0.4	575.16	3000	2.35
06/07/2004	188	4.39	5.26	6.01	20.20	0.4	525.85	3000	3.37
20/07/2004	202	2.73	3.27	3.74	21.06	0.4	504.55	3000	1.34
04/08/2004	217	3.44	4.12	4.61	23.59	0.4	447.63	5000	2.33
23/08/2004	236	4.46	5.35	6.00	21.14	0.4	502.57	5000	3.71
27/08/2004	240	5.02	6.01	7.08	20.27	0.4	524.18	3000	4.47
30/08/2004	243	3.09	3.71	4.28	21.04	0.4	505.14	3500	1.71
03/09/2004	247	2.82	3.38	3.80	21.03	0.4	505.24	3000	1.43
07/10/2004	281	5.74	6.87	7.44	17.69	0.4	596.65	3000	5.41

* calculated as 3-day average prior to the sampling time

A3.2 Lake Ontario site

Table A3.2 Input data for calculation oxygen transfer velocities (k_{O2}, m d^{-1}) for sampling days in Lake Ontario.

date	Julian day	wind speed* at 10 m	peak wind speed* at 10 m	surface water temp*	salinity	Schmidt number Sc (O_2)	fetch	oxygen transfer velocity
dd/mm/yy		m s^{-1}	m s^{-1}	degree C	ppt	none	m	m d^{-1}
13/05/2003	133	5.69	8.46	4.20	0.15	1360.00	6000	2.58
26/05/2003	146	2.89	3.81	7.17	0.15	1116.88	6000	0.73
09/06/2003	160	2.96	4.05	10.13	0.15	923.01	6000	0.85
23/06/2003	174	2.30	3.25	14.00	0.15	730.14	6000	0.57
08/07/2003	189	2.45	3.74	14.92	0.15	692.77	6000	0.67
22/07/2003	203	2.40	3.65	15.50	0.15	670.66	6000	0.65
05/08/2003	217	2.09	2.86	17.89	0.15	590.07	6000	0.53
18/08/2003	230	3.72	5.15	23.16	0.15	456.38	6000	1.91
03/09/2003	246	3.21	4.02	20.32	0.15	522.49	6000	1.33
10/05/2004	131	3.25	4.25	7.37	0.15	1102.47	6000	0.94
18/05/2004	139	2.34	3.46	10.30	0.15	913.41	6000	0.53
01/06/2004	153	3.99	5.21	12.46	0.15	799.51	6000	1.65
15/06/2004	167	3.04	4.19	14.66	0.15	702.92	6000	1.02
06/07/2004	188	3.35	4.87	14.51	0.15	709.00	6000	1.24
20/07/2004	202	2.17	3.00	20.07	0.15	529.02	6000	0.60
04/08/2004	217	2.62	3.97	20.52	0.15	517.50	6000	0.89
23/08/2004	236	3.29	4.98	9.60	0.15	954.55	6000	1.03
25/08/2004	238	4.31	5.73	11.71	0.15	836.98	6000	1.89
30/08/2004	243	2.75	4.02	16.88	0.15	622.05	6000	0.89
03/09/2004	247	2.92	3.88	19.20	0.15	552.13	6000	1.07
07/10/2004	281	4.00	6.09	12.03	0.15	820.55	6000	1.65

* calculated as 3-day average prior to the sampling time

Appendix A4: Data for the comparison of two P-I curves derived from oxygen and ^{14}C methods.

A4.1 General Description of the Appendix 1

This Appendix contains a brief description of the methods and the results (Table A4.1) of two experiments with Hamilton Harbor water run on 18-Aug-2004 to obtain an oxygen P-I curve (oxygen evolution vs. light intensity) for the purpose of comparison of its photosynthetic parameters P^B_m, α^B and I_K with those ones derived from P-I curve obtained from ^{14}C method (assimilation rates of inorganic carbon vs. light intensity).

A4.1 Methods

A4.1.1 Oxygen method

The water handling and titration procedures were similar to those described in the light and dark bottle experiment in Chapter 2 but the incubator was different. The temperature-controlled insulated Fish tank was used for light incubations instead of a Percival incubator. The Fish tank was a glass aquarium (h x w x l = 32 x 32 x 60 cm) light- and temperature- insulated from all sides except one side that was kept clear. The incubator received a running water of the incubation temperature from the temperature-controlled water bath. The water inflow was located above the water level in the tank and the outflow was from the bottom on the opposite side. A light source consisted of two 500 W Halogen Quartz bulbs (type: T3 500W, 120 volts) placed in front of the clear side of the aquarium. The removable light-screens were used to split the volume of the tank into several light sections providing a light gradient ranging from 8 to 320 μE m^{-2} s^{-1}. The screens were made from the perforated plastic and allowed water to move freely from one side of the tank to another (opposite) side. Twenty BOD bottles were filled with the lake water: four "time-zero" bottles that were immediately fixed with Winkler reagents for initial DO concentrations and 16 light bottles. Light bottles were placed inside the incubator and incubated under different irradiance for 6 hours. The levels of PAR at all bottle positions were measured three times (at time zero, 3 hours and 5 hours

later) with a Biospherical PAR quantum sensor (Biospherical, inc., USA) that was recalibrated annually by a manufacturer. The incubation time for all bottles was 6 hours.

A4.1.2 ^{14}C method

The method used exactly the same procedure and incubation time (1-hour) as the ^{14}C method described in Chapter 3. The light source for the light gradient incubator (photosynthetron) was 300W Halogen Projector lamp.

A4.2 Results

Table A4.1 Comparison of the P-I curve experiment results derived from oxygen and ^{14}C methods.

^{14}C method		oxygen bottle method	
irradiance	production	irradiance	production
μmol m^{-2} s^{-1}	mgC $mgChl^{-1}$ hr^{-1}	μmol m^{-2} s^{-1}	mgO_2 $mgChl^{-1}$ hr^{-1}
1.37	0.05	8.93	0.83
3.92	0.10	9.80	1.25
13.21	0.34	12.00	0.97
22.56	0.41	19.33	2.04
37.60	1.13	25.67	0.09
65.40	2.07	43.00	3.99
88.29	2.65	43.60	5.97
89.93	3.21	56.33	4.29
94.83	3.66	95.33	10.83
150.42	3.90	134.33	12.21
183.12	5.02	144.33	12.82
241.98	5.05	266.00	20.23
291.03	5.58	301.00	21.27
304.11	5.88	305.33	21.62
425.10	6.51	314.00	22.11
533.01	6.63		
556.10	6.11		
621.30	6.00		