Primary production and nutrient dynamics of urban ponds

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ABSTRACT

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In urban areas, stormwater management ponds (SWPs) are built to mitigate polluted runoff. Although these ponds are increasing in numbers, their ecology is not well understood. Physical and chemical characteristics of 17 SWPs in the City of Ottawa were measured to determine the drivers of phytoplankton biomass (Chl *a*) and primary production (PP). While total phosphorus was the best predictor of algal biomass in the ponds (as in lakes), the imperviousness of the catchment could also predict Chl. *a*. Planktonic PP in two ponds measured seasonally was more closely related to water residence time than to nutrient concentrations with rates approaching at times the theoretical maximum for aquatic systems. In one pond, whole ecosystem metabolism, estimated using diel changes in dissolved oxygen and $\delta^{18}O$-O_2, suggested that these hypereutrophic systems were net sinks for carbon in the summer but likely sources to the atmosphere at other times of the year.

Key Words: Storomwater management ponds, urban pond, phytoplankton primary production, whole ecosystem metabolism, chlorophyll *a*, nutrients, water residence time, trophic state, urban limnology, PoRGy, $\delta^{18}O$.

RÉSUMÉ

Productivité primaire et dynamique des nutriments dans les bassins de rétention urbains

Muriel Rolon Dos Santos Mérette

Dans les milieux urbanisés, les bassins de rétention d'eau (BR) sont construits pour gérer le ruissellement de surface pollué. Bien que le nombre de ces bassins construits soit à la hausse, leur écologie n'est pas bien comprise. Les caractéristiques physiques et chimiques de 17 BR de la Ville d'Ottawa ont été mesurées pour déterminer les indicateurs de biomasse phytoplanctonique (Chl *a*) et de productivité primaire. Tandis que le phosphore a fourni la meilleure estimation de biomasse (comme dans les lacs), la superficie imperméable du bassin versant a peut aussi prédire la Chl *a* dans les BR. La productivité phytoplanctonique était liée, de façon saisonnière, d'avantage au temps de résidence de l'eau qu'aux concentrations de nutriments et a atteint des taux approchant le maximum théorique pour les systèmes aquatiques. Dans un des bassins, le métabolisme de l'écosystème, mesuré par des changements d'oxygène dissous et $\delta^{18}O$-O_2, suggère que ces systèmes hypereutrophes sont des puits de carbone pendant l'été, mais sont probablement des sources de carbone à l'atmosphère à d'autres périodes de l'année.

Mots clés: Bassin de rétention d'eau, gestion du ruissellement de surface, productivité phytoplanctonique, métabolisme de l'écosystème, chlorophyll *a*, nutriments, temps de résidence de l'eau, statut trophique, limnologie urbaine, PoRGy, $\delta^{18}O$.

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ASW: Air-saturated water

BR: Bassin de rétention

C:N: Particulate carbon to nitrogen ratio

C:P: Particulate carbon to phosphorus ratio

Chl *a*: Chlorophyll a (phytoplankton biomass)

DAGP: Daily areal gross planktonic photosynthesis

DANP: Daily aerial net primary productivity

DAR: Daily areal respiration

DOC: Dissolved organic carbon

DVGP: Daily volumetric gross planktonic photosynthesis

DVR: Daily volumetric respiration

G: Air–water gas exchange with the atmosphere (reaeration)

GP/R: Gross primary production to respiration ratio

GPP: Gross primary production

HNP: Hourly net primary production

HR: Hourly community respiration

HVGP: Hourly volumetric gross primary production

$\mathbf{I_k}$: Saturation PAR

k: Gas transfer velocity

K: Light extinction coefficient

m: Linear function of water temperature

N: Nitrogen

$\mathbf{NH_4^+}$: Ammonium

$\mathbf{NO_2^-}$: Nitrite

$\mathbf{NO_3^-}$: Nitrate

ORP: Oxidative-reductive potential

P: Phosphorus

P:R: Primary production to respiration ratio

PAR: Photosynthetically available radiation

$\mathbf{P^B_m}$: Chlorophyll-dependent rate of photosynthesis at optimal PAR

P_{max}: oxygen production at light saturation

POC: Particulate organic carbon

PON: Particulate organic nitrogen

POP: Particulate organic phosphorus

PP: Primary production

PPB: Productivité primaire brute

PQ: Photosynthetic quotient

R: Respiration

R_{20}: nominal R rate at 20°C

RP: Reactive phosphorus

Sc: Schmidt number

SPC: Specific conductivity

SWP: Stormwater management pond

TDP: Total dissolved phosphorus

TKN: Total Kjeldahl nitrogen

TN: Total nitrogen

TP: Total phosphorus

TSS: Total suspended solids

U_1: Wind speed at 1m height

U_{10}: Wind speed at 10 m height

VSMOW: Vienna Standard Mean Ocean Water

WRT: Water residence time

z: Depth

z_{mix}: Epilimnion depth

α^B: Chlorophyll dependent slope of the photosynthesis versus PAR curve at low irradiance levels

α_R: Community respiration isotopic fractionation factor

$\delta^{18}O\text{-}O_2$: Isotopic signature of dissolved oxygen

$\delta^{18}O$: Isotopic signature of oxygen

$\delta^{18}O\text{-}H_2O$: Isotopic signature of oxygen in water

CHAPTER 1. General Introduction

Impacts of urbanization on aquatic ecosystems- The human population continues to rise and, increasingly, people are migrating from rural areas to cities. In 2008, for the first time in history the urban population equalled the rural population worldwide (United Nations, 2008). Overall, 70% of people are expected to live in urban areas by 2050 (United Nations, 2008; Luck *et al.,* 2009). In Canada alone, the urban population has more than doubled in the last 50 years and is expected to further increase (Statistic Canada, 2006). This urban development has been accompanied by significant impacts on aquatic ecosystems (e.g. House *et al.,* 1993; Paul and Meyer, 2001), often to the very systems that cities depend on for their water supply and other uses. Impacts include changes to regional water temperatures (LeBlanc *et al.,* 1997) as well as to the natural hydrological cycle (Marselek *et al.,* 2006). In the process of urbanization, land surfaces are hardened by asphalt or concrete in the form of roads, parking lots and buildings, leading to an increase in overall imperviousness (e.g. Leopold, 1968). An increase in imperviousness of watersheds usually leads to greater surface runoff of water with consequent flooding, erosion and pollution of downstream areas.

Stormwater management is central to mitigating these impacts. Since the 1960's, one solution has been to retain runoff in detention ponds, also commonly called stormwater management ponds (SWPs) or urban ponds, which are becoming mandatory in new urban developments in many jurisdictions in North America (Comings *et al.,* 2000; Brabec *et al.,* 2002). The design of SWPs varies from simple sedimentation basins to complex constructed wetlands that provide green space and recreational opportunities. In theory, SWPs serve to mitigate flooding and associated erosion as well as improve water quality since urban runoff can contain high loads of suspended sediments and high concentrations of pollutants (e.g. heavy metals, hydrocarbons, pathogenic bacteria, salt and nutrients) that can be detrimental to downstream aquatic life (Whipple, 1979; Latimer *et al.,* 1986; Van Buren *et al.,* 1997; Likens and Buso, 2010). In some instances, natural ponds in urban areas are actually SWPs as early planners relied intentionally or inadvertently on their features for low cost treatment of urban runoff (Vymazal, 2005).

In comparison to natural ponds, urban ponds exhibit much more variability in their hydrological regimes (Chiandet, 2009). For example, the Monahan pond in the City of Ottawa, Canada has a water residence time varying from one to 37 days depending on the weather conditions (Goulet *et al.,* 2001). As a result, in part because of hydrological variability, the retention of elements can also be highly variable (Tuttle *et al.,* 2008). Nutrient removal rates as high as 90% have been reported (USEPA, 1983), but much lower removals of phosphorus, nitrogen and carbon are more common (Cahoon, 1994; Van Buren *et al.,* 1997; Comings *et al.,* 2000; Mallin *et al.,* 2002). Although, hydrological factors are important in explaining the retention of elements, it is becoming clear that biological processes also play an important role (Goulet *et al.*, 2001).

Aquatic primary productivity and respiration- In aquatic ecosystems, aquatic plants including algae and macrophytes, play a critical role in the retention and transformation of nutrients and pollutants either directly through absorption or indirectly through microbial activity. This is because primary production or the fixation of carbon through photosynthesis is intimately linked to the major nutrient cycles of nitrogen and phosphorus. However, very few studies have addressed the biological processes that take place in urban ponds (except Chiandet and Xenopoulos, 2010) even though there is an increasing realization that they harbor biodiversity in cities (Le Viol, 2009; Scher and Thery 2005). Another reason for examining primary production in urban ponds is that these small water bodies have recently been highlighted as potential carbon sinks globally (Downing *et al.,* 2008). Studies on small water bodies have shown that they are very important in terms of carbon cycling compared to forested systems in part due to their role as traps for much larger watersheds, which result in faster processing rates than on land (Cole *et al.,* 2007; Prairie, 2008). For example, organic carbon burial rates appear greater in small eutrophic impoundments compared to terrestrial systems (Downing *et al.,* 2008).

To the author's knowledge, only one study has quantified primary production in stormwater ponds (Munira and Moniruzzaman, 2009) and this study did not explicitly examine factors that drive primary production. Gaining a better understanding of this basic biological process is essential in order to determine what controls nutrient retention in stormwater retention basins. On the one hand, high algal production is believed to lead to greater storage of nutrients due to more sedimentation of organic material into pond sediments (Hoffmann, 1998). On the other hand, excessive microbial respiration of algae reduces oxygen levels at the water-sediment interface especially in deeper systems, which consequently reduces redox potentials and nutrient sorption to sediments (Palmer-Felgate *et al.*, 2011). In such circumstances, dissolved nutrients accumulate and may be exported from urban ponds into downstream ecosystems (Palmer-Felgate *et al.*, 2011).

Hydraulic residence time- Aside from nutrients, physical factors related to the hydrology of urban ponds are likely important in regulating the metabolism of urban ponds. Water residence times may have a positive or negative effect on metabolism and consequently, on nutrient retention and water quality of urban ponds (Tuttle *et al.,* 2008). Cycles of increased inlet flow rates due to storm events followed by longer hydraulic residence time between storms may stimulate aquatic metabolism by accelerating nutrient uptake, photosynthesis, respiration and production rates of aquatic producers (Stevenson, 1996) and in turn positively influence nutrient retention. The inflow is a significant source of nutrients, so in theory, higher inlet flow rates likely support higher aquatic productivity as demonstrated by Cronk and Mitsch (1994) in wetland systems. However, during extreme storm events or prolonged periods of rain, a high inflow can translate into short water residence times and transport of phytoplankton and nutrients through the pond resulting in low nutrient removal. Intermediate water residence times are likely to lead to optimal retention of nutrients.

Estimating primary production in aquatic ecosystems- Measuring the balance between primary production (PP) and respiration (R) is fundamental to understanding of carbon flow and food web dynamics in all aquatic systems (Wetzel, 2001). In the past, various methods have been used to estimate algal production. As most methods can be time consuming and/or expensive, surrogate measures such as the estimation of primary production from chlorophyll *a* have been used (Morin *et al.,* 1999). However, these estimates have a lower accuracy and do not address whole system metabolism and the fate of carbon as other contributors to metabolism are not taken into account.

When more accurate estimates of phytoplankton PP and R are needed, conventional methods such as dark-light bottle incubations are used (Wetzel and Likens, 2000). Changes in oxygen production or carbon uptake are usually measured on isolated samples that are incubated for brief periods of time *in situ* or under simulated natural conditions of temperature and light (Wetzel and Likens, 2000). This method has been widely used in calculating phytoplankton productivity for the past 50 years. However, it can be labour intensive and several assumptions must be made. Also, because with this method only pelagic samples are incubated, whole ecosystem metabolism estimates of PP and R are not made as benthic and littoral components are not included.

If whole ecosystem metabolism is of interest, *in situ* changes and mass balance methods involving dissolved oxygen and stable isotopes of oxygen can be used to estimate PP and R (Holtgrieve *et al.,* 2010). When analysing dissolved O_2 and $\delta^{18}O$ of the dissolved O_2 ($\delta^{18}O$-O_2) it is possible to estimate PP and R representative of pelagic and benthic habitats and also to include the air–water gas exchange (G) that drives dissolved oxygen in surface waters (Venkiteswaran, 2007).

The isotopic composition of dissolved oxygen in aquatic ecosystems is the result of three major processes: PP, R and G. Dissolved atmospheric oxygen has a $\delta^{18}O$ of 23.5‰ (vs. the Vienna Standard Mean Ocean Water (VSMOW)) and there is a 0.7‰ equilibrium fractionation during gas dissolution (Benson and Krause, 1984). Therefore, gas exchange drives the $\delta^{18}O$-O_2 towards 24.2‰. Because aquatic photosynthesis is a non-fractionating process (Guy *et al.,* 1993), O_2 produced by photosynthesis through the photolysis of water has the same isotopic value as the oxygen atoms of water molecules from which it is derived that are depleted in $\delta^{18}O$. During R, the uptake of the light isotope of oxygen is approximately 20‰ greater than the uptake of the heavy isotope of oxygen and thus R enriches the dissolved oxygen pool in the heavy isotope ^{18}O (Kiddon *et al.,* 1993). In the simplest sense, when R dominates over PP, dissolved oxygen will be under saturated and $\delta^{18}O\text{-}O_2$ > 24.2‰. When PP exceeds R, dissolved oxygen will be supersaturated and $\delta^{18}O\text{-}O_2$ < 24.2‰. When G dominates over PP and R, dissolved O_2 is close to saturation and the $\delta^{18}O\text{-}O_2$ is close to 24.2‰ (Quay *et al.,* 1995). The main advantage of the stable isotope approach is that it is less labour intensive and that it quantifies not only PP and R, but also G. However, almost all previously published O_2 stable isotope studies have assumed that the aquatic ecosystem was at steady state and that neither the O_2 concentrations nor its isotopic ratios changed significantly over timeframes that ranged from hours to months (Quay *et al.,* 1993, 1995; Wang and Veizer 2000, 2004; Russ *et al.,* 2004; Luz and Barkan 2000; Hendricks *et al.,* 2005; Sarma *et al.,* 2005). This steady state assumption implies there is no significant concentration or isotopic response to a diel light cycle. So although point measurements of a $\delta^{18}O\text{-}O_2$ can give good estimates of P:R ratios, diel O_2 concentrations and isotope dynamics can be used to better account for the temporal changes of metabolism (e.g. Fry, 2006).

Thesis Rationale **-**There are few comprehensive studies of urban ponds that include measurements of biological processes (except for Chiandet, 2009). Furthermore, most studies have focused on the behaviour of only one individual pond (e.g. Bayley *et al.*, 2005) and noted their uniqueness. There is a need to collectively understand the ecology and impacts of SWPs on downstream aquatic systems as more and more of these systems are being built in cities, at great expense in some cases.

This thesis was part of a larger project on the ecology of urban ponds across Ontario with the overall goal of assessing the biogeochemical sensitivity of aquatic ecosystems to patterns of urbanized land use. In this thesis, the impact of Ottawa urban ponds and their biological function (e.g. primary productivity) was examined at the landscape or city wide scale as well as on a seasonal and diurnal scale.

The thesis objectives were:

1) To determine if urban ponds in the city of Ottawa are impacting the water quality of downstream ecosystems and to determine the relationship between indicators of primary production (e.g. Chl *a*) and pond water quality (e.g. total phosphorus, reactive phosphorus, nitrate, ammonium and conductivity) as well as catchment characteristics (Chapter 2).

2) To determine the seasonal variability of planktonic primary production and respiration of two urban ponds in relation to potential drivers (e.g. nutrients, light penetration, temperature, and hydraulic residence time) (Chapter 3).

3) To determine the diurnal variation in O_2 and $\delta^{18}O$-O_2 in order to evaluate whether urban ponds might be sinks or sources of CO_2 and to evaluate the relative importance of phytoplankton to the ecosystem metabolism of a pond (Chapter 4).

CHAPTER 2. Limnology of urban ponds

Introduction

Stormwater management ponds (SWP's) are commonly used as a best management practice to mitigate the effects of runoff from highly urbanized landscapes (Schueler, 1994; MOE, 2003). Although designed primarily for control of water flow during storm events, urban ponds are now also used to reduce chemical pollution and to protect water quality of downstream ecosystems (e.g. Novotny, 1995). Their numbers are rising in North America as cities grow, with increases of up to 65% over 5 years in some coastal zones (USES, 2004). However, little is known about the basic limnology of these shallow water bodies except that they receive high pollutants loads at concentrations frequently exceeding water quality guidelines. There is considerable variation in pollutant retention or transformation among ponds (e.g. Cahoon, 1994; Mallin *et al.,* 2002) and in some cases, they can be important sources of pollution to receiving systems (e.g. Van Buren *et al.,* 1997).

Urban ponds may differ from natural ponds because of the unique characteristics of the urban landscape. The most obvious one is the amount of catchment area covered by impervious surfaces (i.e. roads, parking lots, roof tops). Impervious cover increases with increasing urbanization and results in higher runoff volumes due to less water infiltration (Schueler, 1994). Consequently, imperviousness leads to higher nutrient loading (May *et al.,* 1997; Roy, 2005), higher water temperatures (Galli, 1990), and changes in dissolved oxygen in urban aquatic systems (May *et al.,*, 1997). In northern climates, increases in road salt usage in the catchment may also lead to increases in the salinity and conductivity of receiving waters (Kelly, 2008).

Imperviousness may also increase sediment inputs (Schueler, 1994) and thus have an impact on water clarity and light penetration.

Water column depth may also be more variable than natural ponds and affect pond stratification. Deeper ponds would stratify more than smaller shallower ponds with thermally isolated bottom waters becoming more anoxic from microbial activity in the sediments (Wetzel, 2001). In the case of urban ponds, thermal stratification combined with high algal productivity could lead to significant internal loading and hence a reduced retention of nutrients such as phosphorus.

Urban ponds are usually dominated by significant areas of open water and have a less prominent littoral zone. In the pelagic zone of aquatic systems, planktonic algae are largely responsible for taking up dissolved nutrients from the water column and mediating many chemical transformations that influence whole ecosystem functions (Korner and Vermaat 1998). To date, phytoplankton and nutrient dynamics in urban ponds have received little attention. Most studies have focused on hydraulics (e.g. Werner and Kadlec, 1996; Shaw *et al.,* 1997) and sediment toxicity with respect to heavy metals (e.g. Marselak and Marselak, 1997; Goulet and Pick, 2001) while water chemistry and biology have received little study. There is evidence to suggest that differences in biological processes might explain the variation in pollutant retention seasonally within ponds (Goulet and Pick, 2001).

To address this gap in knowledge, a set of stormwater ponds were sampled in the City of Ottawa, Canada to determine the relationship between water quality (e.g. total phosphorus, reactive phosphorus, nitrate, ammonium and conductivity) as well as catchment characteristics and algal biomass. In lakes, algal biomass and productivity is largely controlled by phosphorus (Wetzel, 2001) and a similar relationship was expected of these urban ponds. Furthermore, the presence of thermal or chemical stratification was examined in relation to physical characteristics of pond and catchment and how this might relate to water quality. Shallower ponds with smaller catchment: pond area and/or, imperviousness to pond area were expected to stratify less and retain more nutrients.

Materials and Methods

Ponds and landscape characteristics - 17 ponds were chosen among approximately 94 wet ponds operating in the City of Ottawa in 2009 based on their easy access, security (gated facility) and low number of inlets (Figure 2.1). The ponds selected were built between the 1970's and 2004 to mitigate the effects of runoff from surrounding suburban residential developments, lightly industrialized areas and main roads. The ponds varied in size and shape as well as in catchment area (Figure 2.2). They typically consisted of a main cell with a surface area between 0.0003 km^2 and 0.049 km^2 and a mean depth of 1.27 m (Table 2.1). The catchment areas (0.11 - 4.08 km^2) varied in size with approximately 10.3% to 46.7% of impervious cover (Table 2.1).

SWP catchment areas were provided by the City of Ottawa Surface Water Manangement Services Branch and the Water Environment Protection Program Branch. Impervious cover GIS layers were also provided by the City of Ottawa for 2005 and were updated using Canadian geospatial data from DMTI (2009) by University of Ottawa honour student Larkin Mosscrop (2010). As there was some development from 2005 to 2009 in the catchments, an estimate of additional houses and roads built during this time had to be made. By comparing the 2009 DMTI images to 2005 GIS layers, the number of additional houses and roads were calculated. House imperviousness was calculated by averaging the impervious cover area of 15 houses in the watershed and then multiplying this by the amount of missing houses. Missing road surfaces were also calculated by multiplying their length by the average width of the road. These numbers were then compared to the average area of a road segment in the watershed to ensure the calculation was correct.

***Field sampling* -** Sampling was conducted at the center of the main cells in all ponds once in June and once in August 2009 from a canoe. All ponds were sampled within two weeks of each other and weather forecasts were consulted to avoid major rain events within at least two days before sampling and to ensure sunny skies. A Hydrolab minisonde 4*a* was used to record O_2 saturation, O_2 concentration, temperature, specific conductivity (SPC), pH and oxidative-reductive potential (ORP) from subsurface to the bottom at 0.25 m intervals. To normalize for the large seasonal water temperature differences, all O_2 data were analysed as percent saturation, corrected for local barometric pressure. Pond depth was also measured each time. The photosynthetically available radiation (PAR) was measured using a Li- 250A light meter with a LI-193SA spherical underwater quantum sensor. Readings were taken in air and at the subsurface followed by readings at 0.25 m intervals down to 1 m or until light was less than 1% of incident light. The light extinction coefficient (K) was estimated as the slope of the regression of ln (PAR) on depth (z) (Kirk, 1994). Estimates of water clarity were also taken with a 20 cm, black/white Secchi disc.

Surface and bottom water samples were taken at each site using a Van Dorn PVC Beta™ vertical bottle. Water samples were stored in 2L Nalgene® bottles and kept in a cooler with ice for a maximum of 24 h. Subsamples was then taken to measure turbidity (2020 LaMotte turbidity meter), nutrients, total suspended solids (TSS) and chlorophyll *a* concentrations. Grab samples were also collected at the outlet of the pond and analyzed for nutrients.

Nutrient analyses and algal biomass- Surface, bottom and outlet water were analyzed for nutrients by the Regional Municipality of Ottawa-Carleton, Surface Water Quality Laboratories. These included total phosphorus (TP), reactive phosphorus (RP), nitrite (NO_2^-), nitrate (NO_3) and total Kjeldahl nitrogen (TKN) following standard methods of the Ontario Ministry of Environment (Eaton *et al.,* 2005). Detection limits were 20 µg/L for NO_3^- , 3 µg/L for NH_4^+, 2 µg/L for RP, 20 µg/L for TKN and 5 µg/L for TP.

Surface water samples were filtered through Whatman GF/F filters (~ 0. 7 µm pore size, 47mm) which were then frozen for analyses of chlorophyll *a* (Chl *a*). Chl *a* was determined fluorometrically with a Cary Eclipse Spectrofluorometer after cold methanol extraction of filters for 24 h in the dark (Marker *et al.,* 1980). Duplicate samples were within 15% of one another. The filtrate from the above filtrations was then further filtered through 0.22 µm pore size pre-rinsed polycarbonate filters (GE Osmotics) for analysis of dissolved organic carbon (DOC). DOC was analysed by combustion (as in Wilson & Xenopoulos 2008; O.I. Analytical Aurora Model 1030 TOC analyzer, College Station, TX, U.S.A.).

A portion of the surface water sample was also filtered through ashed and pre-weighed Whatman GF/F (~ 0.7 µm pore size, 25mm) filters for particulate organic (seston) carbon (POC), nitrogen (PON) and phosphorus (POP) measurements and through Whatman GF/F (47mm) filters for total suspended solids (TSS) analysis. Filters were analysed for seston POC and PON using a CN elemental analyzer (Elementar Vario El III). POP was measured by persulfate digestion (as in James *et al.,* 2007). The filters were dried at 50ºC for 72h hours and re-weighed. The difference divided by filtrate volume for the GF/F 47 mm filters gave TSS (thus estimating suspended inorganic material as well as organic matter such as algae).

***δ^{18}O analysis* –** To provide an index of photosynthetic activity, water samples were collected for isotopic composition of oxygen in water, $\delta^{18}O-H_2O$, and isotopic composition of dissolved oxygen, $\delta^{18}O-O_2$. Because aquatic photosynthesis is a non-fractionating process (Guy *et al.,* 1993), when respiration (R) dominates over primary production (PP), dissolved oxygen will be under saturated and $\delta^{18}O-O_2 > 24.2‰$. When PP exceeds R, dissolved oxygen will be supersaturated and $\delta^{18}O-O_2 < 24.2‰$.

$\delta^{18}O-O_2$ and $\delta^{18}O-H_2O$ samples were taken from the surface water sample using a syringe. The water was then injected into sterilized 30mL Exetainer® vials making certain no air bubbles were formed. All $\delta^{18}O$ samples were preserved with $HgCl_2$ to approximately 150 ppm and refrigerated at 4°C before analysis (within 3 months).

$\delta^{18}O-H_2O$ and $\delta^{18}O-O_2$ were measured at the G.G. Hatch Isotope Laboratory (University of Ottawa). To measure the isotopic composition of oxygen in water, samples were reacted with a few milligrams of copper and charcoal for 24 hours prior to analysis. Then 0.2 ml of sample was flushed with a gas mixture of 2% CO_2 in helium. The CO_2 was extracted and cleaned for analysis on a Finnigan MAT Delta plus XP + Gasbench with a routine analytical precision of ± 0.1%.

To measure the isotopic composition of dissolved oxygen, a helium headspace was created and a subsequent isotope analysis of the extracted $O_{2(g)}$ was achieved using an isotope ratio mass spectrometer (Barth *et al*., 2004) . The routine analytical precision for isotopic composition of dissolved oxygen analysis was of ±0.2‰.The $^{18}O/^{16}O$ isotope ratios in water and the dissolved oxygen are by convention expressed in ‰ with :

$$\delta^{18}O = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O\,/^{16}O)_{VSMOW}} - 1\right)X1000$$

where VSMOW is the international Vienna Standard Mean Ocean Water.

***Pond stratification* –** Ponds were considered to be stratified thermally if there was at least a 2ºC difference between surface and bottom water temperature. Chemical stratification (dissolved O_2, SPC and ORP) was considered to occur when a difference of 20% or more was observed between surface and bottom water layers.

***Statistical analysis* -** Correlation analysis was used to determine relationships between algal biomass estimated as Chl *a* and surface water chemical and physical parameters as well as catchment characteristics. Data were log transformed, when appropriate, to satisfy the assumptions of normality and homogeneity of variance. The dependent variable Chl *a* was log transformed for all correlation and regression analyses. Pearson correlations were used to determine multicollinearity between independent variables and to determine relationships between physical and chemical variables (Table 2.2). Single linear correlations between independent variables (turbidity, TSS, light extinction coefficient, Secchi depth, water temperature, pond depth, catchment: pond area, imperviousness: pond area, TP, RP, TKN, NH_4^+, NO_3^-, TN:TP and SPC) and the dependent variable Chl *a* were examined. Single correlations between independent variables related to physical characteristics (pond depth, Secchi depth, catchment: pond area and imperviousness: pond area) and pond stratification (percent difference between bottom and top layers) were also performed.

Stepwise multiple linear regressions were used to develop the best predictive model for algal biomass (Chl *a*) in the urban ponds. When strong multicollinearity was present between variables, the parameters chosen for the multiple regression analyses were chosen based on biological and statistical significance. Results did not differ between forward and backward stepwise regressions; the most influential variables were sought via forward stepwise multiple linear regression (McGarigal *et al.,* 2000) with a variable retention criterion of $p = 0.01$.

Results

Physical characteristics - The 17 stormwater ponds (SWP) varied about 2.2 orders of magnitude in their catchment to pond area ratios with SWP-1930 having the lowest ratio (35) and SWP-1628 the highest (5098) (Table 2.1). Imperviousness also varied with imperviousness to pond area ratios ranging from a maximum of 2086 at SWP-1628 and a low of 5 at both SWP-1409 and SWP-1227 (Table 2.1). One pond, SWP-1628, had catchment to pond area 39 times higher than the average pond and an imperviousness to pond area 56 times higher. As a result, this pond was very much an outlier in correlations and regression analysis and was excluded from statistical analysis.

Water clarity was also highly variable: turbidity was highest at SWP-1328 with values reaching 53.96 NTU in June and lowest at SWP 1620 (Table 2.3), which was consistent with the corresponding measurements of suspended solids (TSS, Appendix A). Secchi depth reached the bottom in five ponds in June and six in August, so these 11 Secchi data were excluded from further analyses. In contrast, in over a third of the ponds, less than 5% of incident light reached the bottom. Mean light extinction coefficient was on average 2.18 m^{-1} during June and August (Table 2.3).

Stratification - In general water temperature was higher in August than in June (Figure 2.3). A difference of more than 2ºC was observed between surface water temperature and bottom water temperature in 11 ponds in June and 9 ponds in August (Figure 2.3). Dissolved oxygen (O_2) stratification also occurred in more than half of the ponds: 11 ponds in June had a difference of more than 20% in dissolved O_2 between the bottom and surface layers while in August this was seen in 10 ponds (Figure 2.4). Fewer ponds were stratified with respect to specific conductivity (SPC) (Figure 2.3) and oxidative-reductive potential (ORP) (Figure 2.4) with 3 - 6 ponds in June and 2 - 5 in August showing more than a 20% difference between top and bottom.

Nutrient concentrations – Surface water total phosphorus (TP) levels varied over a little more than one order of magnitude in the 17 ponds (Table 2.3) There was generally no significant difference between bottom and surface TP. However, TP at the outlet of the ponds exceeded surface water TP on 9 occasions in June and 6 occasions in August. Outlet concentrations were on average 57.4±39.9 μg/L (median of 49.5 μg/L) (Appendix B). The reactive phosphorus (RP) levels were usually above detection in all ponds with a maximum concentration of 34 μg/L occurring at SWP-1902 and SWP-1328 (Table 2.3). In most ponds, RP concentrations were lower at the surface compared to bottom (Figure 2.5).

Nitrate concentrations were high in these ponds averaging 421± 458 μg/L and were usually lower at the outlet than in the pond (Appendix B). Surface nitrate concentrations were occasionally lower than bottom concentration although most of the time they remained constant throughout the water column (Figure 2.5). Ponds had varying levels of total nitrogen (TN) (419 to 2789 μg/L). On average, less than 30% of TN occurred as nitrate and over 70% as total Kjeldahl nitrogen (TKN). Surface water TN:TP ratios ranged from 9.5 to 103.

Particulate organic nitrogen (PON) was higher in the ponds than particulate organic phosphorus (POP) with average PON:POP ratio of 36.4±66 by mol (Appendix A). Total suspended solid was high in the ponds and a quarter was as particulate organic carbon (POC) (Appendix A). Most of the TP was as POP and about 35% of TN was PON.

Relationships between physical and chemical variables - Table 2.2 shows the relationships between physical and chemical variables. These relationships helped in deciding what independent variables would be included in the stepwise multiple regression to predict Chl *a* (Table 2.3). TKN was not included because it was significantly correlated with TP. Secchi depth and turbidity were also not included because of their correlation with light extinction. All three variables are measurements of the light regime. Furthermore, turbidity was also correlated with various nutrient parameters which were retained in the multiple regressions (Table 2.3). Specific conductivity was another variable that was not included in the regression due to its relationship with ammonium. Imperviousness to pond area was highly correlated to catchment to pond area and was chosen as the variable to represent the landscape characteristic as it takes into account the portion of the land that is connected to the ponds. There also was a significant relationship between RP and TP. RP was therefore not included in the regression when TP was included, and vice versa.

***Algal biomass* –** Epilimnion chlorophyll *a* (Chl. *a*) ranged from 3.90 to 445 μg/L in the 17 ponds in June and August and averaged 82.66 ± 95.16 μg/L. Chl. *a* was significantly correlated to several physical, chemical and watershed characteristics: TP, TKN, Secchi depth, TN:TP, light extinction coefficient, imperviousness: pond area, RP and turbidity (Table 2.3). A first stepwise multiple regression analysis between Chl. *a* and chosen independent variables (including TP) (Table 2.3) was done. TP was found to be the main predictor of Chl *a* across the ponds explaining 66% of the variation in algal biomass [Log Chl *a* = 1.35 Log TP + 3.46, $p<0.001$] (Figure 2.6). However, when RP was considered in a second stepwise instead of TP, imperviousness to pond area and the light extinction coefficient were significant predictors of Chl. *a*. (Table 2.4). Together, these two variables explained 47% of the variance in Chl. *a* [Log Chl *a* = (0.521 Log Imperviousness: pond area) + (0.963 Log Light extinction coefficient) + 0.651, $p<0.001$].

Discussion

***Pond water quality* -** In 80% of the ponds, the total phosphorus (TP) concentrations exceeded Ontario Provincial Water Quality Objectives (CCME, 2002) of 30 μg/L intended to prevent excessive algal growth (Figure 2.6). This guideline was also exceeded at the outlet in 35% to 53% of the ponds where outlet concentrations tended to be higher than in pond concentrations (Appendix B). Negative phosphorus and positive nitrate removals have been shown in other studies of stormwater ponds during baseflow periods and stormevents (Van

Buren *et al.,* 1997). These results indicate that the ponds may not only be exporting phosphorus but that they have the potential to impair downstream aquatic systems, depending on how impacted these receiving systems are at the point where SWPs discharge.

Nitrate concentrations were well within the Canadian Water Quality Guidelines of 13 mg/L (CCME, 2002), and the concentrations were typical of stormwater ponds reported from other cities (Mallin *et al.,* 2002; Woodcock *et al.,* 2010; Mayer *et al.,* 1996). However, these concentrations were higher than what has been found in natural ponds (Chiandet, 2009). Nitrate was retained in the ponds as concentrations decreased from within the ponds to the outlets. This can be attributed to algal uptake in the epilimnion and to denitrification which would take place mainly in the sediment (Wetzel, 2001) as shown by lower nitrate concentrations at the pond surface (Figure 2.5).

Water column stratification - Thermal stratification was observed in the majority of the ponds even though these systems were very shallow (Figure 2.3). In fact, even the shallowest of ponds (0.5 m) showed some thermal structure. Water clarity and pond depth have been shown to predict stratification (e.g. Condie and Webster, 2002; Xenopoulos and Schindler, 2001). Here this relationship was also observed as stratified ponds were significantly correlated with the light extinction coefficient ($r=-57$, $p<0.04$) and marginally correlated with pond depth ($r^2=0.33$, $p=0.05$). In clear ponds, solar radiation penetrates farther, distributing heat to a greater depth and decreasing stratification. Interestingly, pond catchment characteristics did not have an effect either on thermal stratification or on SPC stratification. Conductivity was higher at the bottom of only a few ponds. Furthermore, these stratifications did not have an effect on nutrient concentrations found within the pond or at the pond outlet.

Water column stratification with respect to SPC was observed in some of the ponds sampled (Figure 2.3). Most of the SPC in urban temperate areas can be explained by the chloride content due to the use of salt as de-icing agents (Kelly, 2008). The changes in salinity in the water column lead to density changes that cause a resistance to mixing. In this study, SPC levels of up to 2797 μS/cm were found in the bottom water of the SWPs falling within the range previously reported for SWPs in Southern Ontario (Chiandet, 2009). Environment Canada and Health Canada have assessed road salt as "toxic" under the Canadian Environmental Protection Act (EC and HC, 2001). SPC values of 1500 μS/cm can have negative impact on rivers (Goss *et al.,* 2003). Five of the studied ponds exceeded this threshold and may likely lead to increases in SPC in downstream ecosystems.

Differences in only a few degrees in water temperature can lead to thermal stratification in the water column (Xenopoulos and Schindler, 2001) and prevent bottom water layers from mixing with surface water during periods of low wind. This can cause dissolved (O_2) to decrease at the sediment water interface. As shown in Figure 2.4, 41% ponds had dissolved O_2 saturations at the bottom below 46% saturation (4.0 mg/L). This tendency has been observed in constructed wetlands (Kadlec and Knight, 1996). Dissolved O_2 concentrations below 4 mg/L are considered harmful to fish but the Canadian water quality guidelines for the lowest acceptable dissolved O_2 levels are 5.5 mg/L in warm-water ecosystems (CCME, 2002). Most of the bottom water of the ponds in this study were below 5.5 mg/L in August.

Higher RP concentrations were observed at the bottom of most ponds compared to the surface (Figure 2.5). This may indicate significant algal uptake at the pond surface but can also point towards a release of RP from the sediment. Low dissolved O_2 concentrations at the pond bottom may lead to a decrease in the reductive potential (ORP) and the dissolution of phosphorus-bearing metal hydroxides, in particular Fe-bound phosphorus (Christophoridis and Fytianos, 2006), resulting in internal loading of phosphorus in shallow systems (Jensen *et al.,* 1992). ORP values reached 48 mV at the bottom of pond SWP-1306 (Figure 2.8). Many pond systems utilize bottom draw outflows, which could cause not only a discharge of low dissolved O_2, but also a significant release of pollutant to receiving waters (Schueler and Galli, 2000).

Planktonic algal biomass as estimated by chlorophyll a - Algal biomass was on average higher and more variable in the ponds than in natural shallow lakes and wetlands (Voros and Padisak, 1991; Bayley and Prather, 2003; Tilahun and Ahlgren, 2010). Chlorophyll *a* (Chl *a*) exhibited a range of two order of magnitude and was within the ranges found in two studies of SWPs (Khondker and Kabir, 1995; Chiandet, 2009). Chl *a* appeared to be mainly driven by TP concentrations in the SWPs (Figure 2.6). Phosphorus is the most important factor in lake eutrophication (Schindler *et al.,* 1971) and its relationship with algal biomass has been well established (Wetzel, 2001). However, the slope of this relationship appeared steeper for SWPs than what has been reported in lakes (slope coefficient of 1.35 v.s. 0.86) (e.g. Wagner, 2011). This could be related to the dynamic hydrology of these ponds that help to supply higher concentrations of bioavailable phosphorus that then stimulate algal growth. Higher turbidity of urban systems could also limit light penetration that could have a positive effect on pigment production (Richardson *et al.*, 1983) and account for steeper TP vs. Chl. *a* slope.

Although, RP was not found to be the strongest predictor of Chl *a*, a significant relationship was observed (Table 2.3). RP is the bioavailable form of phosphorus and in theory would be a better predictor than TP of Chl. *a* as a proportion of the TP was particulate phosphorus derived in part from suspended algae, creating potential for circular reasoning in its application (Biggs, 2000). However, in lakes, RP is usually drawn down by algae and other organisms to the point where it is at or below detection and cannot be used in practice to predict algal biomass. In SWPs, RP is abundant and readily available: plant and algal uptake in the ponds do not seem to draw it down to its detection limit and a positive relationship was observed.

When TP was excluded from the regression analysis, the imperviousness to pond area and light extinction were found to have a significant effect on algal biomass and could explain 47% of the variability (Table 2.4). Pollutant loads have been shown to increase with increasing watershed imperviousness (e.g. Schueler, 1994) as the opportunity for water to pick up dissolved and particulate constituents on paved surfaces increases. Imperviousness cover has therefore been linked with degradation in stream water quality in urban areas (Schueler, 1994; Lewis and Grimm, 2007). In this study, positive relationships between TKN, TP and TN:TP and imperviousness to pond area were observed. This suggests that the more impervious cover a catchment area has relative to the pond area, the more soluble and particulate matter will be washed into the ponds and be readily available for algal uptake. Interestingly, imperviousness to pond area was a better predictor of Chl *a* than catchment to pond area. Pond catchment area contained some vegetated and permeable surfaces where nutrients could have been retained whereas nutrients from impervious surfaces were more directly connected to the ponds. Light extinction was related to nutrients (TP and TKN) and water turbidity. As these parameters were also correlated with Chl *a*, it is not surprising that light extinction was a predictor of Chl *a*. As nutrients are abundant in these systems and high amounts of total suspended solids were recorded (Appendix A), it is possible that light might be limiting algal growth in the most eutrophic ponds.

Based on Chl *a* and TP values, 24% of SWPs in the City Ottawa were considered to be mesoeutrophic while over 75% of ponds were eutrophic to hypereutrophic (Wetzel, 2001). These urban ponds are therefore likely very productive systems and may play an important role in carbon sequestration. In fact, $\delta^{18}O\text{-}O_2$ results provide evidence of high primary productivity (Figure 2.7). The $\delta^{18}O\text{-}O_2$ values in ponds were considerably below the atmospheric equilibrium (24.2‰) and dissolved O_2 were mostly above saturation at times reaching almost 200%. Therefore, not only was algal biomass very high in ponds but the $\delta^{18}O\text{-}O_2$ suggests primary production exceeded respiration in most ponds.

Tables

Table 2.1 Physical characteristics of selected stormwater ponds (SWPs) in the City of Ottawa in 2009. Ponds were digitized and inlet numbers determined from DMTI satellite images from 2009. Volume was calculated by formula V= Surface area*depth. Year was obtained from the City of Ottawa as well as the GIS layers for the calculation of pond and catchment area using ArcGIS (ESRI, 2006).

Pond #	Pond Name	Inlet #	Year built	Average Pond depth (m)	Pond Area (km^2)	Catchment Area (km^2)	Imperviousness coverage (%)	Catchment: Pond area	Imperviousness: Pond
SWF-1139	Lebreton Flats, Northeast Pond	1	2004	1.45	0.001	0.11	29.94	103.5	13.1
SWF-1206	Kanata Town Center	2	Late 1990s	1.02	0.01	0.54	19.82	54.4	10.8
SWF-1207	Insmill Park	1	Mid 1990s	1.65	0.011	0.79	33.86	74.1	25.1
SWF-1211	Kanata Beaver	1	Late 1970s or 1980s	2.10	0.022	1.47	42.25	66.4	27.8
SWF-1215	Shirley's Brook	2	1980s	1.51	0.004	1.23	46.57	328.4	152.1
SWF-1227	Morgan Grant	2	Early 2000s	1.04	0.011	0.44	12.35	40.2	5.0
SWF-1306	Glen Cairn-Castlefrank	1	2000	1.80	0.005	0.75	30.29	150.3	45.3
SWF-1309	Walter Baker Park, SWF-2	1	2000	0.90	0.006	0.64	16.39	108.1	14.7
SWF-1320	Sweetnam-Eileen	1	1990s	1.15	0.001	0.23	43.47	184.9	69.3
SWF-1328	Monahan Wetlands	4	1978, 1996, 2000	1.05	0.049	4.08	34.71	82.7	28.6
SWF-1409	Stonebridge	1	1999	1.15	0.021	1.71	10.3	82.1	5.0
SWF-1410	Strandherd	2	1998	1.30	0.029	3.21	13.16	110.8	7.3
SWF-1610	Saratoga	1	Late 1970s	1.35	0.001	0.5	39.55	347.0	119.7
SWF-1611	Riverside-Hackett	1	Early' 1980	1.13	0.003	NA	NA	NA	NA
SWF- 1628	Valour	1	2000	0.65	0.0003	1.79	40.93	5098.4	2086.9
SWF-1902	Taylor Creek	1	Late 1980s	0.50	0.001	0.19	17.5	185.8	24.1
SWF-1930	Avalon-Aquaview	1	2000	1.84	0.033	1.16	31.31	35.4	8.5

NA: Not available

Table 2.2 Pearson cross-correlations of independent variables (n= 22 - 34) for 17 stormwater ponds in the City of Ottawa. Independent variables presented are pond depth, catchment: pond area, imperviousness: pond area, secchi depth, light extinction coefficient, ammonium (NH_4), nitrate (NO_3^-), reactive phosphorus (RP), total phosphorus (TP), total phosphorus to total nitrogen ratio (TP:TN), specific conductivity (SPC), temperature (Temp.) and turbidity. Significant correlations are indicated by: * p ≤ 0.05, ** p≤ 0.01 and *** p ≤ 0.001.

	Log Catchment area: pond area	Log Imperviousness: pond area	Secchi depth	Log Light extinction	Log NH_4^+	Log NO_3^-	Log RP	Log TKN	Log TP	Log TN:TP	Log SPC	Log Temp.	Turbidity
Pond depth	-0.15	0.18	0.57**	-0.17	-0.15	-0.14	-0.10	0.13	0.04	-0.05	-0.26	0.29	-0.15
Log Catchment area: pond area		0.803***	-0.23	0.25	0.15	-0.27	0.33	0.25	0.417*	-0.44*	-0.13	-0.25	-0.15
Log Imperviousness: pond area			-0.22	0.15	0.27	-0.14	0.35	0.43*	0.51**	-0.41*	-0.02	-0.01	0.01
Secchi depth				-0.71***	-0.43*	-0.18	-0.61**	-0.43*	-0.478*	0.20	-0.54**	0.01	-0.53**
Log Light extinction					0.14	-0.40	0.37*	0.51**	0.57***	-0.58***	0.28	-0.316	0.35*
Log NH_4^+						0.19	0.28	0.26	0.20	0.06	0.50**	0.07	-0.05
Log NO_3^-							0.06	-0.10	-0.22	0.59***	0.27	-0.01	0.15
Log RP								0.45**	0.63***	-0.53**	0.04	0.24	0.48**
Log TKN									0.90***	-0.63***	0.20	0.08	0.45**
Log TP										-0.83***	0.07	0.00	0.45**
Log TN:TP											0.06	0.05	-0.24
Log SPC												-0.12	0.16
Log Temp.													0.224

Table 2.3 Characteristics of 17 stormwater ponds surface water nutrients, temperature and specific conductivity (SPC) sampled in June and August 2009 are presented. Independent variables presented were correlated with surface water Log chlorophyll *a* (Chl. *a*) (n= 23-34) and significant correlations are indicated by: * p ≤ 0.05, ** p≤ 0.01 and *** p ≤ 0.001

Independent variable	Mean (±SD)		Range	r-values
Total phosphorus (µg/L)[1,2,***]	58	±46	15 - 171	0.83
Total Kjeldahl nitrogen (µg/L)[1,***]	885	±406	380 - 2030	0.82
Secchi depth (m)[**]	0.83	±0.38	0.30 - 1.80	-0.58
TN:TP[***]	33	±26	9.5 - 103	-0.56
Light extinction coefficient[1,2,**]	2.18	±1.23	0.64 - 5.23	0.55
Imperviousness: pond area[1,2,3*]	37	±43	5 - 152	0.41
Reactive phosphorus (µg/L)[1,4*]	9	±7	2 - 34	0.39
Turbidity (NTU)[*]	7.34	9.29	0.96 - 53.96	0.36
Catchment: pond area[1,3]	130	±94	35 - 347	0.27
Specific conductivity (µS/cm)	1108	±638	286 - 2809	0.21
NO_3^- (µg/L)[1, 2]	367	±448	20 - 2092	-0.20
NH_4^+ (µg/L)[1, 2]	51.2	±44.8	3 -141	0.08
Mean pond depth (m)[2]	1.27	±0.44	0.40 - 2.10	0.06
Water temperature (ºC)[2]	20.68	±3.92	12.31 - 25.68	-0.02

[1] Variables were log transformed
[2] Candidate variables in step-wise forward multiple regression
[3] SWP-1628 was excluded as an outlier
[4] Only a candidate variable in step-wise when TP not candidate

Table 2.4 Multiple regression analysis of variation in Chl *a* and pond characteristics when TP was not considered. Partial *t*-values indicate the size of the statistical effects of the independent variables when all other variables (Table 2.3) were considered. Independent variables indicated by [1] were log transformed before entering into the model. Chl *a* was also log transformed.

Independent variable	Regression coefficient	Partial *t*	p
Intercept	0.651	2.44	0.023
Imperviousness: Pond area[1]	0.521	2.97	<0.01
Light extinction coefficient[1]	0.963	2.77	<0.01

Figures

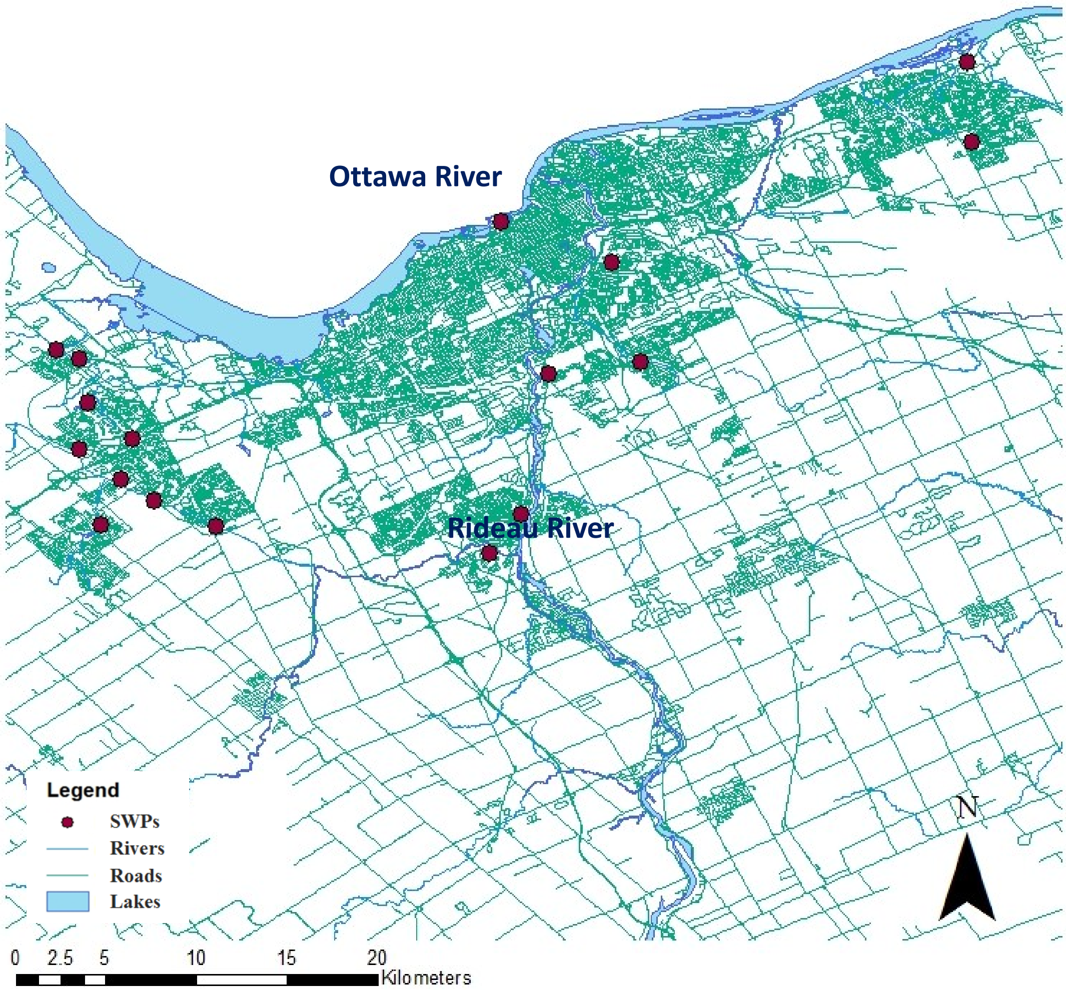

Figure 2.1 Stormwater pond (SWP) distribution across the City of Ottawa in 2009. Composed data points created in ArcGIS and river and road data from Streetview (2009).

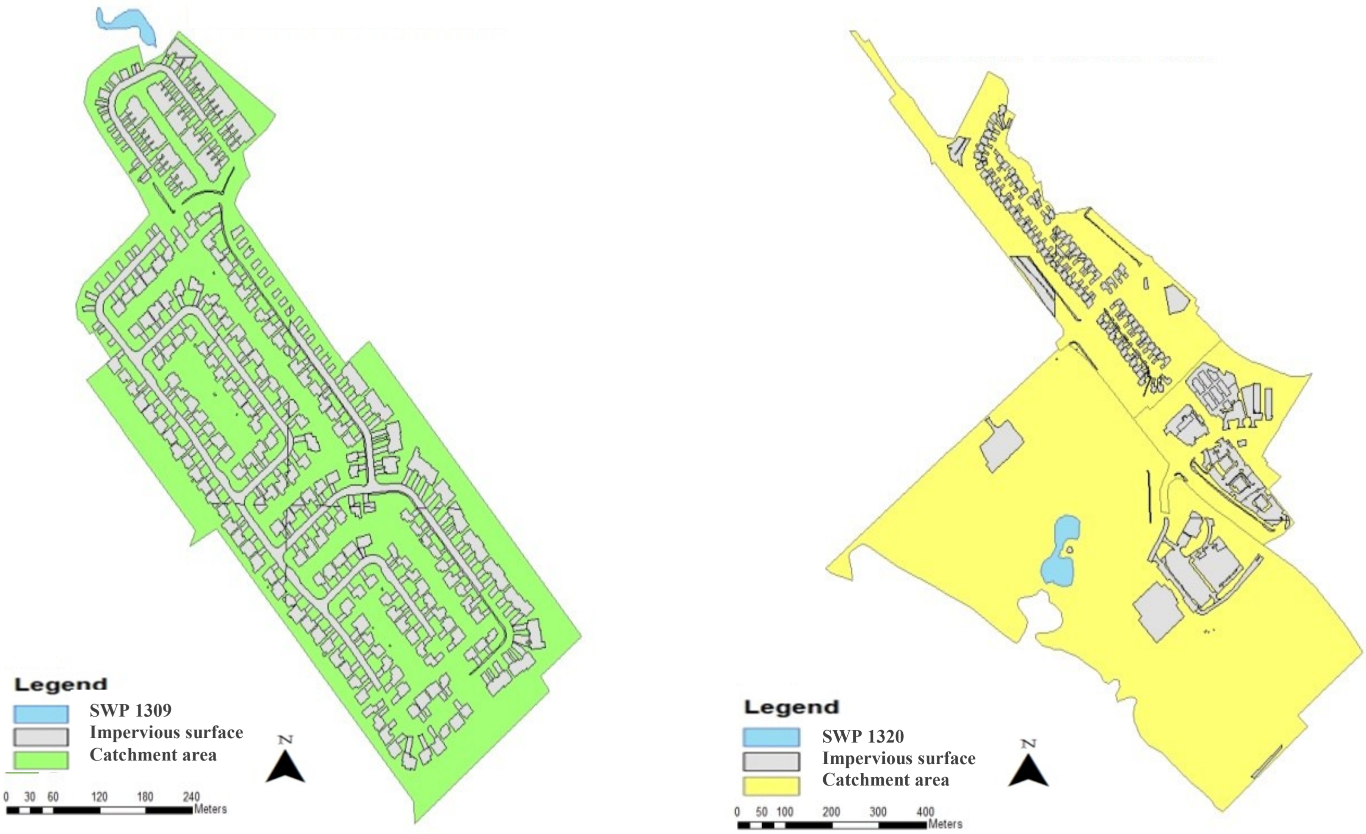

Figure 2.2 Example of two of the 17 stormwater ponds (SWPs) sampled in the city of Ottawa in June and August, 2009. Map was created in ArcGIS using GIS layers provided by the City of Ottawa.

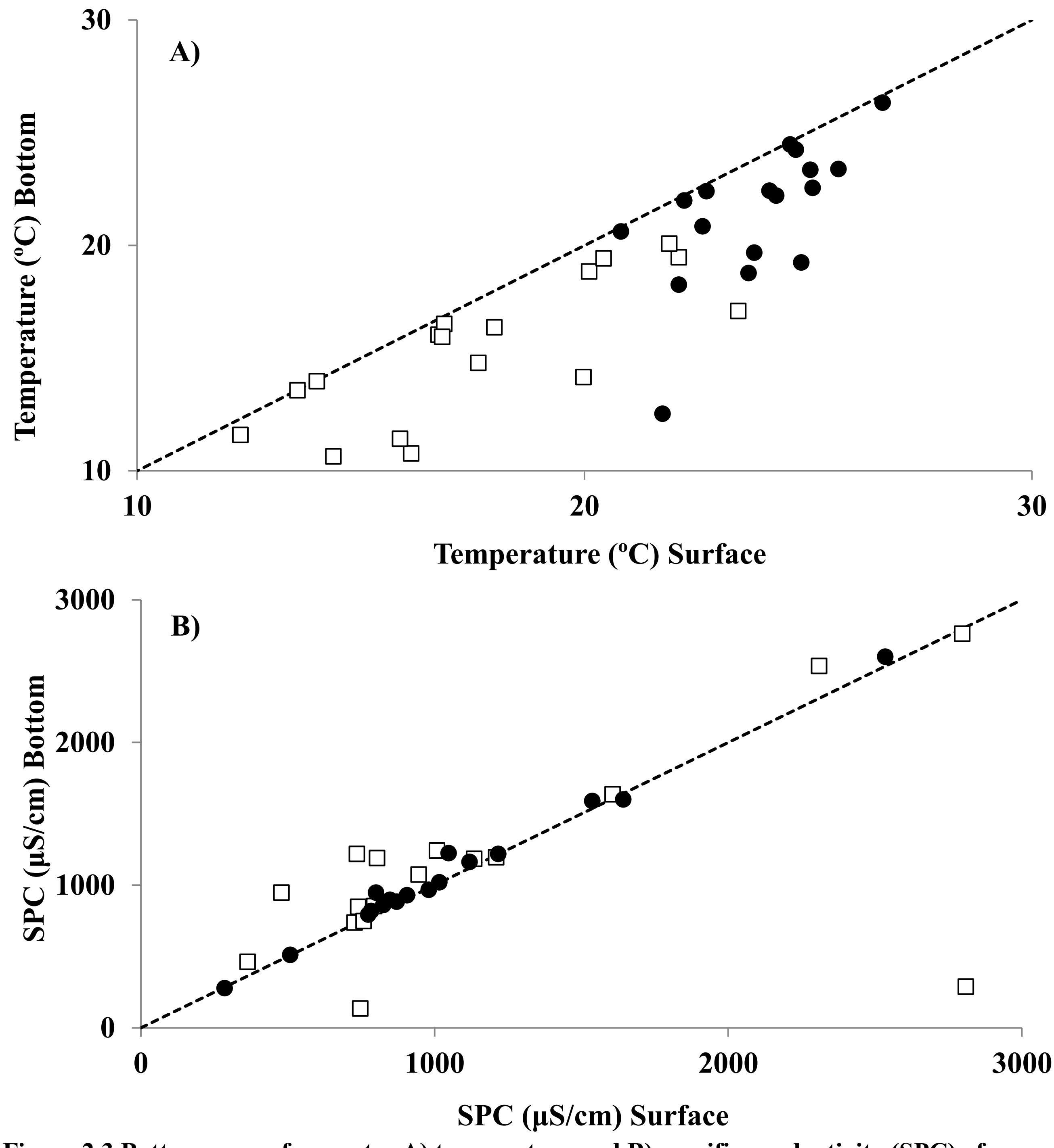

Figure 2.3 Bottom vs. surface water A) temperature and B) specific conductivity (SPC) of 17 stormwater ponds in June (□) and August (•), 2009. The solid lines denote 1:1 relationships.

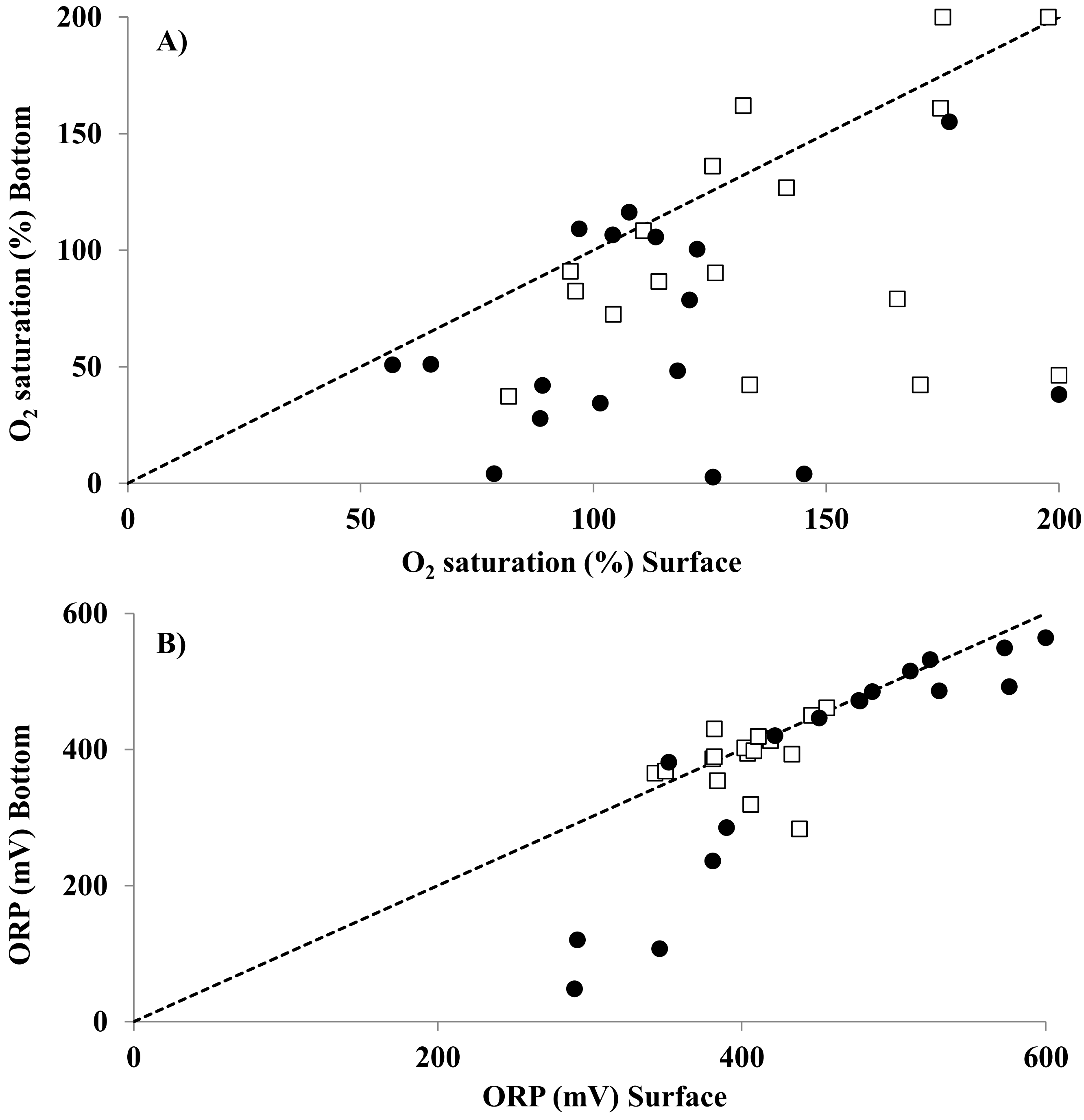

Figure 2.4 Bottom vs. surface water A) dissolved oxygen (O_2) saturation and B) oxidative-reductive potential (ORP) of 17 stormwater ponds in June (□) and August (•), 2009. The solid lines denote 1:1 relationships.

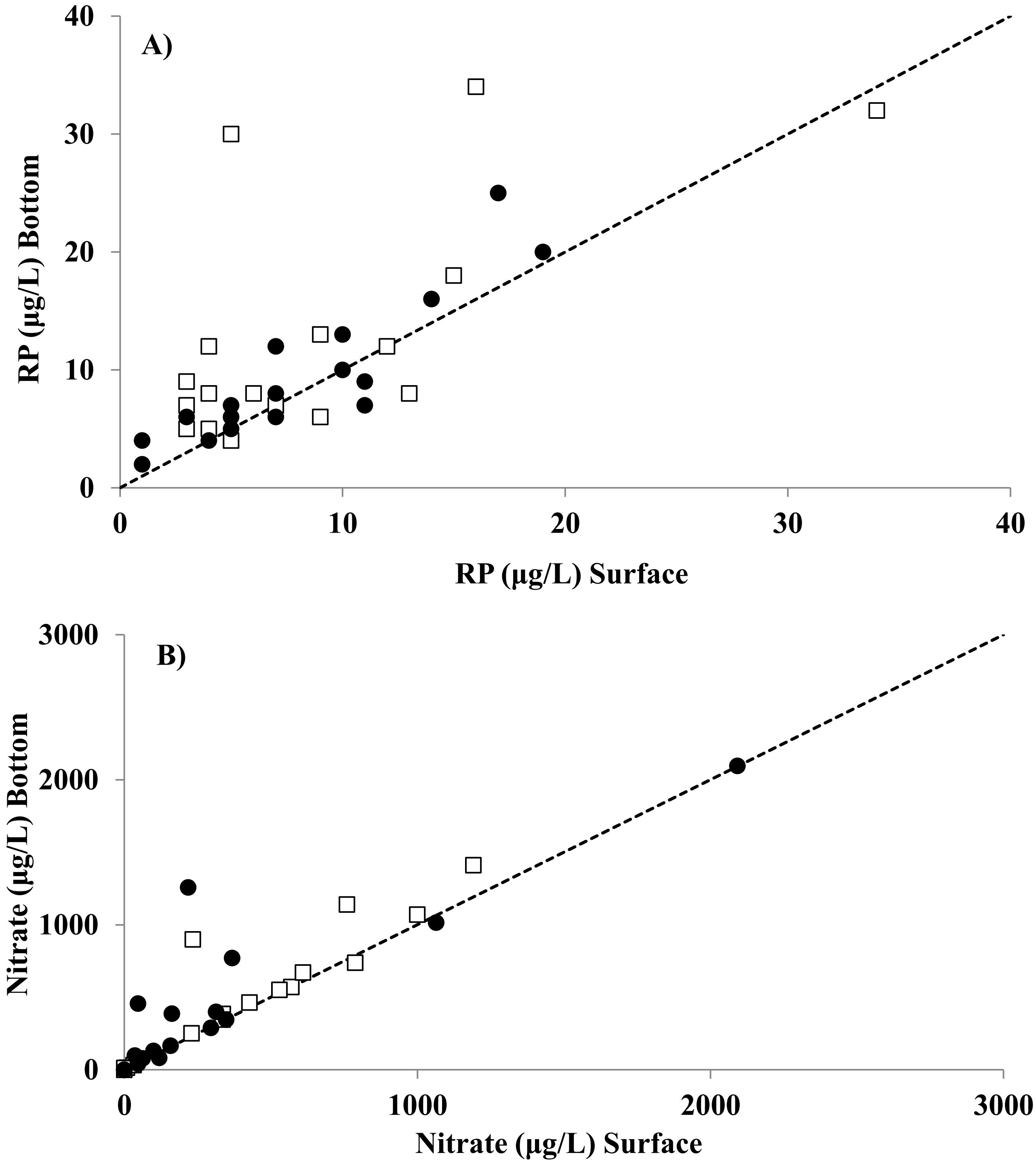

Figure 2.5 Bottom vs. surface water A) reactive phosphorus (RP) and B) nitrate of 17 stormwater ponds in June (□) and August (•), 2009. The solid lines denote 1:1 relationships

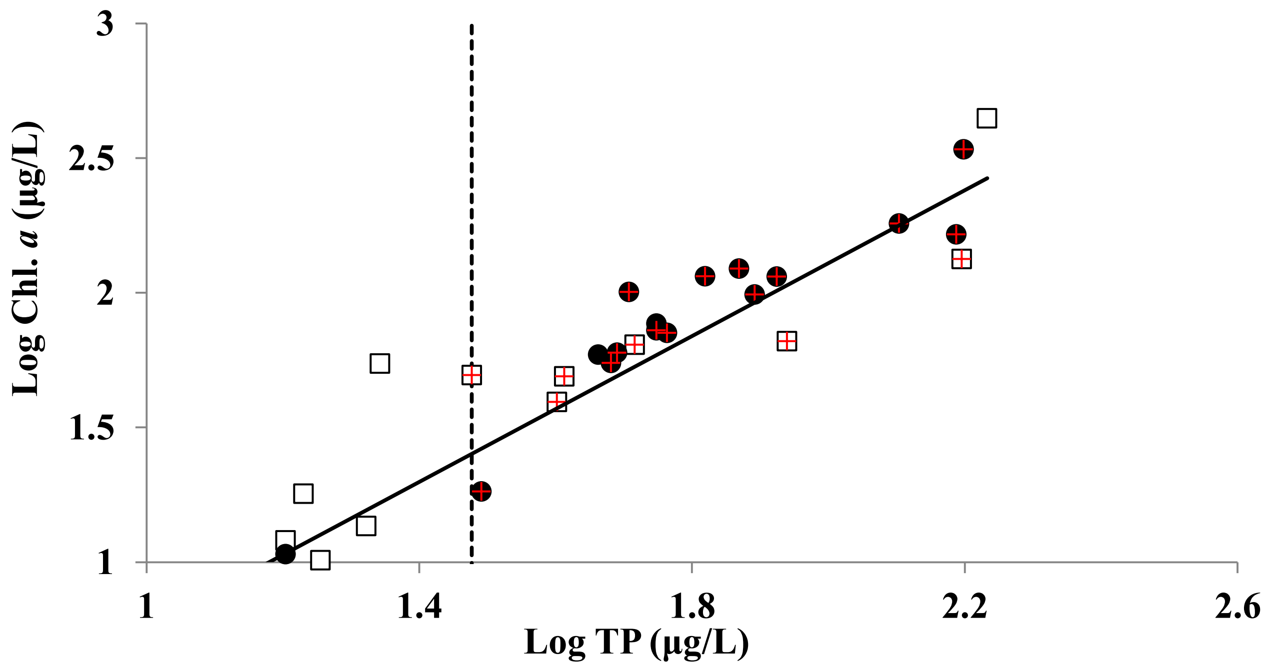

Figure 2.6 Relationship between Log chlorophyll *a (*Chl. *a*) and surface water Log total phosphorus (TP) (r^2=0.66) of 17 stormwater ponds in the City of Ottawa in June (•) and August (□), 2009. The dashed line represents the Ontario provincial guideline for surface water TP (30 µg/L). The + represent ponds with outlet TP concentrations also exceeding guidelines.

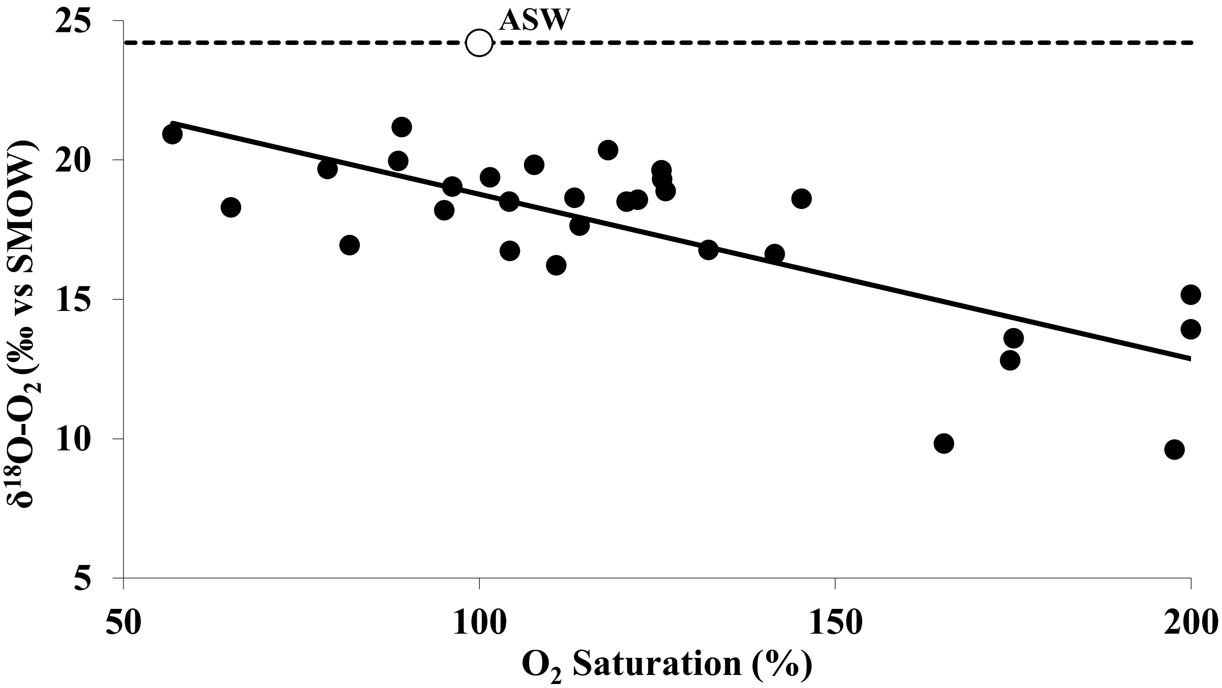

Figure 2.7 Relationship between $\delta^{18}O$-O_2 and O_2 saturation of 17 stormwater ponds in June and in August, 2009. Variables were significantly correlated ($p \leq 0.001$, $r^2 = 0.59$). The dashed line represents the equilibrium air–water saturation. The air-saturated water (ASW) is represented by an open circle.

CHAPTER 3. Seasonal variability of planktonic primary production and respiration in two urban ponds: influence of nutrients and water residence time

Introduction

Primary production (PP) has been measured in aquatic ecosystems for many decades (Kalff, 2001; Wetzel, 2001). The factors that regulate PP have been thoroughly studied and include both deterministic factors (irradiance, temperature as related to latitude) and stochastic factors (e.g. nutrient supply, water transparency) (Lewis, 2011). However, relatively few studies have been conducted on small lakes and ponds (<1 km^2), yet these systems are far more numerous across the globe than previously thought (Downing *et al.,* 2006). Their rates of carbon and other element processing appear more intense than previously thought and may have global significance (Downing, 2010).

In urban areas, stormwater management ponds or urban ponds are increasingly common; in North America the number of these facilities is on the rise (USES, 2004) and can be a requirement for new developments (Wisner, 1997). These ponds are built as a means of controlling flooding and treating polluted runoff (MOE, 2003). In residential areas, urban ponds also often provide green space and recreational amenities thus increasing property values (Baxter *et al.,* 1985; USEPA, 1995). However, their capacity to mitigate pollution though retention or transformation of elements can be highly variable, particularly with respect to phosphorus (Schueler, 1994).

Few studies have been conducted on the ecology of urban ponds with the exception of one recent study (Chiandet and Xenopoulos, 2010) and there have been no measurements of primary production. Such measurements may help explain the high variability in nutrient retention observed in urban ponds since primary production is tightly linked to nutrient cycling (Wetzel, 2001).

Compared to natural ponds, urban ponds are characterized by much higher nutrient concentrations stemming from polluted runoff (Chiandet and Xenopoulos, 2010). Their hydrological regimes are highly dynamic and unstable (e.g. Goulet *et al.,* 2001), driven by precipitation events and the degree of imperviousness of the associated catchments. If erosion is significant in the catchment, turbidity from suspended particles may limit light penetration and primary production. Biologically, some ponds may behave like wetlands if a significant littoral zone and macrophytes are present. In wetland systems, the hydrological regime has a strong influence on primary production (Mitsch and Gosselink, 1993): marshes that have variable water residence times tend to have higher primary production than stillwater wetlands with longer water residence times such as bogs (Mitsch and Gosselink, 1993).

Considering the high nutrient levels typical of urban ponds and the dynamic nature of the hydrological regime, I hypothesized that physical factors related to light availability and water residence time control the seasonal variation in primary production in these systems, in contrast to most lake ecosystems. Specifically the objectives of this study were to 1) estimate the planktonic primary production and respiration of two urban ponds during the growing season and

2) identify the environmental factors regulating PP through sampling and analysis of pond chemical, physical and biological characteristics.

Materials and Methods

***Pond and landscape characteristics* -** Two ponds (Figure 3.1) were chosen among approximately 94 wet ponds operating in the City of Ottawa based on their easy access, security (gated facility), low number of inlets and continuous gaging of both inlet and outlet. Outlet flow was controlled at both ponds to maximize water residence time.

Stonebridge pond (45º 15′ 37.7″ N /-75 43′ 7.7″ W) was constructed in 1999 and Strandherd pond (45º 16′ 39.5″ N /-75 42′ 14.8″ W) in 1998 to manage runoff from the impacts of surrounding suburban residential developments. Stonebridge was also built to mitigate the effects of runoff from an 18-hole golf course. Both ponds both consist of a sediment forebay and a main pond with a surface area of 0.021 km^2 and 0.029 $km^2$and an average depth of 1.11 m and 1.30 m respectively. Stonebridge has one major inlet that drains a catchment area of about 1.71 km^2 with approximately 10.3% of impervious cover, while Strandherd has two inlets that drain a larger catchment area of 3.21 km^2 with approximately 13.16% of impervious surface (calculated in 2008 using ArcGIS 10.0). Catchment: pond area is 110:1 for Strandherd pond and 81:1 for Stonebridge pond.

***Field sampling* -** Sampling was conducted at the center of the main cells at both ponds twice a week from June to August 2009 from a canoe. Stonebridge pond was subsequently sampled monthly from September to October 2009. Pond depth was measured each time since depth was required to compute water residence time and areal primary production. A Hydrolab minisonde 4*a* was used to record oxygen (O_2) saturation, O_2 concentration, temperature, specific conductivity (SPC), pH and oxidative-reductive potential (ORP) from subsurface to the bottom at 0.25 m intervals. To normalize for the large seasonal water temperature differences, all O_2 data were analysed as percent saturation, corrected for local barometric pressure. The photosynthetically available radiation (PAR) was measured using a Li- 250A light meter with a LI-193SA spherical underwater quantum sensor. Readings were taken in air and at the subsurface followed by readings at 0.25 m intervals down to 1 m or until light was less than 1% of incident light. Light depth profiles were necessary in order to compute primary production using the Fee computer program (Fee 1998, PSPARMS Version 4.0).

A water column sample was collected using an integrated sampler made out of a plastic tube with a weight and a rope at one end and estimates of water clarity were taken with a 20 cm, black/white Secchi disc. Integrated water samples were stored in 2L Nalgene® bottles and kept in a cooler with ice for a maximum of 24h. A subsample was then used to measure turbidity (2020 LaMotte turbidity meter), nutrient, total suspended solid (TSS) and chlorophyll *a* concentrations. A surface water grab sample was taken for stable oxygen analyses to provide an index of photosynthesis activity through the season (Methods in Appendix C).

Grab samples were also taken at the inlet and outlet of the pond and used for nutrient analyses. Once a week two 20 L dark polyethylene containers were used to collect surface water at mid-morning for light-dark bottle incubations in the laboratory using a rotating temperature controlled incubator similar to the one described in Shearer *et al.* (1985).

Flow and Water residence time - Continuous daily flow (discharge) measurements were recorded at the inlets and outlets of both ponds by the City of Ottawa using permanently installed flow meters. The data were made freely available for this project. Daily water residence time (WRT) was calculated by dividing the pond volume by the mean daily outlet flow. WRT was calculated for every day of the sampling period (WRTs) but the mean over 7 (WRT_7) and 14 (WRT_{14}) days prior to the day primary production was calculated were also computed.

Nutrient analyses and algal biomass- A subsample of the within pond, inlet and outlet water was analyzed by the Regional Municipality of Ottawa-Carleton, Surface Water Quality Laboratories for nutrients. These included total phosphorus (TP), reactive phosphorus (RP), nitrite (NO_2^-), nitrate (NO_3) and total Kjeldahl nitrogen (TKN) following standard methods of the Ontario Ministry of Environment (Eaton *et al.,* 2005). Detection limits were 20 μg/L for NO_3^-, 3 μg/L for NH_4^+, 2 μg/L for RP, 20 μg/L for TKN and 5 μg/L for TP.

Pond water samples were filtered through Whatman GF/F filters (~ 0. 7 μm pore size, 47mm) which were then frozen for analyses of chlorophyll *a* (Chl *a*). Chl *a* was determined fluorometrically with a Cary Eclipse Spectroflurometer after cold methanol extraction of filters for 24 h in the dark (Marker *et al.,* 1980). Duplicate samples were within 15% of one another.

The filtrate from the above filtrations was then further filtered through 0.22 μm pore size pre-rinsed polycarbonate filters (GE Osmotics) for analysis of other fractions of dissolved nutrients: dissolved organic carbon (DOC, by combustion (as in Wilson & Xenopoulos 2008; O.I. Analytical Aurora Model 1030 TOC analyzer, College Station, TX, U.S.A.) and total dissolved phosphorus (TDP, persulfate digestion and molybdate blue-abscorbic acid spectrophotometric method (Clesceri *et al.,* 1998; Biochrom Ultrospec500; Biochrom, Cambridge, UK)).

A portion of the each water sample was also filtered through ashed and pre-weighed Whatman GF/F 25mm filters for particulate (seston) carbon (POC), nitrogen (PON) and phosphorus (POP) measurements and through 47mm filters for total suspended solids (TSS) analysis. Filters were analysed for seston POC and PON using a CN elemental analyzer (Elementar Vario El III). POP was measured by persulfate digestion (as in James *et al.,* 2007). Filters were dried at 50ºC for 72h ours and re-weighed, the difference divided by filtrate volume for the GF/F 47 mm filters gave TSS (thus estimating suspended inorganic material as well as organic matter such as algae).

Photosynthesis and respiration from bottle incubations - Within two hours of sampling, pond water was gently transferred in the laboratory into a larger container with 12 tube outlets to minimize bubbling. Clear (26) and dark (4) 300ml BOD bottles were filled by placing the tube outlets at the bottom of each bottle and flushing with approximately three times the bottle volume prior to filling. Initial dissolved O_2 concentrations were measured in 4 to 6 clear bottles with a YSI 52 oxygen meter with a self-stirring BOD probe. Given the high algal biomass of the pond, the BOD probe was sufficiently sensitive to measure photosynthesis and respiration and was quicker than chemical measurements of O_2 via Winkler titration. Clear bottles were placed in a water tank incubator equipped with a Phillips MH1000 (1000 W) metal-halide lamp that provided 7 irradiance levels ranging from 28.2 to 339.6 $\mu mol/m^2/s$, and a compressor to adjust the temperature. The photosynthetic available radiation (PAR) at each irradiance level was measured at several points near replicate bottles with a Li- 250A light meter with a LI-193SA spherical underwater quantum sensor. Bottles were incubated at ± 2°C of the *in situ* temperature for 3.5 to 4 hours. For respiration measurements, two dark bottles were incubated for a short period (3.5 to 4 hours) and two others were incubated for a longer period of time (24 to 49.5 hours). At the end of each incubation, the dissolved O_2 concentration was measured in each bottle.

The hourly net primary production (HNP) and hourly community respiration (HR) was calculated from the changes in dissolved oxygen concentration in clear and dark bottles during the incubation. Daily volumetric (DVR) and areal (DAR) respiration rates were calculated assuming that respiration rates measured from water sampled in the morning were representative of the entire diel period. Equal dark and light respiration was assumed and hourly volumetric gross primary production (HVGP) was calculated as HNP + HR.

The HVGP vs. PAR curves were then used to calculate photosynthetic parameters using the Fee computer program (Fee 1998, PSPARMS Version 4.0). The chlorophyll-dependent rate of photosynthesis at optimal PAR ($P^B{}_m$, mg O_2 mg Chl^{-1} h^{-1}), the chlorophyll dependent slope of the photosynthesis versus PAR curve at low irradiance levels (α^B, mg O_2 mg Chl^{-1} E^{-1} m^2) and the saturation PAR (I_k, µmol m^{-2} h^{-1}) were calculated on all dates (Appendix D). To estimate the amount of photosynthesis from June to November 2009, the computer program YTOTAL was used with estimated daily PAR from latitude and longitude coordinated (Version 4.0, Fee 1998). This program uses chlorophyll concentrations, $P^B{}_m$ and α^B (all linearly interpolated from the entered data) and the fraction of the measured solar PAR that reaches each depth to calculate the photosynthesis versus depth profiles. Finally, daily volumetric gross planktonic photosynthesis rates (DVGP) were calculated from bottle incubation measurements and PAR data using YTOTAL. Daily areal gross photosynthesis rates (DAGP) were calculated by multiplying DVGP by the epilimnion depth (z_{mix}) which was the same as pond depth in most cases. Oxygen units were transformed into carbon units for comparison purposes with the literature using a photosynthetic quotient (PQ) of 1 (mole O_2 per mole C produced or respired (Fee, 1998).

Statistical analysis - Correlation analysis was used to determine relationships between the calculated daily areal gross primary production (DAGP) and meteorological, physical, chemical and biological parameters. Independent variables of chlorophyll *a*, turbidity, temperature and daylight hours used for statistical analyses were measured on the same sampling day as DAGP. However, other independent variables such as nutrients, WRT and specific conductivity (SPC) were considered when averaged over 7 days or 14 days prior to DAGP sampling. These lag times were used as the two ponds are highly dynamic with mean water residence times of 7 days for Stonebridge and 14 days for Strandherd. Correlations using these lagged variables provided better relationships with DAGP than when using variables measured on the same day as DAGP. The subscript 7 is used for Stonebridge variables that have been lagged 7 days, 14 for Strandherd variables that have been lagged 14 days and S for variables that have not been lagged.

Data were log transformed, when appropriate, to satisfy the assumptions of normality and homogeneity of variance. The dependent variable DAGP was log transformed for all correlation and regression analyses. Pearson correlations were used to determine multicollinearity between independent variables (Appendix E). Single correlations between independent variables (chlorophyll $a_{(s)}$, turbidity$_{(s)}$, water temperature$_{(s)}$, day light hours$_{(s)}$, pond depth$_{(s)}$, $TP_{(7 \text{ or } 14)}$, $RP_{(7\text{or } 14)}$, $TKN_{(7\text{or}14)}$, $NH_4^+{}_{(7\text{or}14)}$, $NO_3^-{}_{(7\text{or}14)}$, $SPC_{(7\text{or}14)}$ and $WRT_{(7\text{or}14)}$) and the dependent variable (DAGP) were performed.

Stepwise multiple linear regressions were used to develop the best predictive model for primary production within each pond. When strong multicollinearity was present between variables, the candidate parameters in the stepwise regression were chosen based on biological theory. For example, pond depth$_{(s)}$ was not included in the stepwise regression due to its correlation with WRT_7 (Appendix E, Table E1). Also $SPC_{(7\text{or } 14)}$ and $TP_{(7\text{or } 14)}$ were not included because of their significant correlation with $RP_{(7\text{or } 14)}$ (Appendix E, Table E1). Results did not differ between forward and backward stepwise regressions; the most influential variables were sought via forward stepwise multiple linear regression (McGarigal *et al.,* 2000) with a variable retention criterion of $p = 0.01$.

Results

***Physical variables* –** The inlet flows reached a maximum of 4.23 X 10^4 m^3/day at Stonebridge and 7.18 X 10^4 m^3/day at Strandherd during 2009. Water residence time ($WRT_{(s)}$) was significantly different between ponds ($p<0.001$) and was highly variable during the season, from less than a day to about 53 days (Appendix F). On average water was retained longer at Strandherd (14.2 days) in comparison to Stonebridge (6.8 days) (Appendix F). Pond depth$_{(s)}$ was significantly correlated with $WRT_{(7)}$ at Stonebridge ($r = -0.80$, $p < 0.001$) while this relationship was not significant at Strandherd ($r = -0.26$, $p = 0.08$) with $WRT_{(14)}$(Appendix E). Irradiance$_{(s)}$ at the subsurface was usually lower at Strandherd pond and highest during the end of July and beginning of August at both ponds. Although Secchi depth readings were taken, on many dates light reached the bottom of the pond so accurate measurements were not possible. $\text{Turbidity}_{(s)}$ was more variable at Strandherd (0.9 - 23.4 NTU) than Stonebridge (1.81- 9.4 NTU), but was on average quite similar (5.91 vs. 6.0 NTU).

The surface water $\text{temperatures}_{(s)}$ ranged from 13.5ºC and 25.4ºC (Table 3.1; Table 3.2) in Stonebridge from June to August and dropped to a low of 5.4 ºC in November. Strandherd followed a similar seasonal pattern but reached slightly higher temperatures (~1º C) on average (Table 3.2). In general, $\text{SPC}_{(7\text{ or }14)}$ was much more variable throughout the summer at the Strandherd pond with a maximum of 1325 µS/cm compared to a maximum of 925 µS/cm from June to August at Stonebridge (Table 3.1; Table 3.2). Thermal stratification was not observed in Stonebridge for much of the sampling period although some chemical stratification arose (Appendix G). In contrast, Strandherd showed a stronger chemical and thermal stratification with lower dissolved oxygen, temperature and higher $\text{SPC}_{(s)}$ at the bottom. Although both ponds did not reach highly reducing conditions, ORP was generally lower at the bottom at both ponds (Appendix G).

Chemical variables- Within the ponds, dissolved concentrations of $\text{RP}_{(s)}$ were close to detection (2 µg/L) most of the summer. In contrast, dissolved inorganic nitrogen concentrations were normally above detection limits. $NO_3^-{}_{(s)}$ peaked from mid-July to the beginning of August in both ponds whereas $\text{TP}_{(s)}$ peaked from the end of June to beginning of July at Strandherd and at the beginning of July and beginning of November at Stonebridge (Figure 3.2; Figure 3.3).

These peaks usually corresponded to periods of high precipitation: July was the rainiest month of summer 2009 (~183 mm of rain). $TP_{(s)}$ concentrations were on average higher at Stonebridge (57 µg/L) than at Strandherd (45 µg/L) from June to August. During most of the sampling period, $NO_3^-{}_{(s)}$ and $RP_{(s)}$ inlet concentrations of the two SWP's exceeded outlet concentrations (Figure 3.2; Figure 3.3). However, the opposite arose for $TP_{(s)}$ and $TKN_{(s)}$, where higher concentrations were found at the outlets.

Dissolved organic carbon (DOC) concentrations were similar between the two ponds (about 5 mg/L) with Strandherd having slightly higher concentrations (Appendix F). Total suspended solids of these urban ponds were relatively high (5 – 80 mg/L) (Appendix F) compared to natural ponds (average 2.09) (Chiandet, 2008; Unpublished data) whereas particulate C:N (by mol) (6 – 14) (Appendix F) were low compared to other freshwater lentic ecosystems (Chiandet and Xenpolous, 2010).

Algal biomass - Macrophytes dominated by *Myriophyllum spicatum* (Eurasian watermilfoil) covered 60-80% of both ponds most of the summer. However, during rainy periods, these macrophytes were not visible from the pond surface. Phytoplankton biomass (Chl $a_{(s)}$) showed strong seasonal variation and was highest in Strandherd in the beginning of July (173 µg/L) and highest in Stonebridge in the beginning of August (164 µg/L). Both ponds had the lowest concentrations of Chl $a_{(s)}$ (~ 12 - 13ug/L) at the beginning of the sampling period (Table 3.1; Table 3.2). Periods of high Chl $a_{(s)}$ seemed to coincide with the rainy period observed in July. A positive relationship between $TP_{(s)}$ and Chl $a_{(s)}$ was observed at Strandherd (Figure

3.4). At Stonebridge, this relationship was not significant (p=0.86) although positive up to $TP_{(s)}$ of 82 μg/L; at higher levels of $TP_{(s)}$, Chl $a_{(s)}$ was very low.

Planktonic Primary Production and respiration - Daily aerial gross primary production (DAGP) ranged from 321 to 6171 mg C/m^2/day at Stonebridge (Figure 3.6) and from 272 to 7618 mg C/m^2/day at Strandherd. Mean summer DAGP from June to August was not significantly different between Stonebridge and Strandherd: 2808 vs. 2727 mg C/m^2/day respectively (p = 0.92). In contrast, although there was no significant difference between summer daily aerial respiration (DAR) rates between the two ponds, on average Strandherd mean DAR was twice that of Stonebridge; 1240 vs. 602 mg C/m^2/day respectively. Pond temperature$_{(s)}$ had a positive effect on DAR, however, this relationship was not significant at both ponds. Significant positive relationships were also observed between DAR and DAGP (p<0.001, r =0.57 for Stonebridge and 0.86 for Strandherd) (Figure 3.5). Planktonic DAGP tended to exceed DAR with mean GP:R ratios of 10.51 for Stonebridge and 3.06 for Strandherd (Figure 3.5; Appendix F). $\delta^{18}O\text{-}O_2$ values for both ponds were below +24.2‰ (the air-water equilibrium value) and dissolved oxygen mostly above 100% saturation consistent with significant levels of primary production (Appendix C).

At Stonebridge, DAGP was significantly correlated with several physical, nutrient, and biological measures. $WRT_{(7)}$, mean pond depth$_{(s)}$, Chl $a_{(s)}$ and water temperature$_{(s)}$ all showed notable correlations with DAGP (Table 3.1). Correlations with $WRT_{(s)}$ and $WRT_{(14)}$ were either not significant or not as significant. Multiple regression analysis however, determined that $WRT_{(7)}$ was the main predictor of DAGP for this pond from June to October and explained 91%

of the variability in primary productivity [Log DAGP= 4.12- 1.01 $LogWRT_{(7)}$, $p<0.001$], where $WRT_{(7)}$ had a negative relationship with DAGP (Figure 3.7). $WRT_{(7)}$ was still a strong predictor of DAGP (70%) when only the summer time frame was considered (June-August). Nutrients were included in the stepwise regressions for biological reasons but did not seem to have an effect on DAGP. Although DAGP and Chl $a_{(s)}$ were significantly correlated in this pond, $WRT_{(7)}$ seemed to override this relationship.

Strandherd pond DAGP however, had a significant positive relationship with daylight $hours_{(S)}$ and significant negative relationship with $WRT_{(14)}$ (Table 3.2). $WRT_{(s)}$ and $WRT_{(7)}$ proved to be not significant or not as significant. However, with the stepwise procedure, the regression found that daylight $hours_{(s)}$ and water $temperature_{(s)}$ were the main predictors explaining about 69% of the variability in primary productivity [Log DAGP= 0.08water $temperature_{(s)}$ + 0.35 daylight $hours_{(s)}$ +10.40, $p=0.02$]. Again, nutrients did not appear to have a significant effect on DAGP.

Discussion

Planktonic production and respiration rates - The rates of planktonic primary production estimated for Stonebridge and Strandherd stormwater management ponds were at the high end of rates measured in shallow lakes from around the world (Table 3.3). According to Wetzel (2001), lakes with a mean daily aerial net primary productivity (DANP) above 1000 mg C m^2/day are classified as eutrophic. With mean DANP rates between 1488 – 1566 mg C m^2/day, Stonebridge and Strandherd are both clearly eutrophic to hypereutrophic. In fact, the max daily areal rates measured (6171 and 7618 mg C/m^2/day) approached the theoretical maximum rates estimated as 8 to 13 g C/m^2/day under optimal conditions (Melack and Kilham, 1974; Talling 1982; Uhlmann 1978 and Lewis, 2011). When considering the same time frame, from June to August, Stonebridge and Strandherd's daily aerial gross production rates (DAGP) were similar (2727 vs. 2808 mg C/m^2/day) however DANP was higher at Stonebridge than Strandherd (1800 vs. 1488 mg C/m^2/day) reflecting higher respiration at Strandherd.

Daily aerial respiration (DAR) was twice as high at Strandherd than at Stonebride (1240 vs. 602 mg C/m^2/day respectively) during the summer months. Although not significant, temperature had a positive effect on respiration in these ponds. Surface water temperature was slightly higher at Strandherd (~1 ºC difference) than at Stonebridge in the summer likely because of the longer water residence time. However, this difference was probably not sufficient to explain the difference in respiration.

Respiration rates measured in bottle experiments represent both bacterial and algal activity. In both ponds, respiration rates were correlated with daily aerial gross primary production (DAGP); 74% and 32% of DAR in Strandherd and Stonebridge respectfully could be explained by algal production (Figure 3.5). This could suggest that bacterial respiration was more important in Stonebridge. Stonebridge had slightly more particulate organic carbon (POC) than Strandherd but the difference was not significant. Dissolved organic carbon entering the pond, another potential substrate for bacterial respiration, was not significantly different between ponds and in fact there appeared to be more consumption of this element in Strandherd (5.26 mg/L at inlet vs. 4.06 mg/L at outlet) than at Stonebridge (5.18 mg/L at Inlet vs. 5.59 mg/L at outlet) suggesting more bacterial respiration.

Drivers of planktonic production - At Stonebridge, the single most significant factor that explained the seasonal variation in DAGP was water residence time averaged over the previous week ($WRT_{(7)}$). From June to October, this relationship was negative and highly significant (Table 3.1). Although cell biomass, temperature and light showed positive relationships as might be expected (Table 3.1), the multiple regression analysis pointed to a much stronger effect of $WRT_{(7)}$.

Stonebridge pond may be acting like a chemostat where increased inflows positively affect algal production due to increased nutrient inputs to the system (Peterson, 1996; Stevenson, 1996). But, inflows were rarely high enough to lead to the washing out of planktonic algae. In flowing water wetlands fluctuating or constant water inputs from rivers have also been reported to have positive effects on primary production due to the significant nutrient loading (Nixon, 1995; Tuttle *et al.,* 2008). Cronk and Mitsch (1994) also showed that constructed wetland primary production benefited from having medium to high flows compared to still water wetlands.

At Strandherd, although $WRT_{(14)}$ showed a negative trend with DAGP (Figure 3.7), $WRT_{(14)}$ was not a significant driver of DAGP. Strandherd mean $WRT_{(s)}$ was much longer than at Stonebridge, 14 days compared to 7 days. As a consequence of water staying longer in the pond, this system may function more like a lake where other factors drive DAGP (e.g. Prézelin *et al.,* 1991; Gervais and Behrendt, 2003). Light availability and temperature turned out to be the main factors explaining the seasonal variation of DAGP in this pond. However, WRT may not have had an effect on DAGP simply because the sample size was lower in Strandherd due to the shorter time period of investigation.

Strandherd also stratified more often than Stonebridge, which is consistent with a longer water residence time. Water temperature, dissolved oxygen and ORP were lower at the bottom of the pond whereas conductivity was higher as observed in lake systems (Appendix G). Furthermore, a positive significant relationship between $TP_{(s)}$ and Chl $a_{(s)}$ was observed at Strandherd (Figure 3.4). This is also consistent with a still water aquatic system. The summer Chl *a* concentration of temperate lakes can be predicted quite accurately from concentrations of total phosphorus (TP) (e.g. Dillon and Rigler, 1974; Schindler, 1978). In contrast, at Stonebridge, due to its more dynamic hydrology, this relationship was not significant ($p = 0.86$) although the trend was positive up to $TP_{(S)}$ of 82 µg/L. At higher levels of $TP_{(s)}$, Chl $a_{(s)}$ tended to be lower due to coincident shorter $WRT_{(7)}$.

Nutrient concentrations - Unlike lake ecosystems, nutrients appeared less important than physical factors (WRT, temperature and light) in explaining the seasonal variation in DAGP (or DAR, not shown)even when time lags were considered. This might be because nutrient concentrations were very high in both urban ponds with $TP_{(s)}$ concentrations exceeding Ontario provincial guidelines (30 µg/L) for the protection of aquatic life about 80% of the time (Figure 3.4).

Nitrogen and phosphorus concentrations were highest in July and the beginning of August likely because of high precipitation events. In 2009 Ottawa received 37% more rain during the summer when compared to the 30 year average, with July receiving the most precipitation (183 mm). Both mean total phosphorus and nitrogen concentrations were high in these two urban ponds (0.05 mg/L and 1.19 mg/L respectively). Low particulate C:N and C:P (Appendix F) also points to high concentrations of N and P found within these urban ponds compared to natural ponds (Sterner *et al.,* 2008). Mean TN:TP at Stonebridge was 18.75 and was lower on average than at Strandherd with a ratio of 32.18 (Appendix F) suggesting that Stonebridge may have more denitrification (i.e. more N removal).

Both ponds did not retain TP and TKN well for most of the growing season with outflow concentrations exceeding inflow concentrations (Figure 3.2 and 3.3). However, retention of RP and NO_3^- was evident (Figure 3.2 and 3.3) and likely the result of algal and plant uptake, as well as denitrification in the case of nitrate. Export of TP might be attributed to previous time frames when TP would have accumulated in the system and internal loading. Less TP removal was also observed at Stonebridge than Strandherd. This is probably in part because of slightly higher TP inputs at Stonebridge due to its proximity to an 18-hole golf course.

GP:R ratios - Throughout the sampling period planktonic GP:R was >1 at both ponds (Appendix F). This suggests that pelagic zones of these systems is predominantly autotrophic. Strandherd however seemed less autotrophic than Stonebridge (GP:R of 3.06 compared to 10.51). As a result, these two urban ponds may be sinks for carbon. However, planktonic metabolism alone is not sufficient to provide an estimate of the whole ecosystem metabolism as other organisms such as macrophytes, are likely to be important contributors to overall metabolism. The seasonal O_2 vs. ^{18}O-O_2 cross plot (Appendix C) would suggested that the whole pond primary production exceeded community respiration throughout the growing season except on a few occasions where $\delta^{18}O\text{-}O_2$ values approached +24.2‰ (the air-water equilibrium value) and O_2 concentrations were below 100% saturation (Appendix C, Figure C). Whole ecosystem measurements must be taken in to account in order to accurately determine if these eutrophic stormwater management ponds are sink or sources of carbon. This requires diurnal measurements of $\delta^{18}O\text{-}O_2$ and/or O_2 changes (Chapter 4).

Tables

Table 3.1 Characteristics of Stonebridge Pond, from June to October 2009. Independent variables presented were correlated with Log daily areal gross primary production (DAGP) (n= 14 - 17). Significant correlations are indicated by: * p ≤ 0.05, ** p≤ 0.01 and *** p ≤ 0.001.

Independent variable	Median	Range	r-values
Chlorophyll $a_{(S)}$ (µg/L)$^{1,\,**}$	65	12 - 164	0.63
Day light$_{(S)}$ (Hours)^{2}	14.1	9.3 - 15.7	0.17
WRT$_{(7)}$ (Days)$^{1,\,2,\,3***}$	5.8	0.9 - 19	-0.96
Mean Pond Depth$_{(S)}$ (m)**	1.2	0.6 - 1.7	0.67
Turbidity$_{(S)}$ (NTU)^{1,2}	6.0	1.8 – 53.4	0.50
Water Temperature$_{(S)}$ (ºC)$^{2,\,*}$	19.7	5.4 - 25.4	0.54
Specific Conductivity$_{(7)}$ (µS/cm)	753	377 - 925	-0.34
Total Phosphorus$_{(7)}$ (µg/L)^{1}	51	20 - 196	0.46
Reactive Phosphorus$_{(7)}$ (µg/L)^{2}	7	2 - 32	0.14
$NO_3^-{}_{(7)}$ (µg/L)$^{1,\,2}$	160	14 - 967	-0.17
$NH_4^+{}_{(7)}$ (µg/L)$^{1,\,2}$	36	4 - 420	-0.4

[1] Variables were log transformed
[2] Candidate variables in step-wise forward multiple regression
[3] Mean water residence time over 7 days previous to primary production sampling

Table 3.2 Characteristics of Strandherd Pond, from June to August 2009. Independent variables presented were correlated with Log aerial gross primary production (DAGP) (n= 11 - 23). Significant correlations are indicated by * ($p \leq 0.05$).

Independent variable	Median	Range	r-values
Chlorophyll $a_{(S)}$ (µg/L)[1,]	86	13 – 173	0.39
Day light$_{(S)}$ (Hours)[2, *]	15.2	13.9 - 15.7	0.68
WRT$_{(14)}$ (Days)[2, 3]	16.3	2.2 - 24.7	-0.65
Mean Pond Depth$_{(S)}$ (m)	1.3	1.4 - 1.6	0.30
Turbidity$_{(S)}$ (NTU)[1,2]	3.52	0.9 – 29.4	0.25
Water Temperature$_{(S)}$ (ºC)[2, *]	21.4	14.9 - 26.2	0.52
Specific Conductivity$_{(14)}$ (µS/cm)	875	298 - 1325	-0.23
Total Phosphorus$_{(14)}$ (µg/L)	40	13 - 86	0.46
Reactive Phosphorus$_{(14)}$ (µg/L)[1,2]	2	2 - 23	0.31
$NO_3^-{}_{(14)}$ (µg/L)[1, 2]	411	62 - 1177	-0.08
$NH_4^+{}_{(14)}$ (µg/L)[1, 2]	50	3 - 260	-0.06

[1] Variables were log transformed
[2] Candidate variables in step-wise forward multiple regression
[3] Mean water residence time over 14 days previous to primary production sampling

Table 3.3 Seasonal range in daily mean gross phytoplankton primary production (DAGP) of different shallow lakes compared to Stonebridge pond DAGP range of summer 2010.

Lake/Pond	**Comment**	**Net phytoplankton production range (mg C m^{-2} day^{-1})**	**Mean daily net primary production (mg C m^{-2} day^{-1})**
Lawrence, Michigan, USA*	Oligotrophic	5 - 497	99
Goose, Indianna, USA*	Small kettle lake, Mesotrophic	166 - 1753	729
Müggelsee, Berlin, Germany**	Polymictic lake, mesoeutrophic to slightly eutrophic	640 - 980	NA
Frederiksborg, Denmark*	Eutrophic	12 - 4160	1030
Strandherd Pond, Ottawa, Canada	**Mesotrophic to Hypertrophic**	**80 – 4336**	1488
Stonebridge Pond, Ottawa, Canada	**Mesotrophic to Hypertrophic**	**261 – 3913**	1566
Søbygaard, Jutland, Denmark***	Hypertrophic	3000-12000	NA

*As cited in Wetzel, 2001

** Gervais and Behrendt, 2003

***As cited in Kalff, 2003

Figures

Figure 3.1 Stonebridge (upper panel) and Strandherd (lower panel) urban stormwater ponds. Red arrows indicate water flow and blue lines show the forebay berms. The star indicates the sampling station. Pictures were accessed on September, 2009.

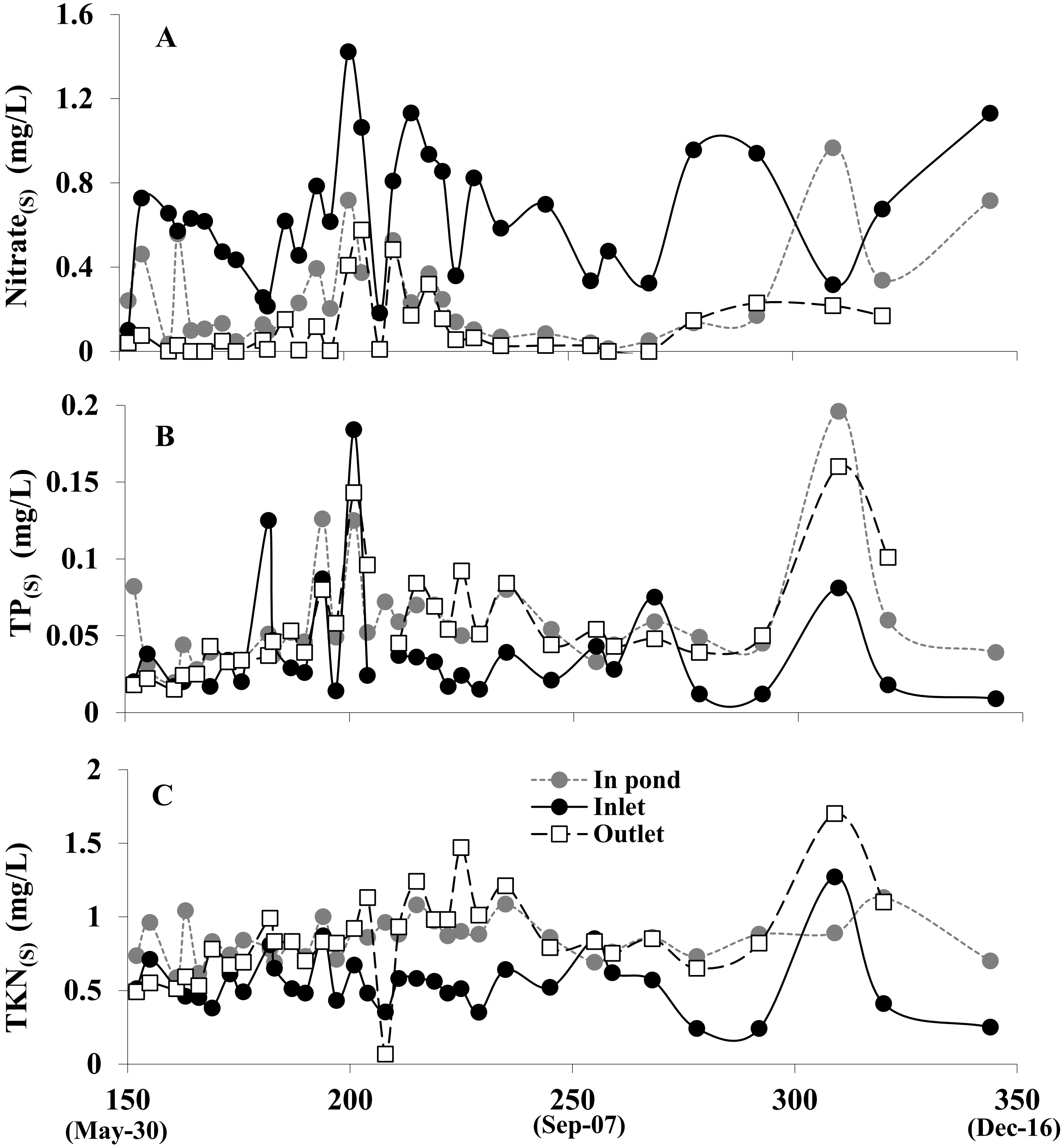

Figure 3.2 Seasonal variation in A) total phosphorus (TP), B) total Kjeldahl nitrogen (TKN) and C) nitrate concentrations at the inlet, outlet and in the middle of Stonebridge pond, Ottawa, ON.

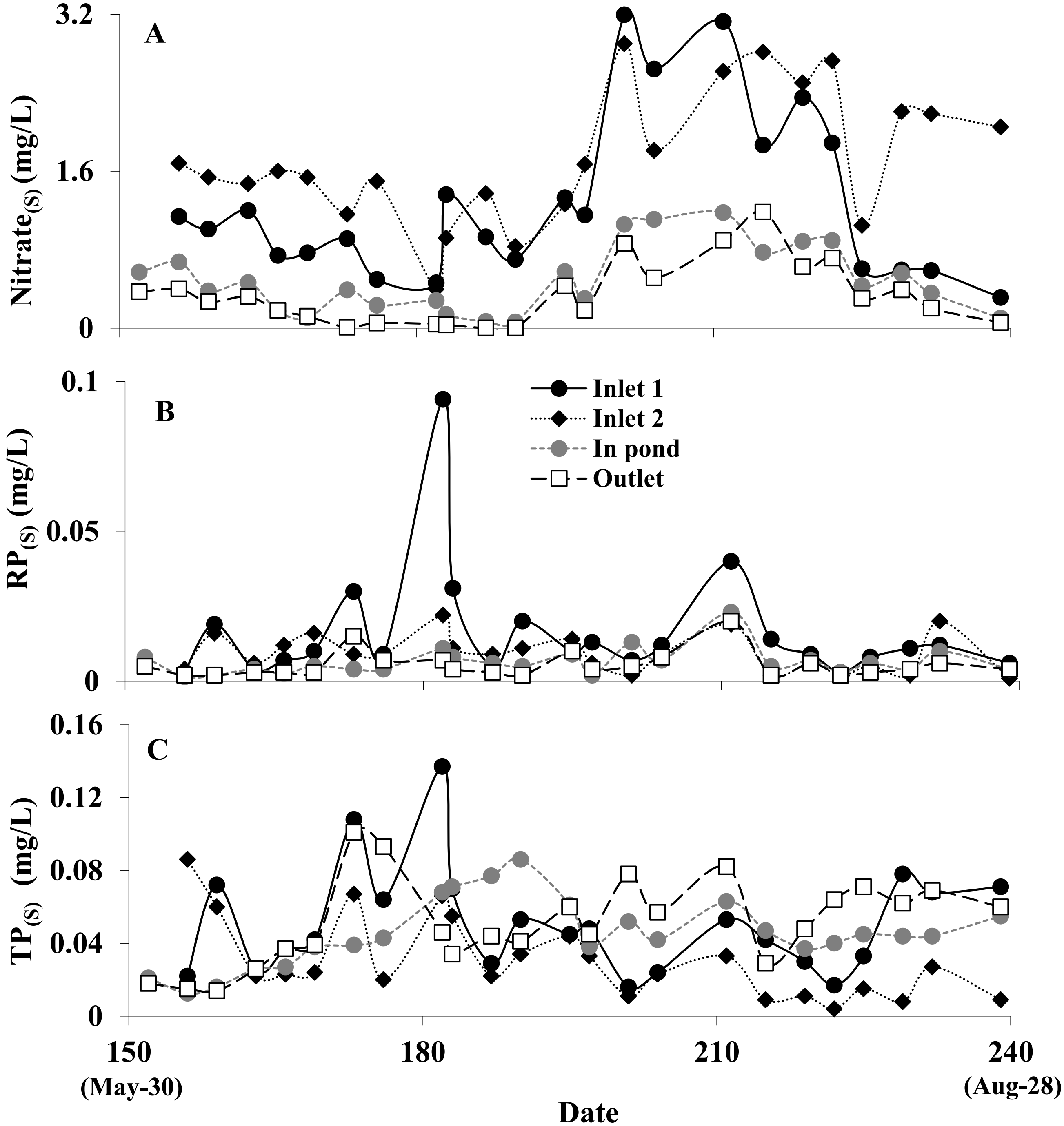

Figure 3.3 Seasonal variations in A) nitrate, B) reactive phosphorus and C) total phosphorus (TP) concentrations at the both inlets (inlet 1 and inlet 2), outlet and in the middle of Strandherd pond, Ottawa, ON.

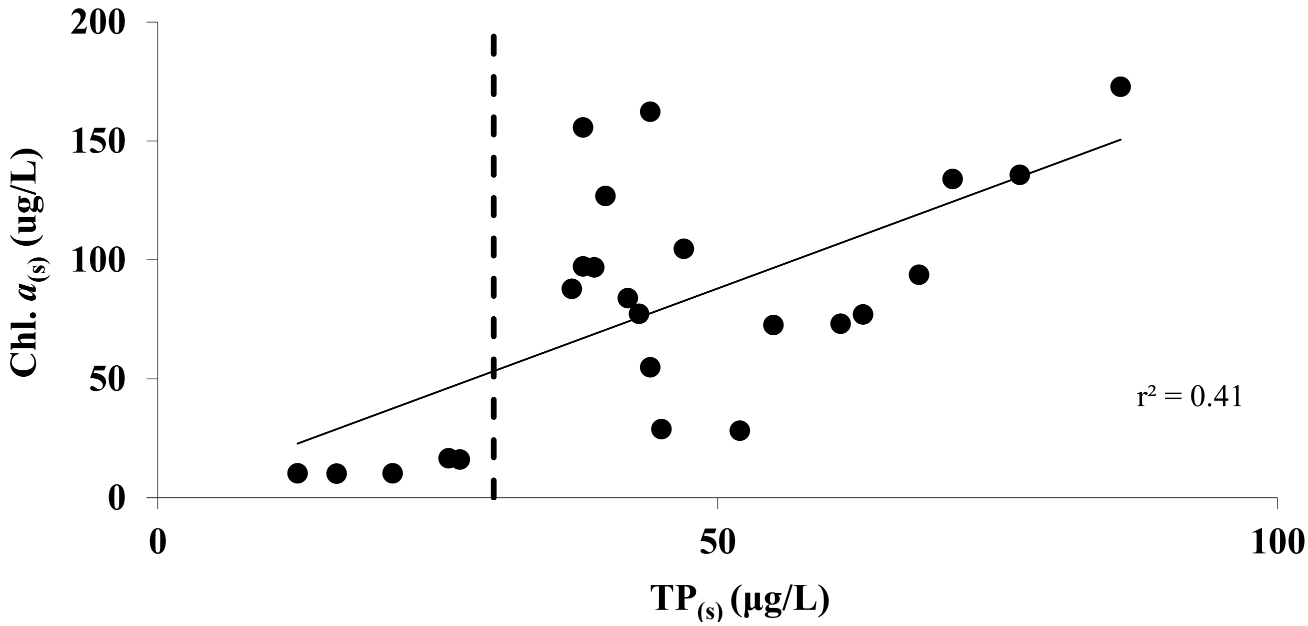

Figure 3.4 Relationship between chlorophyll *a (*Chl. *a*$_{(S)}$) and total phosphorus ($TP_{(S)}$) for Strandherd pond. The dashed line represents the Ontario provincial guideline for surface water $TP_{(S)}$ (30 µg/L) and the solid line represents linear regression line between the two variables. ($p \leq 0.001$).

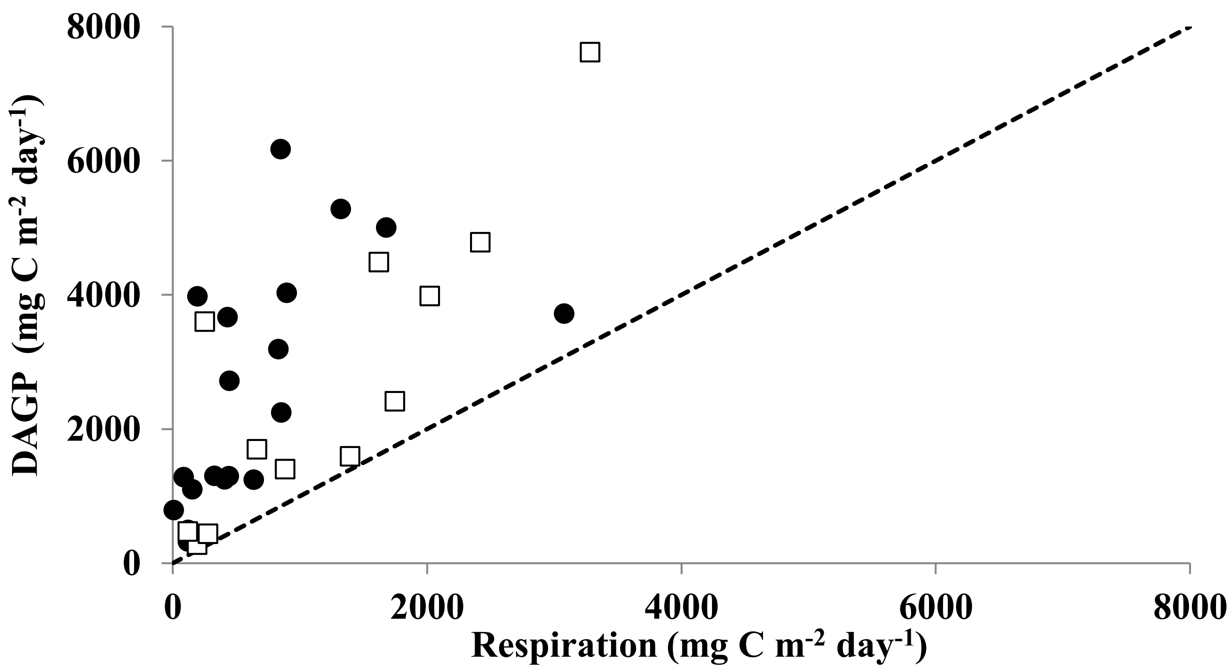

Figure 3.5 Relationship between planktonic gross primary production (DAGP) and respiration of Stonebridge (•) and Strandherd (□) ponds. Variables were significantly correlated ($p \leq 0.001$) for both Stonebridge ($r = 0.57$) and Strandherd pond ($r = 0.86$). The dotted line denotes the 1:1 relationship.

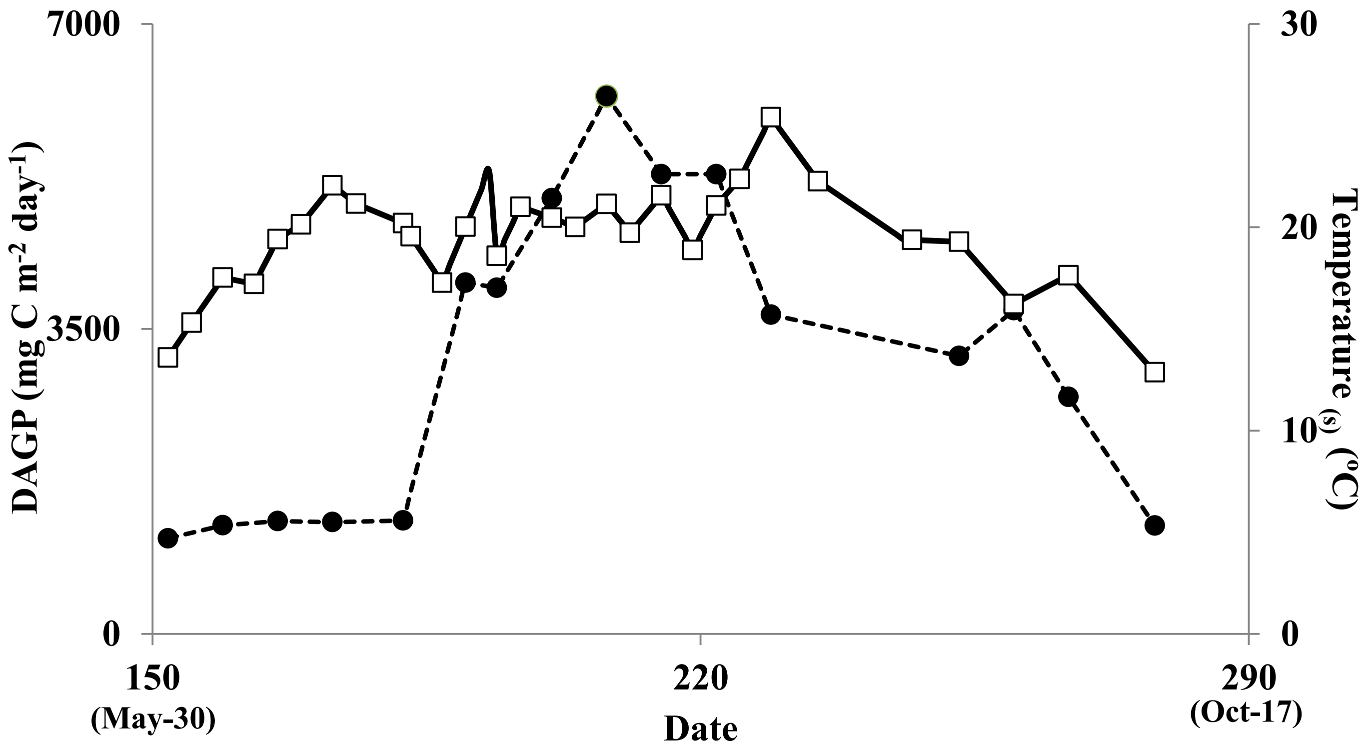

Figure 3.6 Daily planktonic aerial gross primary production (DAGP) (•) and the water temperature$_{(s)}$) (□) at Stonebridge.

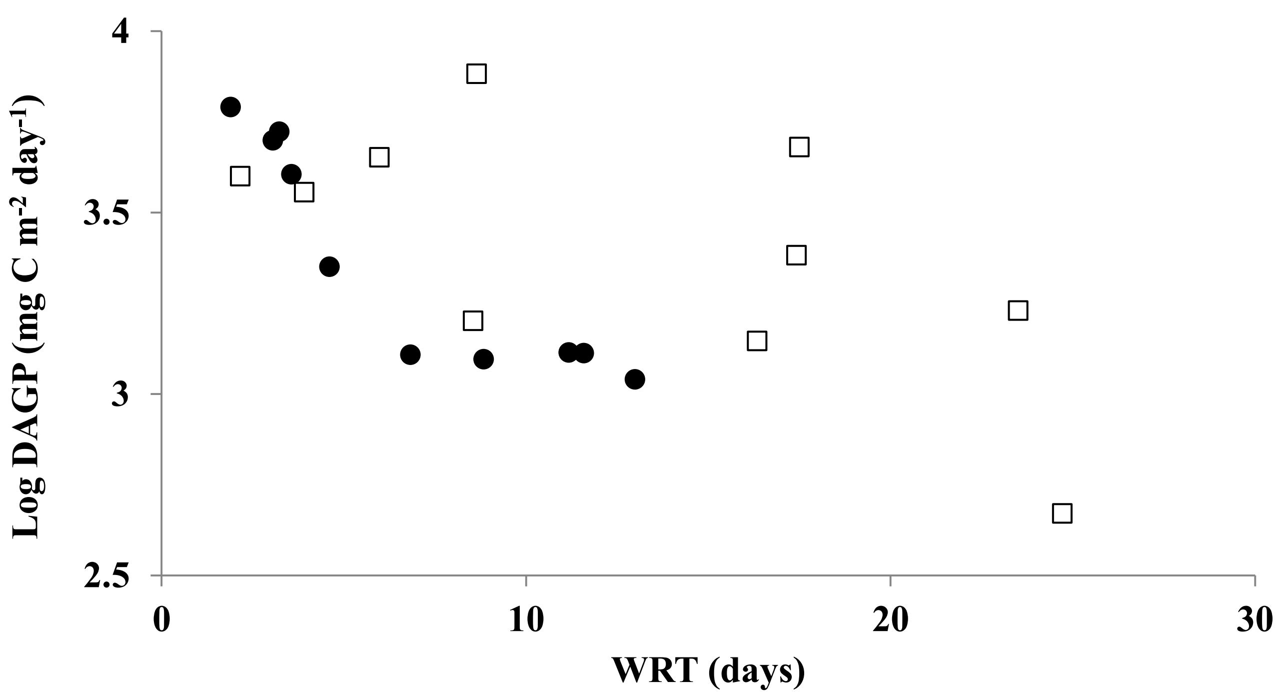

Figure 3.7 Summer daily planktonic aerial gross primary production (DAGP) and mean water residence time of Stonebridge (•) and Strandherd (□). WRT$_{(7)}$ for Stonebridge and WRT$_{(14)}$ for Strandherd is shown.

CHAPTER 4. Whole ecosystem metabolism of an urban pond

Introduction

The metabolism of aquatic ecosystems has been the subject of intensive research to determine if and when these systems are net sources or sinks of CO_2 to the atmosphere. Most recent studies have concluded that lakes are sources of CO_2 and thus largely heterotrophic (e.g. Kling *et al.,* 1992; Cole *et al.,* 1994, 2007) in part because of significant inputs of organic carbon from the drainage basin.

Small water bodies (< 1 km^2) constitute a significant fraction of the earth's freshwater systems (Downing *et al.,* 2006) but their contribution to the carbon cycle has rarely been quantified (Cole *et al.,* 2007, Downing *et al.,* 2008). Recent evidence suggests that small eutrophic water bodies may in fact be sinks for carbon (Finlay *et al.,* 2009; Lazzarino *et al.,* 2009; Balmer and Downing, 2011) as eutrophication increases the conversion rate of inorganic carbon to particulate organic matter (Smith, 1979; Peters, 1986).

Analysing the carbon balance of aquatic systems requires measurements of photosynthesis and respiration to calculate gross and net primary production. There are several approaches for measuring aquatic metabolism (Juranek and Quay, 2005; Yacobi *et al.,* 2007). Early methods of measuring primary productivity consisted of incubating isolated samples of communities *in situ* (e.g. at depths of collection) or under laboratory conditions and measuring the changes in oxygen concentrations or uptake of ^{14}C (Wetzel, 2001). Although the protocols for this method are now standard (Wetzel and Likens, 2000), concerns over the "bottle" approach remain, as the actual light, nutrient cycling and grazing regimes can differ from the natural environment (Wetzel, 2000). Furthermore, as pelagic samples are used, only phytoplankton and bacterioplankton metabolism are measured and the contribution of other primary producers (e.g. macrophytes, attached algae) and other sources of respiration in the system are not considered.

The analysis of the stable isotope composition of dissolved oxygen can provide estimates of whole system metabolism and eliminates the limitations of bottle incubations (Odum, 1956). This method is based on the fact that photosynthesis and respiration have opposing effects on the ratio of the heavier to lighter stable isotopes of oxygen. The two most abundant isotopes, O^{16} and O^{18} have been used to infer the gross primary production to respiration (GP:R) in several different systems. (e.g. Quay *et al.,* 1995, Wang and Veizer, 2000; Russ *et al.,* 2004). A single water sample of dissolved oxygen concentration and isotopic composition can potentially suffice to characterize the metabolic balance of the aquatic system; however actual metabolic rates cannot be calculated. Estimates of GP:R of samples taken at one point in time also depend on steady state assumptions (Quay *et al.,* 1995) whereas most aquatic systems are frequently not at steady state. Collecting several samples within one single diel period can help to constrain these uncertainties as well as produce estimates of absolute gross primary production and respiration over a day-night cycle (Venkiteswaran *et al.,* 2007; Holtgrieve *et al.,* 2010). Although this method enables the measurement of whole ecosystem metabolism, no one method can both estimate whole ecosystem metabolism and identify the contributions from different communities (e.g. phytoplankton vs. macrophytes) to overall productivity.

The aim of this study was to estimate the primary productivity and respiration of an urban pond. A combination of the bottle incubation and the dual isotope method was used to determine the overall metabolism as well as to estimate planktonic vs. non-planktonic contributions (attached algae and macrophytes) to primary production and respiration.

Materials and Methods

Pond and landscape characteristics - Experiments were conducted at Stonebridge pond in the City of Ottawa, Ontario, Canada (45º 15′ 37.7″ N /-75 43′ 7.7″ W) (Figure 4.1). Stonebridge was chosen from a list of 94 possible wet ponds operating in the City of Ottawa based on its ease of access, security (a gated facility so that equipment could be left *in situ*), low number of inlets (1) and ongoing gaging stations at both inlet and outlet.

The pond was constructed in 1999 to manage runoff from the impacts of a surrounding residential development and from 18-hole golf course. It consists of a sediment forebay and a main pond with a surface area of 0.021 km^2 and an average depth of 1.11m. Its one inlet drains a suburban catchment area of about 1.71 km^2 with approximately 10.3% impervious cover (calculated in 2008 using ArcGIS 10.0).

Field sampling - Three 24h-diel experiments were conducted on the following dates; April 29 (early spring), May 28 (mid spring) and July 5, 2010 (summer). Weather forecasts were consulted to avoid major rain events within at least two days before the experiments and to ensure sunny skies. A 2.25 m^2 instrument and sampling platform was installed at the center of the main cell (~1 m depth) and left throughout the sampling season. A Hydrolab minisonde 4*a* and an anemometer (Onset Computer Coorporation, model number SWCA-M003) were attached to the platform. The Hydrolab sonde was fixed mid-depth below the water surface at 0.5 m and recorded O_2 saturation, O_2 concentration, temperature, specific conductivity (SPC), pH and oxidative-reductive potential (ORP) at 15-min intervals throughout the 24h period. The sonde was calibrated in the laboratory for O_2, specific conductivity and pH prior to deployment. To normalize for the large seasonal water temperature differences, all O_2 data are herein reported as percent saturation, corrected for local barometric pressure. The wind velocity was recorded at 30-sec intervals and the photosynthetically available radiation (PAR) was measured using a Li-250A light meter with a LI-193SA spherical underwater quantum sensor. Every hour, an initial reading was taken in air and at the subsurface followed by readings at 0.25m intervals down to 1m or until light was less than 1% of the surface value. Light depth profiles were necessary in order to compute planktonic primary production using the Fee computer program (Fee 1998, PSPARMS Version 4.0).

Using a canoe, water samples for isotopic composition of oxygen in water, $\delta^{18}O\text{-}H_2O$, and isotopic composition of dissolved oxygen, $\delta^{18}O\text{-}O_2$, were collected hourly at a depth of 0.5m at the center of the pond adjacent to the meteorological station using a syringe. The water was then injected into sterilized 30mL Exetainer® vials making certain no air bubbles were formed. All $\delta^{18}O$ samples were preserved with $HgCl_2$ to approximately 150 ppm and refrigerated at 4°C before analysis (within 3 months).

At the beginning, mid-morning, and at the end of each 24h-diel sampling, a water column sample was collected using an integrated sampler made out of a plastic tube with a weight and a rope at one end and estimates of water clarity were taken with a 20 cm, black/white Secchi disc. Integrated water samples were stored in 2L Nalgene® bottles and kept in a cooler with ice for a maximum of 24h. A subsample was then used for nutrient and chlorophyll *a* analyses.

Grab samples were also taken at the inlet and outlet of the pond and used for nutrient analyses. Once a week two 20 L dark polyethylene containers were used to collect surface water at mid-morning for light-dark bottle incubations in the laboratory using a rotating temperature controlled incubator similar to the one described in Shearer *et al.,* (1985).

Nutrient analyses and algal biomass- A subsample of the within pond, inlet and outlet water was analyzed by the Regional Municipality of Ottawa-Carleton, Surface Water Quality Laboratories for nutrients. These included total phosphorus (TP), reactive phosphorus (RP), nitrite (NO_2^-), nitrate (NO_3) and total Kjeldahl nitrogen (TKN) following standard methods of the Ontario Ministry of Environment (Eaton *et al.,* 2005). Detection limits were 20 µg/L for NO_3^- , 3 µg/L for NH_4^+, 2 µg/L for RP, 20 µg/L for TKN and 5 µg/L for TP.

Within pond samples were filtered through Whatman GF/F filters (~ 0. 7 µm pore size, 47mm) which were then frozen for analyses of chlorophyll *a* (Chl *a*). Chl *a* was determined fluorometrically with a Cary Eclipse Spectroflurometer after cold methanol extraction of filters for 24 h in the dark (Marker *et al.,* 1980). Duplicate samples were within 15% of one another.

The filtrate from the above filtrations was then further filtered through 0.22 µm pore size pre-rinsed polycarbonate filters (GE Osmotics) for analysis of other fractions of dissolved nutrients: dissolved organic carbon (DOC, by combustion as in Wilson & Xenopoulos 2008 using an O.I. Analytical Aurora Model 1030 TOC analyzer, College Station, TX, U.S.A.) and total dissolved phosphorus (TDP by the persulfate digestion and molybdate blue-abscorbic acid spectrophotometric method Clesceri *et al.,* 1998) using a Biochrom Ultrospec500, Biochrom, Cambridge, UK)). Total inorganic carbon was analysed at the G.G. Hatch Isotope Laboratory on an O.I. Analytical "TIC-TOC" Analyser (St-Jean, 2003).

A portion of each water sample was also filtered through ashed and pre-weighed Whatman GF/F (~ 0.7 µm pore size filters, 25mm) for particulate (seston) organic carbon (POC), nitrogen (PON) and phosphorus (POP) measurements. Filters were analysed for POC and PON using a CN elemental analyzer (Elementar Vario El III). POP was measured by persulfate digestion (James *et al.,* 2007).

***δ^{18}O analysis* -** $\delta^{18}O$-H_2O and $\delta^{18}O$-O_2 were measured at the G.G. Hatch Isotope Laboratory, University of Ottawa. To measure the isotopic composition of oxygen in water, samples were reacted with a few milliliters of copper and charcoal for 24 hours prior to analysis. Then 0.2 ml of sample was flushed with a gas mixture of 2% CO_2 in helium. The CO_2 was extracted and cleaned for analysis on a Finnigan MAT Delta plus XP + Gasbench with a routine analytical precision of ± 0.1%.

To measure the isotopic composition of dissolved oxygen, a helium headspace was created and a subsequent isotope analysis of the extracted $O_{2(g)}$ was achieved using an isotope ratio mass spectrometer (Barth *al*., 2004) . The routine analytical precision for isotopic composition of dissolved oxygen analysis was of ±0.2‰.

The $^{18}O/^{16}O$ isotope ratios in water and the dissolved oxygen are by convention expressed in ‰ with :

$$\delta^{18}O = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O\,/^{16}O)_{VSMOW}} - 1\right) X1000$$

where VSMOW is the international Vienna Standard Mean Ocean Water.

***Whole ecosystem metabolism modeling, calculating P, R and G from oxygen isotopes* -** The dynamic O_2 stable isotope computer model PoRGy (photosynthesis– respiration–gas exchange) (Venkiteswaran *et al.,* 2007) was used to simultaneously estimate ecosystem gross productivity (GPP), respiration (R) and reaeration rates (G) from field observations of diel changes in dissolved O_2 and $\delta^{18}O$-O_2 as well as other measured and assumed physical and biological parameters (Appendix H). Similar to an isotopic version of the O_2 models used in the past to estimate ecosystem metabolism (Hornberger and Kelly, 1975; O'Connor and Di Toro, 1970; Odum, 1956), PoRGy assesses GPP, R, and G at discrete time steps and models the mass balance of O_2 through time (Eq. 1.1).

$$\frac{dO_2}{dt} = GPP - R + G \qquad (1.1)$$

Where GPP, R, and G are rates as described above and G = k ($O_{2\ saturation} - O_2$), k being the gas transfer velocity coefficient. PoRGy however, also includes a second equation to account for $\delta^{18}O$-O_2 (Eq. 1.2).

$$\frac{d^{18}O^{16}O}{dt} = GPP\left(\alpha_P \, X \, \frac{^{18}O}{^{16}O_{H_2O}}(^{18}O)\right) - R\left(\alpha_R \, X \, \frac{^{18}O}{^{16}O_t}\right) + G_{\ ^{18}O\,^{16}O} \qquad (1.2)$$

Where $\frac{^{18}O}{^{16}O_{H_2O}}$ is the isotopic ratio of H_2O, α_P isotopic fractionation factor during production which equals to 1.000 and α_R is the community respiration isotopic fractionation factor.

PoRGy was used to find the best combinations of 1) the nominal R rate at 20°C (R_{20}), 2) oxygen production at light saturation (P_{max}), 3) k and 4) α_R that provide the best fit of the modelled data to the observed diurnal dissolved O_2 and $\delta^{18}O$-O_2 field data (Venkiteswaran *et al.,* 2007; Wassenaar *et al.,* 2010). PoRGy model was imported to MATLAB 7.6.0 (The MathWorks, Inc., Natick, Massachusetts; http://www. mathworks.com) to enable automated iterative curve-fitting using field data ($\delta^{18}O$-O_2, $\delta^{18}O$-H_2O, O_2, temperature, time, date and location) as well as constrained unknown variables (metabolic rates, k and α_R) (Wassenaar *et al.,* 2010). Unknown parameters were constrained within the model based on literature values. P_{max} and R_{20} were assumed to be in between 0 and 5000 mg O_2 m^{-2} h^{-1} (Wassenaar *et al.,* 2010).

The value of α_R is typically below 1 and was constrained based on literature values between 0.975 and 1.00 (Venkiteswaran *et al.,* 2007). α_R was also calculated directly from dark bottle incubations (Quay *al.*, 1995) and taken into consideration when running the model (Appendix I). To estimate *k*, the *in situ* measurements of wind speeds were used in three common empirical models (Crusius and Wanninkhof, 2003) (Appendix J). This estimate of k was taken into account when running PoRGy. However, given the much greater uncertainty in *k* than for all other covariates (Jha *et al.* 2004), a range of three orders of magnitude of *k*, from 0.001 to 1 m/h, were tested.

Randomizing starting points for unknown variables based on the assumed constraints were used to run PoRGy in Matlab as well as the measured field variables. The output generated consisted of tables of *k*, α_R and GPP, R, and G combinations that minimized the combined sum of squared errors of $\delta^{18}O$-O_2 and O_2 between observed field data and modelled data

(Venkiteswaran *et al.,* 2007). To compare model results with *in situ* field site data, r^2 values were calculated by least squares regressions of field data versus model results for both dissolved O_2 and $\delta^{18}O$-O_2 values. As different combinations of unknown variables provided different results, the model was run 20 times and the results having the highest combined r^2 were averaged as possible model solutions. Out of 20 model runs, the PoRGy model converged to the same results 14 times in April and 16 times in May and June. Results from these model runs were averaged as they also produced the best combination of *P*, *R*, *k*, and a*R* that minimized the combined sum of squared errors between observed field data (O_2 and d $\delta^{18}O$-O_2) and modelled data ($O_2$and $\delta^{18}O$-O_2)$^{.}$

Photosynthesis and respiration from bottle incubations - Within two hours of sampling, pond water was gently transferred in the laboratory into a larger container with 12 tube outlets to minimize bubbling. Clear (26) and dark (4) 300ml BOD bottles were filled by placing the tube outlets at the bottom of each bottle and flushing with approximately three times the bottle volume prior to filling. Initial dissolved O_2 concentrations were measured in 4 to 6 clear bottles with a YSI 52 oxygen meter with a self-stirring BOD probe. Given the high algal biomass of the pond the BOD probe was sufficiently sensitive to measure photosynthesis and respiration and was quicker than chemical measurements of O_2 via Winkler titration. A $\delta^{18}O$ sample was also collected from two of these initial clear bottles to calculate the respiration isotopic fractionation factor. Clear bottles were placed in a water tank incubator equipped with a Phillips MH1000 (1000 W) metal-halide lamp that provided seven irradiance levels ranging from 28.2 to 339.6 μmol/m^2/s, and a compressor to adjust the temperature. The photosynthetic available radiation (PAR) at each irradiance was measured at several points near replicate bottles with a Li- 250A light meter with a LI-193SA spherical underwater quantum sensor. Bottles were incubated at ±

2°C of the *in situ* temperature for 3.5 to 4 hours. For respiration measurements, two dark bottles were incubated over this time frame and two others were incubated for a longer period of time (24 to 49.5 hours). At the end of each incubation, the dissolved O_2 concentration was measured in each bottle and a $\delta^{18}O$ sample was obtained from dark bottles to estimate α_R (Appendix I).

The hourly net primary production (HNP) and hourly community respiration (HR) was calculated from the changes in dissolved oxygen concentration in clear and dark bottles during the incubation (Appendix K). Daily volumetric (DVR) and areal (DAR) respiration rates were calculated assuming that respiration rates measured from water sampled in the morning were representative of the entire diel period. Equal dark and light respiration was assumed and hourly volumetric gross primary production (HVGP) was calculated as NHP + HR.

The HVGP vs. PAR curves were then used to calculate photosynthetic parameters using the Fee computer program (Fee 1998, PSPARMS Version 4.0). The chlorophyll-dependent rate of photosynthesis at optimal PAR ($P^B{}_m$, mg O_2 mg Chl^{-1} h^{-1}), the chlorophyll dependent slope of the photosynthesis versus PAR curve at low irradiance levels (α^B, mg O_2 mg Chl^{-1} E^{-1} m^2) and the saturation PAR (I_k, μmol m^{-2} h^{-1}) were calculated on all dates (Appendix L). To estimate the amount of photosynthesis from April 29 to July 5, 2010, the computer program YTOTAL was used with measured daily PAR (Version 4.0, Fee, 1998). This program uses chlorophyll concentrations, $P^B{}_m$ and α^B (all linearly interpolated from the inputted data) and the fraction of solar PAR that reaches each depth to calculate the photosynthesis versus depth profiles. Finally, daily volumetric gross planktonic photosynthesis rates (DVGP) were calculated from bottle incubation measurements and PAR data using the computer program YTOTAL (Version 4.0, Fee

1998). Daily areal gross photosynthesis rates (DAGP) were calculated by multiplying DVGP by the epilimnion depth (z_{mix}) which was the same as pond depth in most cases. Oxygen units were transformed into carbon units for comparison with the literature using a photosynthetic quotient (PQ) of 1 (mole O_2 per mole C produced or respired).

Results

***Pond physical and chemical characteristics* -** Dissolved concentrations of RP in the pond were close to detection (2 µg/L) on all three dates with the exception of the May experiment (Table 4.1). Pond total phosphorus (TP) concentrations were highest in May (0.119 mg/L). Outlet concentrations usually exceeded inlet concentrations for both fractions but was similar to the within pond concentrations on all dates. Within pond dissolved inorganic nitrogen concentrations, in contrast to RP, were largely above the detection limit except in May. Nitrate (NO_3^-) declined from inlet to outlet on all three dates whereas TKN increased from inlet to outlet and NH_4^+ showed a more variable change (Appendix M).

Particulate organic carbon (POC), particulate organic nitrogen (PON) and particulate organic phosphorus (POP) were highest during the May experiment (by about 10 fold), as was the case for algal biomass estimated from Chl *a* concentrations (Table 4.2). In April and July, POC decreased over the course of the experiment whereas a large increase was observed in May. The mass PON: POP ratios ranged from a low of 5 to a high of 19. Total inorganic carbon did not vary much during the diel experiments. .

Diel variations of in situ measurements**-** On all three dates, temperature usually increased from dawn to late afternoon and then decreased through the night. The overall temperature variation was highest in May with a difference of 4.38ºC (Table 4.1). No specific diel trends were observed with respect to specific conductivity (SPC) and oxidation reduction potential (ORP) (Table 4.1). pH increased throughout the day and decreased at night and the change was very similar to the O_2 diel pattern (Figure 4.2).

On all dates, a significant O_2 diel cycle was observed with photosynthetically produced oxygen raising oxygen concentration during the day and respiration lowering it at night (Figure 4.3). Pond O_2 was mostly supersaturated relative to atmospheric saturation (> 100% saturation) with the highest O_2 occurring around 3PM in late spring (Figure 4.3, upper panel). In fact, O_2 was only undersaturated for a few hours on a couple of occasions (after midnight and in early morning in May and July). The smallest O_2 variation was observed in April and the largest in May when O_2 saturation reached almost 200% by early mid-afternoon.

$\delta^{18}O$-O_2 trends **–** The $\delta^{18}O$-O_2 also exhibited a diel cycle (Figure 4.3), with photosynthetically produced oxygen lowering the $\delta^{18}O$-O_2 values during the day and respiration raising them at night. $\delta^{18}O$-O_2 values for all three dates were below the air-water equilibrium value during the day (+24.2‰) (Fig. 4.3). As with O_2 fluctuations, ranges in $\delta^{18}O$-O_2 values were largest in May (difference of 13.65%) followed by July (difference of 11.91%) and smallest in April (difference of 4.66%). Maximum $\delta^{18}O$-O_2 values occurred in July at around 6AM and minimum values in May before sunset.

It is noteworthy that O_2 and $\delta^{18}O\text{-}O_2$ were highly correlated on April 29 ($r^2 = 0.81$, $p < 0.001$) (Figure 4.3) with lowest $\delta^{18}O\text{-}O_2$ values corresponding to the highest O_2 saturation values. However, although this negative relationship was also significant on May 28 and July 05 ($p < 0.01$), O_2 saturation did not explain as much of the variation in $\delta^{18}O\text{-}O_2$ ($r^2 = 0.40$ and 0.43 respectively for May and July).

Photosynthesis–respiration–gas exchange (PoRGy) model results- The PoRGy model generated the highest maximum areal photosynthetic rates (P_{max}) for May followed by July and April (Table 4.3). On the other hand, the nominal community respiration rate at 20ºC (R_{20}) that generated the best-fit was highest in April with 565 mg $O_2/m^2/h$ (5085 mg $C/m^2/day$) and was lowest on the two other dates at 331 and 268 mg $O_2/m^2/h$ (2979 and 2412 mg $C/m^2/day$) (Table 4.3). α_R followed the opposite trend with lower fractionation values in early spring and higher ones later on in the summer.

PoRGy was run by using a range of *k* values that were calculated using common empirical models for various wind speeds (Appendix J). In order to find the best-fit, the model chose a *k* value at the lowest limit of the constraint ($k = 0.001$) for April whereas this was not the case for the other two dates ($k = 0.117$ and 0.137).

The isotopic respiration fractionation factors (α_R) were also calculated with the bottle incubations and were within previously published ranges for O_2 isotopic fractionation (Kiddon *et al.,* 1993; Quay *et al.,*1995) for all dates (0.972±0.018 (n=2), 0.993 ±0.009 (n=2) and 0.990 ±0.006 (n=3) respectively) (Appendix I) and were not significantly different among the dates ($p > 0.05$).

In general, the PoRGy model was able to reproduce the diel fluctuations of both $\delta^{18}O$-O_2 and O_2 field data and was able to describe most of the variability (Figures 4.4 - 4.6). This was reflected in the r^2 values for all 3 dates (r^2>0.5) (Table 4.4). In July, however, the O_2 data seemed to be noisier than the $\delta^{18}O$-O_2 data in that the changes through time were not as smooth (Table 4.4); the July cross-plot indicated that not all the field data were encompassed by the model output (Figure 4.6, lower panel).

The PoRGy model indicated that daily aerial gross primary production (DAGP) was highest in May followed by July and April (Table 4.4). In contrast, daily aerial respiration (DAR) was fairly similar between dates. DAGP was much lower in April resulting in a lower GP:R. GP:R was almost constant between May and July. The computed gross gas exchange (G) obtained with the model was considerably lower in April relative to May and July resulting in a higher GP:R:G on that day. This was the result of choosing an unusually low *k*. However, even though a low *k* was used in April, the $\delta^{18}O$-O_2 *vs.* O_2 cross plots do show that the range of data was adequately covered by the model output on that day (Figure 4.4).

***Bottle incubations compared to PoRGy* -** Phytoplankton DAGP and DAR was highest in April followed by May and July (Table 4.4). This was not the trend observed for the whole ecosystem DAGP calculated with PoRGy. Bottle based DAGP were about 2 to 5 times lower than whole ecosystem DAGP and bottled based DAR values were about 5 to 9 times lower than whole ecosystem DAR.

Overall bottle incubation derived GP:R was almost 1.5 to 3 fold higher than the PoRGy derived GP:R (Table 4.4). The bottle incubation points towards a predominantly autotrophic (GP:R > 1) ecosystem metabolic balance on all dates whereas the PoRGy model method points to a predominately heterotrophic system in April (GP:R<1) suggesting a greater influence of DAR on that day than on the other summer days. It is important to note that macrophytes dominated by *Myriophyllum spicatum* developed in May and July. In April, although macrophytes were not seen at the pond surface due to high water levels, their presence was noted as they were brought up when the boat anchor was pulled up.

Discussion

Diel variations in O_2 and $\delta^{18}O$- O_2- Dissolved O_2 was predominantly supersaturated (>100% saturation) and $\delta^{18}O$- O_2 values were below +24.2% (the air-equilibrium value) on all three dates indicating high primary production in this urban pond (Figure 4.3). As expected, the lowest $\delta^{18}O$-O_2 values corresponded to the highest O_2 saturation values revealing a sensitive isotopic response to diel changes in photosynthesis and respiration. Diel fluctuations in O_2 and $\delta^{18}O$-O_2 values were observed on all dates (Figure 4.3): the smallest fluctuations arose in April when pond temperatures were lowest whereas the largest fluctuations arose in May when both temperature and total nutrient concentrations were highest, probably due to high inputs of nutrients from the spring.

O_2 saturation vs. $\delta^{18}O$- O_2 plots can graphically illustrate the overall ecosystem metabolism. The more productive a system becomes (k being equal), the larger the diel variation becomes and the further the data lies to the lower left of the cross plot (Figure 4.3)

(Venkiteswaran *et al.,* 2008). When comparing this relationship between the three dates, the April cluster of data is displaced towards the upper right of the cross-plot towards air-saturation conditions suggesting a larger influence of respiration. Whereas in May, the cross-plot of Figure 4.3 clearly shows a greater influence of primary production on the system.

PoRGy model fit - In general, the PoRGy dissolved oxygen isotope model (Venkiteswaran *et al.,* 2007) was able to successfully track the field dissolved O_2 and $\delta^{18}O$- O_2 data (Table 4.4). However, in April, the model fit was lower for the $\delta^{18}O$- O_2 data (r^2=0.49) and in July lower for the O_2 data (r^2=0.50) suggesting that there may be additional factors at play. PoRGy uses average daily values of variables entered in the model (Pmax, R_{20}, k, and α_R) for the entire diel period. If these variables are not constant over 24 h, or changes occurred in the hydrological mixing, then the PoRGy model fits may deviate from observed data (Wassenaar *et al.,* 2010).

In fact, the PoRGy model assumes a constant rate of gas transfer velocity coefficient (k) over the diel cycle and this assumption may be invalid at shallow and wind exposed sites such as this pond. The k value determined by the model that gave the best fit in April and that was used to compute the gas exchange rate was the lowest of the probable range in k (Appendix J). As wind speed was variable in April, using a low k could have had an effect on the model fit of $\delta^{18}O$- O_2 (Venkiteswaran *et al.,* 2008). However, although the fit of the model of $\delta^{18}O$- O_2 and O_2 data were lower on some dates, the $\delta^{18}O$-O_2 vs. O_2 cross plots do show that the range of data is covered by the model output on all days (Figure 4.4 - 4.6).

Whole ecosystem metabolism - Metabolic rates at Stonebridge pond were on average higher than other previously published data for different aquatic systems using the PoRGy Model method (Table 4.5). Respiration and gross production rates were of the same order of magnitude as those measured in the South Saskatchewan River but three to four times higher than rates observed in a wetland system. The highest daily areal gross primary production (DAGP) was measured in May (Table 4.4. in oxygen units and equivalent to 3.8 g C/m^2/day). On this date, the DAGP exceeded the whole system respiration rates and this was also the case in July. In contrast, while April oxygen saturation values (>100%) and ^{18}O-O_2 values (< 24.2‰) pointed towards an autotropic system, daily aerial respiration was the highest amongst the three dates and DAGP was the lowest resulting in a GP:R significantly below one. Pond heterotrophy with high oxygen concentrations in April might have occurred because temperature warming tends to occur faster than oxygen degasing in the spring, creating highly oxic conditions even in a respiration dominated system. The high April respiration rates might have resulted from increased inputs of organic matter from the drainage basin after snow melt or more rapid decomposition (relative to the winter condition) of macrophyte biomass produced in the previous year, although the dissolved organic carbon concentrations were actually quite low (Table 4.1).

The whole ecosystem metabolism calculations suggest that Stonebridge pond may be a sink for carbon during the summer whereas in spring (and likely winter) it may be a source of CO_2. Although most lakes are considered sources of CO_2 to the atmosphere (Duarte and Prairie, 2005; Pace and Prairie, 2005; Rantakari and Kortelainen 2005; Sobek *et al.,* 2005), a recent study of eutrophic ponds, in Iowa suggests that those systems may be sinks when based on measurements of the partial pressure of CO_2 in surface waters (Balmer and Downing, 2011).

Stonebridge is also clearly eutrophic if not hypereutrophic based on the independent measures of total nutrients and algal biomass (Chl *a*).

Using the GP:R:G ratios instead of the conventional GP:R ratio helps describe the vulnerability of an aquatic ecosystem to external stressors as it fully takes into consideration how much re-aeration occurs to attenuate the potential extremes caused by enhanced aquatic metabolism. In Stonebridge, GP:R:G ratios followed the same trend as GP:R in that the former ratios were lowest in April and highest in May (29.19:25.74:1 vs. 34.61:58.07:1) (Table 4.4) revealing that aquatic metabolism was a more important driver of O_2 dynamics than re-aeration in May. However, in July, the importance of gas exchange was more obvious as this ratio dropped to 1.15:0.90:1 reflecting higher wind speeds.

The contribution of plankton to whole ecosystem metabolism – Planktonic DAGP and DAR rates measured with the bottle incubation method were much lower than whole ecosystems rates computed with the PoRGy model (Table 4.4). Given the presence of significant macrophyte beds in the pond this was anticipated. Macrophytes, although not directly measured, covered much of the pond bottom. Interestingly, the highest rates of DAGP and DAR for the plankton were actually measured in April, when the planktonic algal biomass (Chl *a*) was also the highest. Across the three dates, the planktonic GP:R ratios were consistently well above 1 (1.75-2.36) and pointed to net autotrophy in the open water.

The bottle incubations reflected phytoplankton and bacterioplankton metabolism only, whereas the PoRGy method includes the total activity of all primary producers in the system (e.g. macrophytes, attached algae, phytoplankton) and all sources of respiration. In particular, sediments are often the most important source of respiration in aquatic systems with high organic matter content (e.g. Jonsson *et al.,* 2003). Given the shallow nature of urban ponds, sediment respiration is likely a significant source of respiration.

By comparing the two methods, it is possible to calculate the importance of the planktonic community to whole system metabolism or vice versa, the contribution of attached plants (macrophytes and periphyton). In April, planktonic primary production contributed to approximately half of the whole ecosystem primary production (55%). Later in the summer however, this dropped to 20% probably because of higher macrophyte and periphyton biomass and activity. Clearly these communities are also very important to carbon cycling. The contribution of the plankton to respiration was actually lower at 19% in April and dropped further to only 11% of the whole ecosystem respiration in July. In the summer months, most of the respiration (89%) must have come then from the benthic community and/or the sediments.

Both the whole ecosystem and planktonic measurements of diel changes in oxygen suggest that this urban pond might be a sink rather than a source of carbon in the summer, when very high rates of primary production resulting largely from the activity of attached plants can arise. However, it is likely to be primarily a source of CO_2 to the atmosphere in the spring and winter months. Whether such ponds, on an annual basis and on a longer time scale, can be effective sinks for carbon or other macronutrients remains to be determined.

Tables

Table 4.1 Diurnal variation in nutrient concentrations (µg/L) and other parameters at Stonebridge pond on April 29, May 28 and July 05, 2010. Subsurface samples and measurements were taken at the center of the pond. Reactive phosphorus (RP), nitrate (NO^-_3), ammonium (NH^+_4), total phosphorus (TP), total Kjeldahl nitrogen (TKN), dissolved organic carbon (DOC) (mg/L), temperature (ºC), specific conductivity (SPC) (µS/cm) and oxidation reduction potential (ORP) (mV) are presented.

Constituent	29 April	28 May	05 July
TP	30 - 33	86 - 119	35 - 58
RP	2 - 3	6 - 17	2 - 5
NH^+_4	19 - 36	43 - 66	3
NO^-_3	31 - 60	2	41 - 49
TKN	590 - 690	1170 - 1610	770 - 1020
TDP	14 - 15	13 - 16	11 - 15
DOC*	1.99 - 2.67	4.14 - 3.48	6.79 - 6.45
Temp	10.38 -13.02	19.18 - 23.56	20.73 - 22.83
SPC	876 - 895	782 - 1038	689 - 916
ORP	439 - 469	86 - 349	246 - 434

* Units are in mg/L

Table 4.2 Particulate organic nitrogen (PON) (mg N/L), particulate organic carbon (POC) (mg C /L) and particulate organic phosphorus (POP) (mg P/L) as well as chlorophyll *a* (µg/L) at the beginning (t_o) of diurnal experiments at Stonebridge pond on April 29, May 28 and July 05, 2010. Subsurface samples were taken at the center of the pond.

Constituent	29 April	28 May	05 July
PON	0.25	1.61	0.52
POC	3.45	32.63	5.62
POP	0.04	0.23	0.03
Chl *a*	294.56	266.21	173.00

Table 4.3 Photosynthesis–respiration–gas exchange (PoRGy) (Venkiteswaran, 2007) model input parameters. Known variables and input variables such as the oxygen production at light saturation (P_{max}, mg $O_2/m^2/h$), the nominal community respiration rate at 20°C (R_{20}, mg $O_2/m^2/h$), the gas transfer velocity (k) and the community respiration isotopic fractionation factor (α_R) are presented for diel experiments at Stonebridge pond on April 29, May 28 and July 05, 2010.

	Date		
Varables	**April 29**	**May 28**	**July 05**
PoRGy known variable			
Year	2010	2010	2010
Day of the year (Julian day)	119	148	186
Latitude (ºN)*	45.261	45.261	45.261
Longitude (ºW)*	75.719	75.719	75.719
Altitude (m above sea level)	114	114	114
Area (m^2)	21 000	21 000	21 000
Depth (m)	1	1	1
Water T (°C)	10.38 - 13.02	21.18 - 23.56	20.73 - 23.83
$\delta^{18}O$-H_2O (‰ vs. SMOW)	10.61	10.14	8.56
Modelled variables for PORGY model fit			
P_{max}(mg $O_2/m^2/h$)	1668	2496	2209
R_{20} (mg $O_2/m^2/h$)	565	331	268
α_R	0.977	0.995	1
k (m/h)	0.001	0.117	0.137

SMOW, standard mean ocean water

*Required as irradiance is modeled

Table 4.4 Photosynthesis–respiration–gas exchange (PoRGy) model and bottle incubation results. Daily aerial gross primary production (DAGP), daily aerial respiration (R), gross gas exchange (G*) and goodness-of-fit r^2 values for dissolved O_2 and $\delta^{18}O$-O_2 obtained with model are presented.

	Date		
Variables	**29 April**	**28 May**	**05 July**
PoRGy			
DAGP (mg O_2/m^2/day)	5542	10056	9156
DAR (mg O_2/m^2/day)	9299	8870	7174
G* (mg O_2/m^2/day)	160	345	7934
GP:R:G	34.61:58.07:1	29.19:25.74:1	1.15:0.90:1
GP:R	0.60:1	1.13:1	1.28:1
R:GP	1.68:1	0.88:1	0.78:1
r^2 (O_2)	0.68	0.62	0.50
r^2 ($\delta^{18}O$-O_2)	0.49	0.69	0.97
Bottle incubation			
DAGP (mg O_2/m^2/day)	3037	2181	1816
DAR (mg O_2/m^2/day)	1739	1249	768
GP:R	1.75:1	1.75:1	2.36:1
R:GP	0.57	0.57:1	0.42:1

Table 4.5 Hourly aerial gross primary production (HAGP), hourly aerial respiration (HAR) and gas exchange (G) measured with the Photosynthesis–respiration–gas exchange (PoRGy) model of different aquatic systems (Venketeswaran *et al.,* 2007) compared to Stonebridge pond.

Metabolic and G rates ($mg/m^2/h$)	FLUDEX Medium C reservoir, Experimental Lakes Area, northwestern Ontario	Wetland 50,St Denis National Wildlife Area	South Saskatchewan River, 50 km downstream from Saskatoon	Stonebridge urban pond
HAGP	131	105	425	**551**
HAR	168	143	382	**352**
G*	14	41	215	**227**

*The sum of influx and efflux rather than their difference

Figures

Figure 4.1 Stonebridge Pond (SWF-1409), City of Ottawa. White arrows indicate the inlet and outlet (red square) of the pond. The red or shows sampling location. Satellite image was obtained from the City of Ottawa and Google Maps Canada in September, 2009.

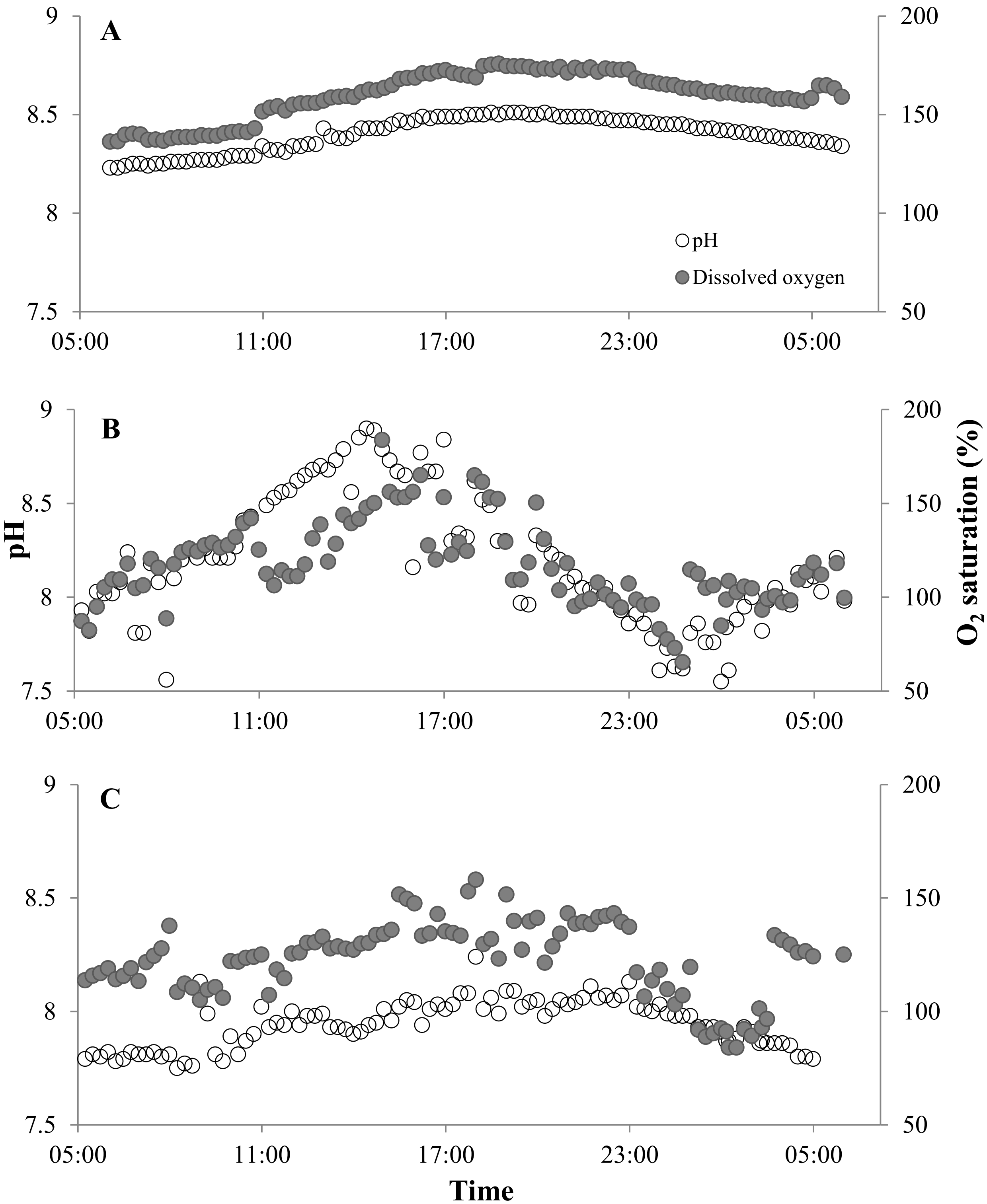

Figure 4.2 Diel O_2 saturation and pH of Stonebridge Pond on A) April 29 B) May 28 and C) July 05 of 2010.

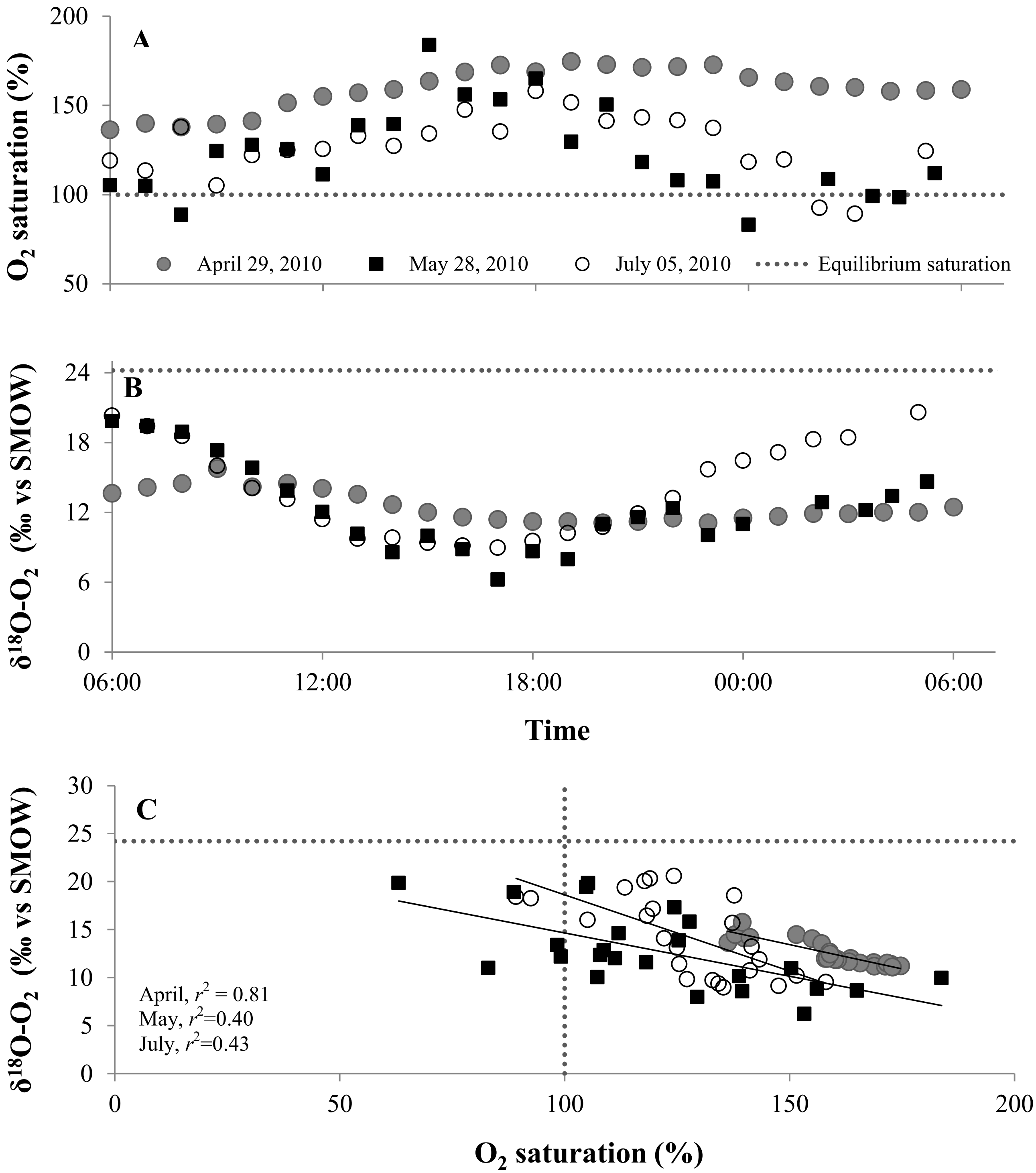

Figure 4.3 Diel change in O_2 saturation and $\delta^{18}O\text{-}O_2$ of Stonebridge Pond on April 29, May 28 and July 05, 2010. The original sampling frequency of O_2 saturation data was reduced to match the hourly $\delta^{18}O\text{-}O_2$ data. Equilibrium air–water saturation is also shown.

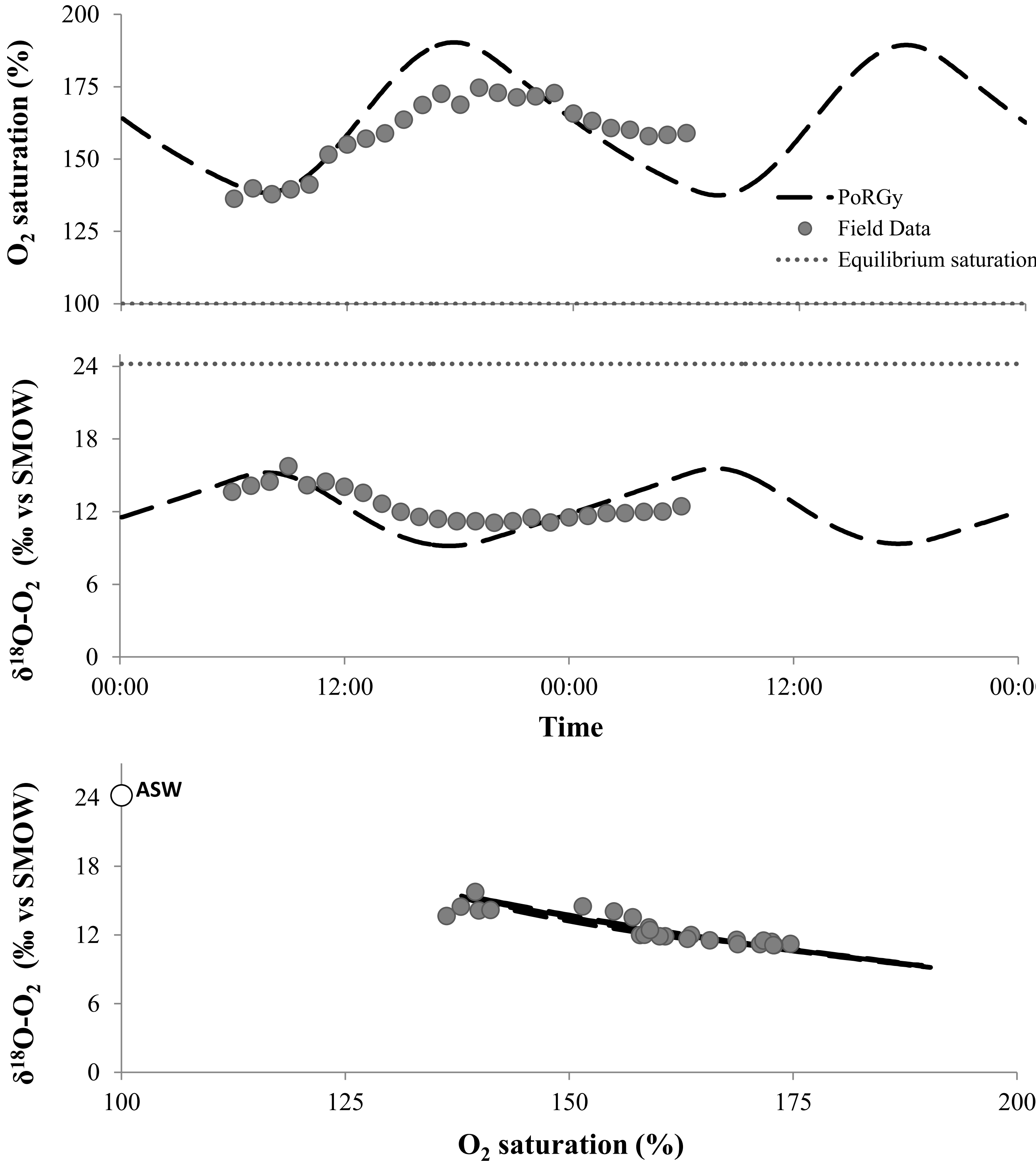

Figure 4.4 Diel field data of O_2 saturation and $\delta^{18}O\text{-}O_2$ and PoRGy model fit of Stonebridge Pond on April 29, 2010. The original frequency of O_2 saturation data was reduced to match the $\delta^{18}O\text{-}O_2$ data. Equilibrium air–water saturation is shown in the temporal plots and air-saturated water (ASW) is shown as an open circle in the cross-plot figure.

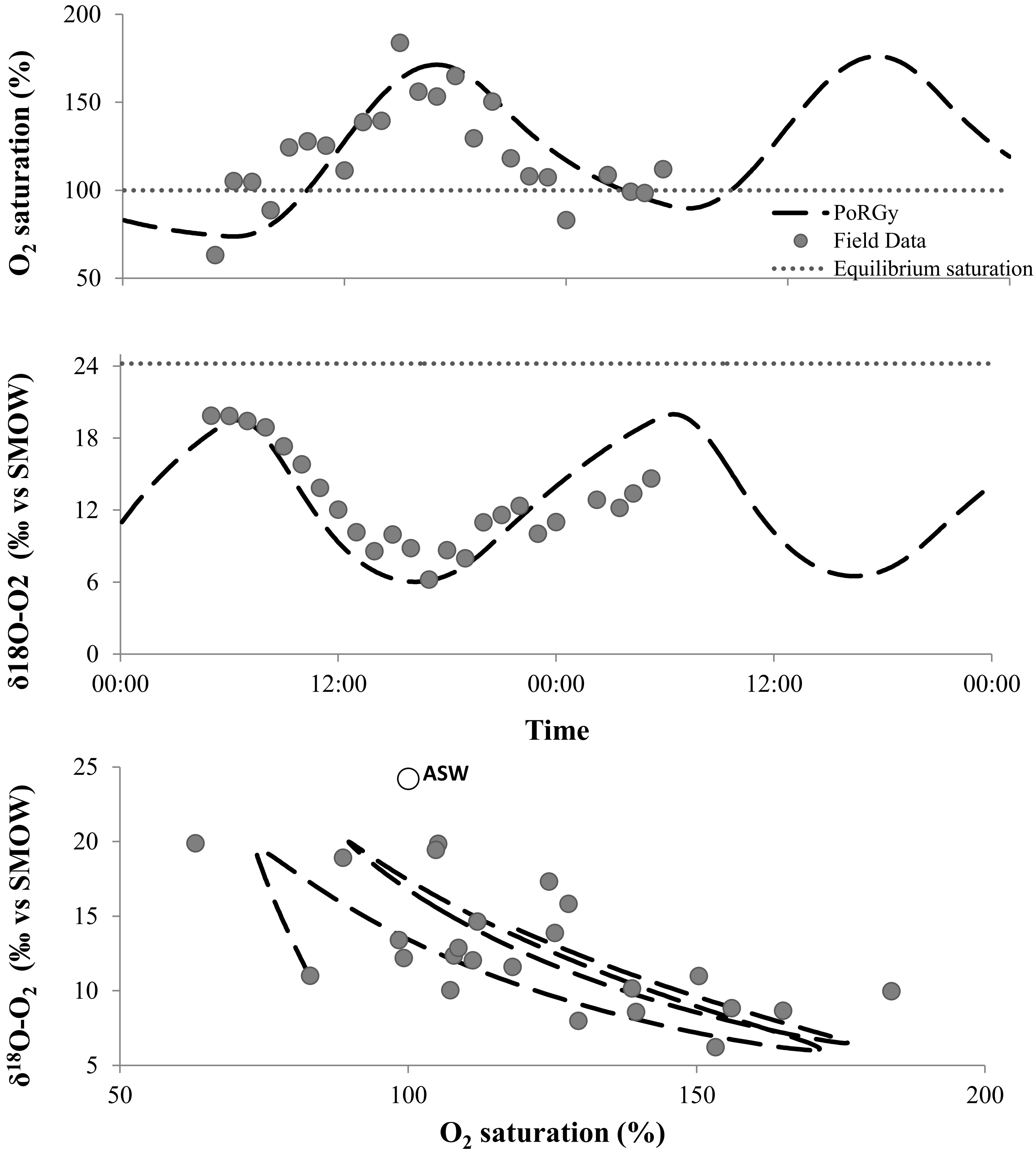

Figure 4.5 Diel field data of O_2 saturation and $\delta^{18}O$-O_2 and PoRGy model fit of Stonebridge Pond on May 28, 2010. The original frequency of O_2 saturation data was reduced to match the $\delta^{18}O$-O_2 data. Equilibrium air–water saturation is shown in the temporal plots and air-saturated water (ASW) is shown as an open circle in the cross-plot figure.

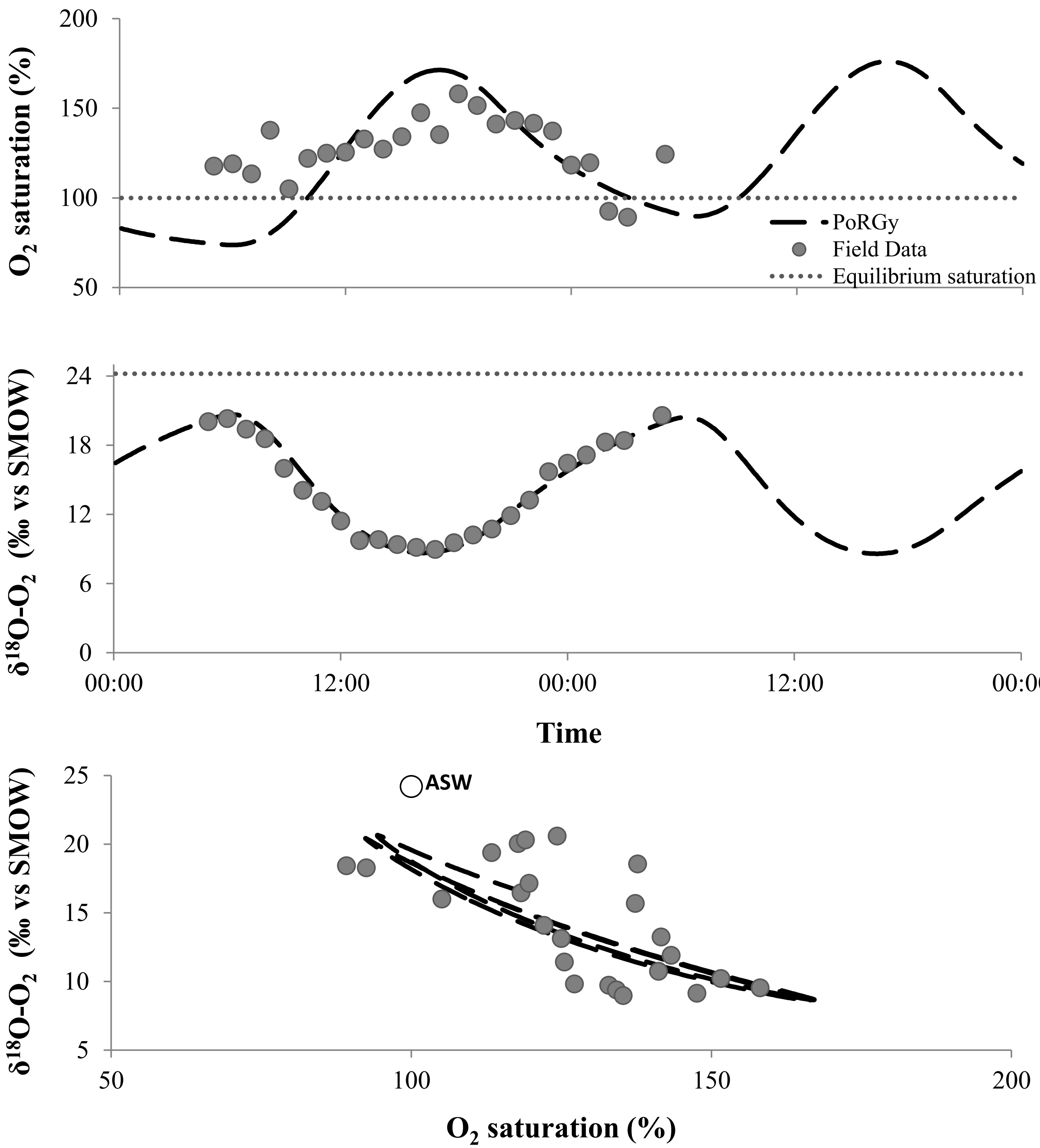

Figure 4.6 Diel field data of O_2 saturation and $\delta^{18}O$-O_2 and PoRGy model fit of Stonebridge Pond on July 05, 2010. The original frequency of O_2 saturation data was reduced to match the $\delta^{18}O$-O_2 data. Equilibrium air–water saturation is shown in the temporal plots and air-saturated water (ASW) is shown as an open circle in the cross-plot figure.

CHAPTER 5. General conclusions

SWPs are used in the City of Ottawa to control the quantity and quality of stormwater discharges to surface waters in residential developments and lightly industrialized areas. More than 94 SWPs were built in the City of Ottawa between 1974 and 2009 (City of Ottawa, personal communication, Jan. 2009). In fact, SWPs are the most common structural beneficial management practices used in Ontario, Canada (OME, 2003). The number of ponds continues to rise as they are considered to be important treatment facilities. However, the Ottawa ponds appear to be discharging high concentrations of phosphorus to downstream aquatic systems.

Outlet nutrient concentrations often exceeded water quality guidelines for the protection of aquatic life in the Ottawa SWP's. The Provincial Water Quality Objectives limit for total phosphorus (TP) is 30 µg/L in surface water because excessive plant and algal growth can occur at concentrations greater than this limit (OME, 1994). In addition, the Canadian Council of Ministers of the Environment (2002) has stated that an increase in 25 mg/L of TSS from background surface water concentrations is unfavourable to stream health. SWM ponds are currently not required to meet these thresholds and might be affecting downstream ecosystems, which should meet these guidelines. Pond performance is graded on percent removal of TP and TSS and not on attaining provincial water quality objectives at the pond the discharge. Future work needs to be done in order to assess the effects of pond discharge on downstream ecosystems.

At a city wide scale, this study showed that algal biomass within the ponds was mainly controlled by total phosphorus. This relationship is well established for lakes (Dillon and Rigler, 1974). However in SWPs, when TP was not included in regressional models, landscape characteristics were shown to predict algal biomass. As impervious cover in the catchment area increases relative to pond size, more nutrients such as TP and TKN are washed into the pond. It remains unclear what is the best range in imperviousness to pond ratio to achieve optimal production that will provide efficient nutrient removal. Further research with respects to impervious cover effects on algal biomass is needed and more ponds should be studied to increase the sample size on which models are based.

At a seasonal scale, within two ponds, plankton primary production rates were typical of eutrophic to hypereutrophic aquatic systems with maximum daily areal rates (6171 and 7618 mg C/m^2/day) approaching the theoretical maximum rates (Melack and Kilham, 1974; Talling, 1982; Lewis, 2011). At the more hydraulically dynamic pond, Stonebridge, water residence time (WRT) had a significant effect on planktonic primary production while in the pond with longer water residence, Strandherd, light availability and temperature turned out to be the main driving variables. Strandherd also had higher respiration rates and more lake like features such as pond thermal stratification and low dissolved O_2 at the bottom. However, nutrient concentrations were similar between the two ponds and with similar differences between inlet and outlet concentrations. OMOE (2003) guidelines suggest a detention time of 24 hours for SWPs to provide adequate time for TSS settling. Further work should examine the removal efficiently of ponds in relation to WRT and internal biological processes such as primary production.

This research also showed that planktonic primary production exceeded respiration not only on a seasonal basis within two ponds, but also on whole ecosystem basis within one pond during the summer. However, during the spring, whole ecosystem metabolism GP:R was less than one, indicating that the pond was a source of carbon to the atmosphere at that time. Whether the ponds are net sinks or sources of carbon on annual basis remains unclear. If P:R ratios in the winter are low, nutrients might be released from the sediment and exported from the systems. In fact, this has been reported for metals (Fe and Mn) in winter in an Ottawa constructed wetland (Goulet and Pick, 2001). Further research on whole ecosystem metabolism of SWP should be carried out in the winter and spring to determine their metabolic balance on an annual scale. The stable isotope method, although effective, is time consuming and would not be the best approach for municipalities. Measuring changes in dissolved O_2 by leaving an oxygen probe *in situ* has been successful in the past, and would be sufficient for this type of study (Mitsch and Day, 2004).

Diurnal experiments showed that plankton contributed less to overall ecosystem metabolism than the macrophyte and periphyton communities. This illustrates the importance of these communities not only to the carbon cycle but to the phosphorus and nitrogen cycles within the ponds. Ponds with more dominant macrophyte communities contribute to sediment stabilisation but also to processing of nutrients. More recently, improved pond designs (e.g. hybrid ponds) with increased macrophyte cover have been proposed in the Stormwater Management Planning and Design Manual (OMOE, 2003) to meet water quality, flooding and erosion concerns. Hybrid wet pond/wetland systems consist simply of a SWP element and a wetland element, connected in series. The system provides for the deep water component which will be least impacted by winter/spring conditions and the shallower wetland component which provides more macrophyte cover and in consequence, enhanced biological removal during the summer months. While these facilities have the potential to remove pollutants (Oberts and Osgood,1991), research focusing on whole ecosystem metabolism and treatment performance is lacking.

APPENDICES

Appendix A: Particulate matter concentrations in surface waters of ponds.

Table A. Particulate matter concentrations of surface water from 17 Ottawa ponds in June and August, 2009. Total suspended solids (TSS), particulate organic nitrogen (PON), particulate organic carbon (POC) and particulate organic phosphorus (POP) are presented as well as POC:PON, POC:POP and PON:POP.

Particulate matter	n	Mean ± SD	Min	Max
TSS (mg/L)	34	8.87±7.31	0.2	36.8
PON (mg N/L)	32	0.47±0.42	0.04	1.76
POC (mg C/L)	34	2.36±1.82	0.46	9.96
POP (mg P/L)	34	0.05±0.04	0.01	0.17
POC:PON (by mol)	32	7.5±2.2	4	14.3
POC:POP (by mol)	34	200.6±286	20.9	1423.1
PON:POP (by mol)	32	36.4±66	3.1	339.1

Appendix B: Nutrient concentrations at pond outlets

Table B. Nutrient concentrations at the outlet of 17 ponds in June and August, 2009.

Nutrient	n	Mean ± SD	Min	Max
NH_4^+ (µg/L)	34	43.8±43.0	3	188
NO_3^- (µg/L)	34	364±664	20	2711
Total Nitrogen (TN)	34	1303±600	485	3171
Total Kjeldahl nitrogen (µg/L)	34	839±282	430	1610
Reactive Phosphorus (µg/L)	34	9.18±6.79	2	29
Total Phosphorus (TP) (µg/L)	34	57.4±39.9	14	203
TN:TP	34	35.48±33.72	7.931	132.121
Dissolved organic carbon (mg/L)	25	4.92±1.04	3.14	9.57

Appendix C: $\delta^{18}O$ analysis

Water samples for isotopic composition of oxygen in water, $\delta^{18}O$-H_2O, and isotopic composition of dissolved oxygen, $\delta^{18}O$-O_2 were collected from the surface waters of the ponds, during mid-morning along with the *in situ* measurements of dissolved oxygen in order to provide an index of photosynthetic activity throughout the season. These were collected from the subsurface grab sample using a syringe. The water was then injected into sterilized 30 mL Exetainer® vials making certain no air bubbles were formed. All $\delta^{18}O$ samples ($\delta^{18}O$-H_2O and $\delta^{18}O$-O_2) were preserved with $HgCl_2$ to approximately 150 ppm and refrigerated at 4°C before analysis (within 3 months) at the G.G. Hatch Isotope Laboratory (University of Ottawa).

To measure the isotopic composition of oxygen in water, samples were reacted with a few milliliters of copper and charcoal for 24 hours prior to analysis. Then 0.2 ml of sample was flushed with a gas mixture of 2% CO_2 in helium. The CO_2 was extracted and cleaned for analysis on a Finnigan MAT Delta plus XP + Gasbench with a routine analytical precision of ± 0.1%.

To measure the isotopic composition of dissolved oxygen, a helium headspace was created and a subsequent isotope analysis of the extracted $O_{2(g)}$ was achieved using an isotope ratio mass spectrometer (Barth *al*., 2004) . The routine analytical precision for isotopic composition of dissolved oxygen analysis was of ±0.2‰.

The $^{18}O/^{16}O$ isotope ratios in water and the dissolved oxygen are by convention expressed in ‰ with :

$$\delta^{18}O = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O\ /^{16}O)_{VSMOW}} - 1\right) X1000$$

where VSMOW is the international Vienna Standard Mean Ocean Water.

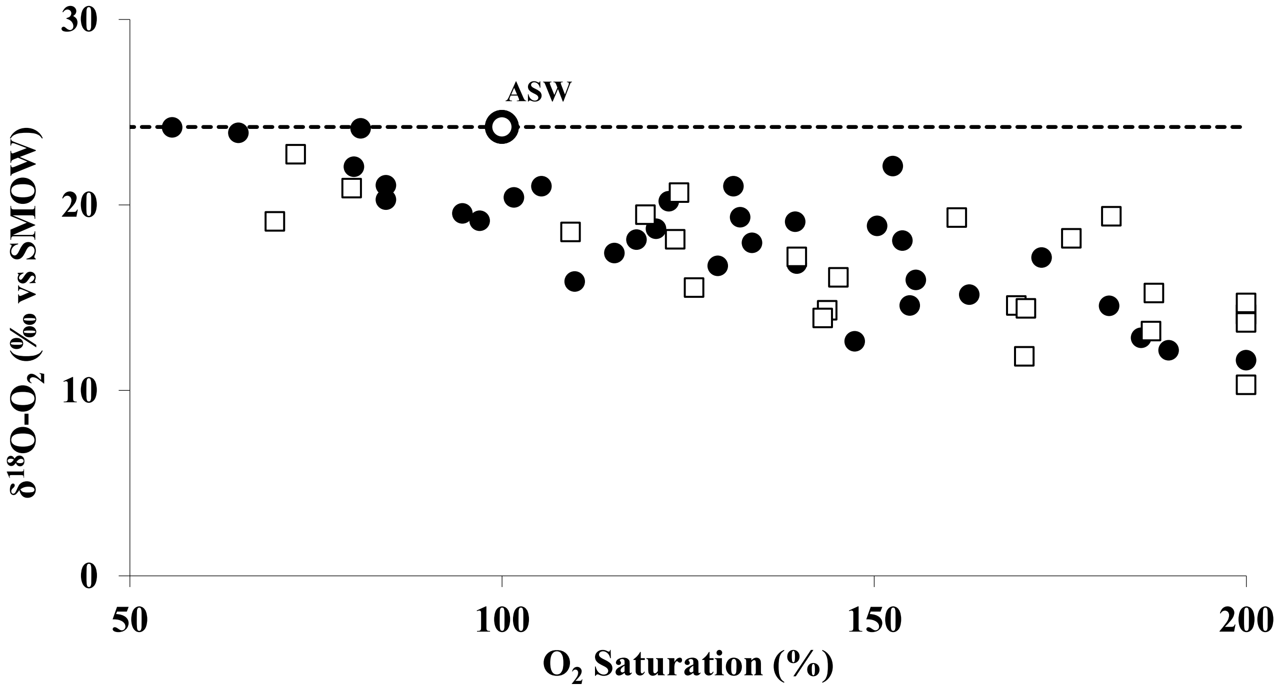

Figure C. Relationship between δ^{18}O-O_2 and O_2 saturation of Stonebridge and Strandherd Pond. Variables were significantly correlated ($p \leq 0.001$) for both Stonebridge (•) ($r^2 = 0.67$) and Strandherd (□) ponds ($r^2 = 0.52$). The dashed line represents the equilibrium air–water saturation. The air-saturated water (ASW) is represented by an open circle.

Appendix D – Fee computer program PSPARMS results and examples of PP vs. I curves

Table D. Range in Fee computer program PSPARMS results of Stonebridge and Strandherd pond. The chlorophyll-dependent rate of photosynthesis at optimal PAR ($P^B{}_m$, mg C mg Chl^{-1} h^{-1}) and the chlorophyll dependent slope of the photosynthesis versus PAR curve at low irradiance levels (α^B, mg C mg Chl^{-1} E^{-1} m^2) are presented.

Pond	α^B (mg C mg $Chl^{-1}E^{-1}m^2$)	$P^B{}_m$ (mg C mg Chl^{-1} hr^{-1})
Stonebridge	0.92 - 21.92	0.54 - 20.02
Strandherd	0.36 - 18.01	0.09 - 11.03

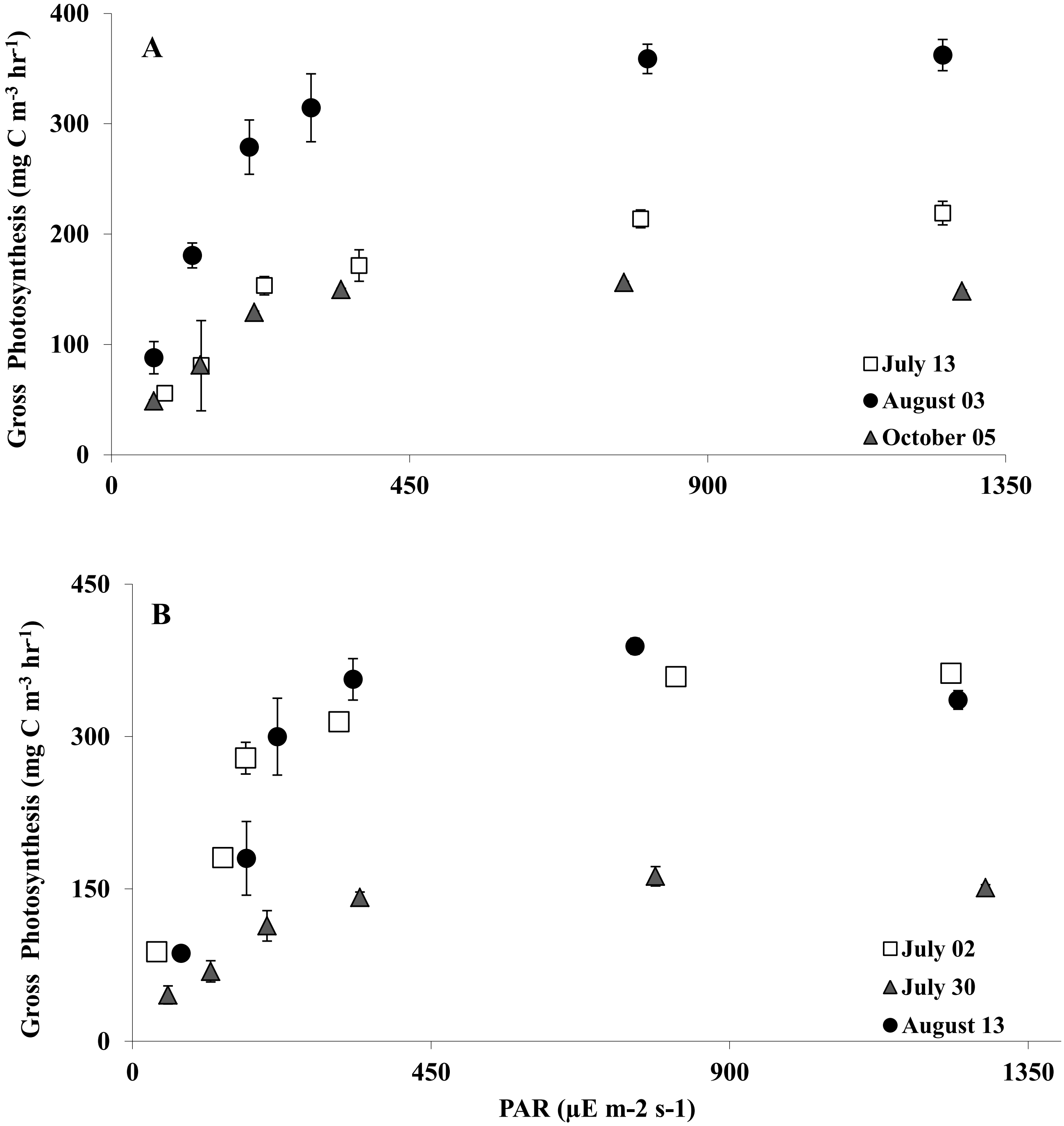

Figure D. Examples of gross photosynthesis vs. PAR relationships of A) Stonebridge pond and B) Strandherd pond.

Appendix E: Pearson cross-correlation between independent variables of Stonebridge and Strandherd ponds.

Table E.1 Pearson cross-correlations of independent variables (n= 14 - 17) of Stonebridge Pond, from June to October 2009. Independent variables presented are Chlorophyll a (Chl $a_{(s)}$), total phosphorus ($TP_{(7)}$), reactive phosphorus ($RP_{(7)}$), nitrate ($NO_3^-{}_{(7)}$), ammonium ($NH_{4(7)}$), specific conductivity ($SPC_{(7)}$), temperature ($Temp._{(s)}$), Day light hours$_{(s)}$, Turbidity$_{(s)}$, Pond depth$_{(s)}$ and mean water residence time over 7 days ($WRT_{(7)}$). Significant correlation are indicated by: * $p \leq 0.05$, ** $p \leq 0.01$ and *** $p \leq 0.001$.

	$TP_{(7)}$	$RP_{(7)}$	Log $NO_3^-{}_{(7)}$	Log $NH_{4(7)}$	$SPC_{(7)}$	$Temp._{(s)}$	Day light hours$_{(s)}$	Log Turbidity$_{(s)}$	Pond depth$_{(s)}$	Log $WRT_{(7)}$
Log Chl $a_{(s)}$	-0.20	-0.14	-0.22	-0.11	-0.30	0.20	0.07	0.17	0.59*	-0.52
$TP_{(7)}$		0.82***	0.56***	-0.08	-0.17	-0.30	-0.32	0.03	-0.21	-0.49
$RP_{(7)}$			0.42*	0.22	-0.59***	0.03	0.18	0.07	0.28	-0.28
Log $NO_3^-{}_{(7)}$				-0.03	-0.28	-0.09	-0.01	-0.05	-0.16	-0.68**
Log $NH_{4(7)}$					-0.08	-0.35	-0.15	0.36	-0.26	0.34
$SPC_{(7)}$						-0.20	-0.43	-0.05	-0.47*	0.49
$Temp._{(s)}$							0.86***	-0.78***	0.17	-0.32
Day light hours$_{(s)}$								-0.70**	0.01	0.28
Log Turbidity$_{(s)}$									0.15	0.19
Pond depth$_{(s)}$										-0.80***

Table E.2 Pearson cross-correlations of independent variables (n= 11 - 23) of Strandherd Pond, from June to August 2009. Independent variables presented are Chlorophyll a (Chl $a_{(s)}$), total phosphorus ($TP_{(14)}$), reactive phosphorus ($RP_{(14)}$), nitrate ($NO_3^-{}_{(14)}$), ammonium ($NH_{4(14)}$), specific conductivity ($SPC_{(14)}$), temperature ($Temp._{(s)}$), Day light hours$_{(s)}$, Turbidity$_{(s)}$, Pond depth$_{(s)}$ and mean water residence time over 14 days ($WRT_{(14)}$). Significant correlation are indicated by * p ≤ 0.05

	$TP_{(14)}$	$RP_{(14)}$	Log $NO_3^-{}_{(14)}$	Log $NH4_{(14)}$	$SPC_{(14)}$	Temp. $_{(s)}$	Day light hours$_{(s)}$	Log Turbidity$_{(s)}$	Pond depth$_{(s)}$	Log $WRT_{(14)}$
Log Chl $a_{(s)}$	-0.12	-0.42	-0.67*	-0.27	-0.43	0.40	0.67*	0.02	0.11	-0.42
$TP_{(14)}$		0.36	0.43	-0.26	-0.48*	-0.30	-0.25	0.34	-0.10	-0.49
$RP_{(14)}$			0.38	0.39	-0.11	0.17	0.39	0.53	0.43	-0.17
Log $NO_3^-{}_{(14)}$				-0.13	-0.06	-0.32	-0.57	-0.13	-0.25	-0.13
Log $NH_{4(14)}$					-0.04	-0.30	-0.04	-0.26	-0.46	0.15
$SPC_{(14)}$						-0.25	-0.38	-0.40	-0.13	0.58
Temp. $_{(s)}$							0.06	-0.46	-0.10	0.52
Day light hours$_{(s)}$								-0.16	0.01	0.53
Log Tubidity$_{(s)}$									0.16	-0.57
Pond depth$_{(s)}$										-0.26

Appendix F: Other parameters measured at Stonebridge and Strandherd pond.

Table F. Parameters measured at Stonebridge (June to October 2009) and Strandherd (June to August 2009) ponds. The sample size is given by "n". The following parameters are presented: Daily aerial gross primary production (DAGP), respiration, DAGP to respiration ratios (GP:R), total Kjeldahl nitrogen (TKN), dissolved organic carbon (DOC), total dissolved phosphorus, total nitrogen to total phosphorus ratios (N:P), total suspended solids (TSS), particulate organic carbon (POC, particulate organic nitrogen (PON), particulate organic phosphorus (POP), Particulate organic carbon to particulate organic nitrogen ratios (C:N), dissolved oxygen saturation (O_2 sat.), pH, oxidative-reductive potential (ORP), PAR irradiance (PAR), Secchi depth, turbidity (PtCo)and water residence time (WRT_s).

Parameter	n		Mean		Min		Max	
	Stone.	Strand.	Stone.	Strand.	Stone.	Strand.	Stone.	Strand.
DAGP (mg C/m^2/day)	19	12	2581	2728	321	272	6171	7618
Respiration (mg C/m^2/day)	19	12	679	1240	8	121	3079	3282
GP:R	19	12	10.51	3.06	1.21	1.14	97.83	14.22
TKN (µg/L)	32	23	853	835	1130	500	545	1520
DOC (mg/L)	25	10	5.1	5.2	2.7	3.1	7.7	12.1
TDP (µg/L)	18	12	12	15	4	5	47	37
TN:TP	19	12	18.75	32.18	9.47	14.37	31.78	55
TSS (mg/L)	18	11	18	20	6	5	46	80
POC (mg/L)	32	23	2.84	2.75	0.6	0.7	5.1	9.61
PON (mg/L)	32	12	0.4	0.3	0.1	0.1	0.7	0.6
POP (mg/L)	16	12	0.0	0.04	0.0	0.02	0.1	0.08
C:N (by mole)	19	12	9	10	6	7	13	14
C:P (by mole)	19	12	82	79	34	41	199	130
O_2 saturation (%)	19	12	121	147	56	72	200	200
pH	19	12	8.3	8.2	7.7	7.5	9.6	9.2
ORP (mV)	19	12	440	410	313	268	561	532
PAR (µE/m^2/s)	15	7	858	504	430	110	1300	1000
Secchi $depth_{(S)}$ (m)	19	12	0.74	0.89	0.20	0.20	1.08	1.30
$Turbidity_{(S)}$ (NTU)	32	23	8.0	5.9	1.8	0.89	53.4	29.4
$WRT_{(S)}$ (days)	133	82	6.8	14.2	0.6	0.3	26	53

Appendix G: Bottom water vs. surface water chemical parameters at Stonebridge and Strandherd pond.

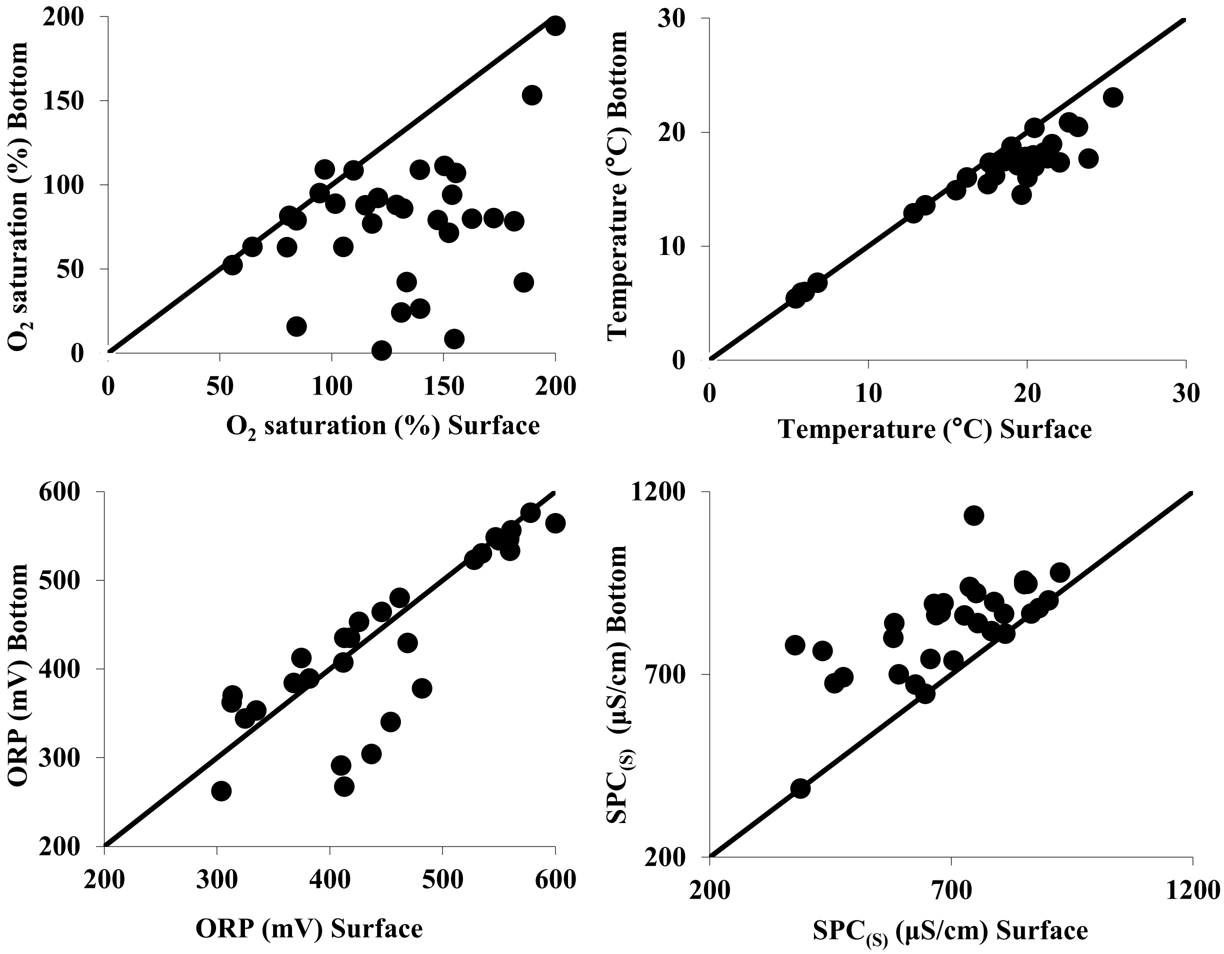

Figure G.1 Bottom vs surface water A) dissolved oxygen (O_2)saturation (DO), B) temperature C) oxidative-reductive potential (ORP), D) specific conductivity ($SPC_{(S)}$)of Stonebridge pond. The solid lines denote 1:1 relationships.

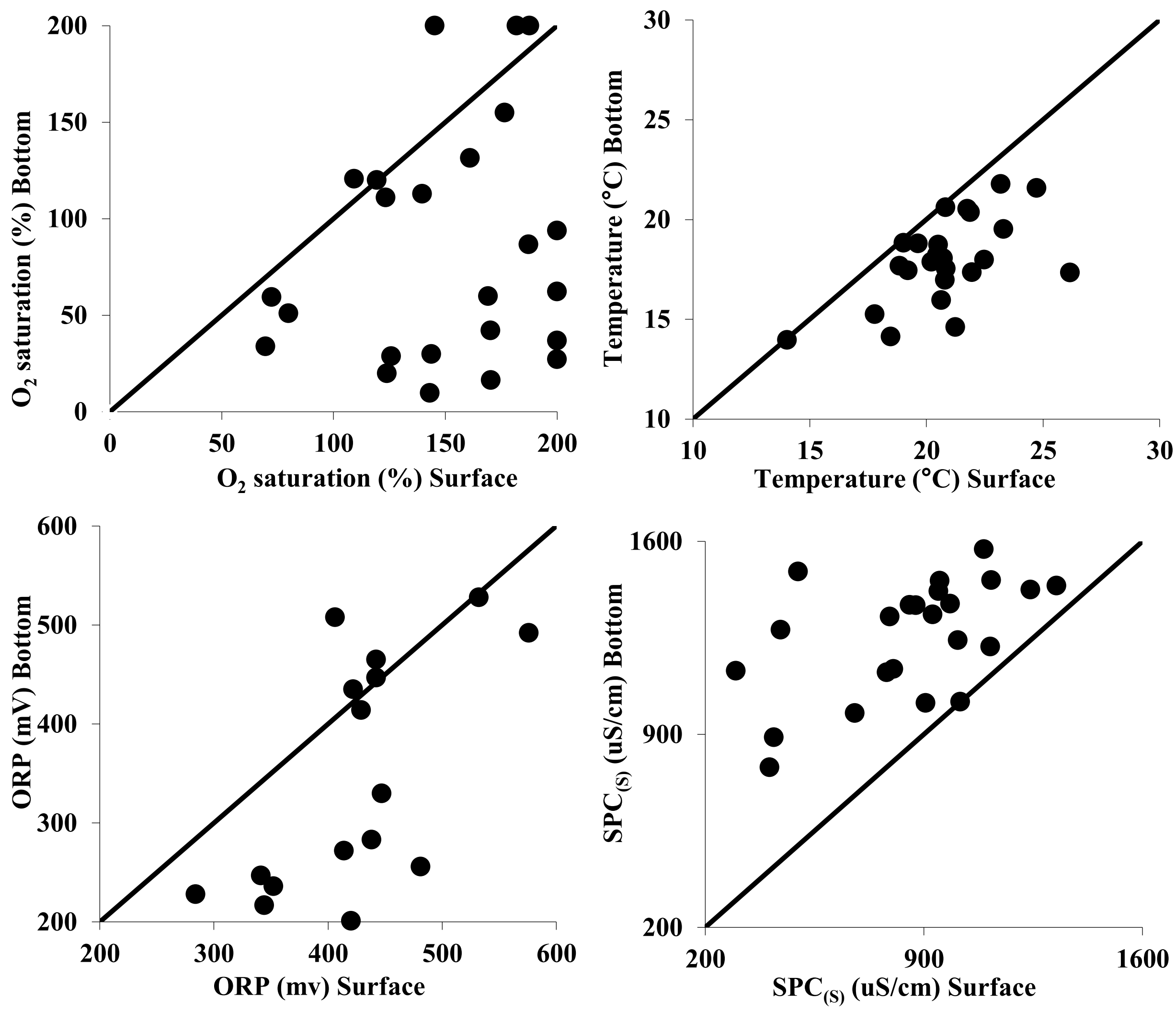

Figure G.2 Bottom vs. surface water A) dissolved oxygen (O_2) saturation, B) temperature C) oxidative-reductive potential (ORP), D) specific conductivity ($SPC_{(S)}$) of Strandherd pond. The solid lines denote 1:1 relationships.

Appendix H – Input Photosynthesis-respiration-gas exchange parameters.

Table H. Input Photosynthesis-respiration-gas exchange (PoRGy) (Venkiteswaran, 2007) parameters. Geographical inputs, measured variables, initial conditions and modelled variables such as the oxygen production at light saturation (P_{max}, mg $O_2/m^2/h$), the nominal community respiration rate at 20°C (R_{20}, mg $O_2/m^2/h$), the gas transfer velocity (*k*) and the community respiration isotopic fractionation factor (α_R) are presented.

Geographical Inputs	Modelled Variables	Measured Variables	Initial conditions
Year	R_{20} (mg $O_2/m^2/h$)	Water temperature (°C)	Dissolved O_2 (mg)
Day of the year (julian day)	α_R	$\delta^{18}O-H_2O$ (‰ vs. SMOW)	$\delta^{18}O-O_2$ (mg)
Latitude (decimal degrees)*	P_{max}(mg $O_2/m^2/h$)		
Longitude (decimal degrees)*	*k* (m/h)		
Altitude (m)			
Aspect*			
Slope *			
Time zone (hours relative to GMT)*			
Daylight savings time (h)*			
Transmissivity*			
Area (m^2)			
Depth (m)			
Salinity (ppt)			

SMOW, standard mean ocean water
PorGy, photosynthesis– respiration–gas exchange (Venkiteswaran *et al.,* 2007)
*Required to model irradiance

Appendix I – Respiration isotopic fractionation factor (α_R)

Respiratory uptake of O_2 substantially enriches the $\delta^{18}O$ pool of the remaining dissolved O_2 (Kiddon *et al.,* 1993). Dark bottle incubation experiments were therefore performed for all 3 diurnal experiments to measure the fractionation effect. The change in dissolved O_2 and $\delta^{18}O$ were consequently measured during 7 dark BOD incubations from the three 24h-diurnal experiments. A value of the isotopic fractionation factor of respiration was determined with the Rayleigh fractionation relationship (Broecker and Oversby 1971; Kiddon *et al.,* 1993; Quay *et al.,* 1995; Wang *et al.,* 2008):

$$\frac{R_t}{R_O} = (O_{2t}/O_{2O})^{(\alpha_R - 1)} \qquad \text{(D.1)}$$

where R is the ^{18}O:^{16}O ratio, *O* and *t* represent initial and at a later time conditions and α_R represents the respiration isotopic fractionation factor.

The α_R calculated (Table I) represents all processes that consumed O_2 in the bottles (phytoplankton respiration, bacteria respiration, methane oxidation, nitrification, Mn oxidation, etc.)

Table I. The changes in O_2 concentration and ^{18}O-O_2 and the respiration isotopic fractionation factor (α_R) during dark bottle incubation experiments on April 29, May 28 and July 05, 2010.

Date	Incubation time (hrs)	$\delta^{18}O_o$	$\delta^{18}O_t$	$(^{18}O:^{16}O)_O$	$(^{18}O:^{16}O)_t$	O_{2o} (mg/L)	O_{2t} (mg/L)	n	Average α_R	
29-Apr-10	3.5	16.01	19.83	0.0020373033	0.0020449631	14.96	11.68	2	0.9719	± 0.018
	48	16.01	24.79	0.0020373033	0.0020549089	14.96	12.13			
28-May-10	4	19.26	25.92	0.0020438202	0.0020571748	10.95	6.65	2	0.9930	±0.009
	70	18.60	18.66	0.0020424967	0.0020426170	10.84	10.09			
05-Jul-10	4	20.56	20.68	0.0020464269	0.0020466675	9.65	9.32	3	0.9899	±0.006
	49.5	20.60	23.75	0.0020465071	0.0020528235	9.53	7.64			
	49.5	20.49	23.71	0.0020462865	0.0020527433	9.79	7.64			

Appendix J – Estimation of gas transfer velocity (*k*).

Several factors must be taken into consideration when calculating reaeration rates (G) (Venkiteswaran 2007). The first factor is the levels of ^{18}O-O_2 saturation that drive ^{16}O:^{16}O or ^{18}O:^{16}O into or out of the system. The second one is the diffusivity of O_2 across the air–water interface, described by the gas transfer velocity, *k*. The third is the level of dissolved O_2 saturation that drive the net flux of O_2 into or out of the system. The final one is the in-situ water temperature because it directly affects all the other factors.

Temperature, dissolved O_2 saturation and $\delta^{18}O$-O_2 were measured. However, *k* must be estimated using common empirical models (Crusius and Wanninkhof 2003). The magnitude of *k* is determined by 1) surface turbulence 2) water viscosity, and 3) solubility of O_2. Temperature (T) and salinity (S) drive water viscosity and solubility as calculated by the Schmidt number (Sc) (Wanninkhof 1992; Holtgrieve *et al.,* 2010).

$$Sc_{O_2}(T) = 1800.6 - 120.10T + 3.7818T^2 - 0.047608T^3 \tag{D.2}$$

The Schmidt number is then adjusted to salinity (Holtgrieve *et al.,* 2010):

$$Sc_{O_2}(T,S) = Sc_{O_2}(T)\ \mathrm{X}\ (1 + \mathrm{S}\ \mathrm{X}\ m) \tag{D.3}$$

where *m* is the linear function of water temperature, $m = 3.286\ \mathrm{X}\ 10^{-5}T + 2.474\ \mathrm{X}\ 10^{-3}$.

To facilitate the estimation of *k*, *k* was adjusted to a Schmidt number (Sc) of 600, where Sc is defined as the kinematic viscosity of water divided by the diffusion coefficient of sulfur hexafluoride (SF6) (Crusius and Wanninkhof 2003). SF6 is inorganic and non-toxic gas that is commonly used as a deliberate tracer in in situ gas exchange experiments. For the normalization of Sc a -2/3 power dependence of Sc was assumed below a wind speed of 3 m s^{-1} (measured at 1 m height) under the assumption that the surface was smooth (Jahne *et al.,* 1987; Crusius and Wanninkhof 2003), and a -1/2 power dependence of Sc was assumed above 3 m s-1 for a surface with waves (Jahne *et al.,* 1984; Crusius and Wanninkhof 2003).

The gas transfer velocity (*k*) can therefore be calculated as follows:

$$k = k_{600}\left(\frac{Sc_{O_2}}{600}\right)^{-0.5\ or-2/3}$$

where K_{600} is the transfer velocity adjusted to Sc = 600. Crusius and Wanninkhof 2003 calculated based on gas transfer in-situ experiments that k_{600} could be estimated by any of the following three relationships between k_{600} and U_{10} (wind speed at 10 m height (in m/s))

Model (1) for $U_{10} < 3.7$ m/s $k_{600} = 0.72U_{10}$ cm/h

for $U_{10} > 3.7$ m/s $k_{600} = 4.33U_{10} - 13.3$ cm/h

Model (2) for winds < or > or above 3.7m/s $k_{600} = 0.228U_{10} + 0.168$ cm/h

Model (3) for $U_{10} < 3.7$ m/s $k_{600} = 1$ cm/h

for $U_{10} > 3.7$ m/s $k_{600} = 514U_{10} - 179$ cm/h

where U_{10}= 1.22 X U_1, U_1 being the speed at 1m.

Using these three empirical models for each diurnal experiment in the summer of 2010, *k* was calculated (Table J.1.; J.2; J.3). The range in *k* obtained by these three relationships where used as the range of input to PoRGy.

Table J.1. Parameters used to calculate the range of gas transfer velocity (*k*) used in PorGy for April 29, 2010. Temperature (T), wind speed at 1m (U_1), wind speed at 10m (U_{10}), the transfer velocity adjusted to Schmidt number (*Sc*) 600 (k_{600}) for models 1, 2 and 3, Sc adjusted to temperature ($Sc_O{}^2$ (T)), Sc adjusted to temperature and salinity ($Sc_O{}^2$ (T,S)), the linear function of water temperature (*m*) and gas transfer velocity (*k*) for model 1, 2 and 3 are presented.

T (°C)	(U_1) (m/s)	(U_{10}) (m/s)	Model 1 for k_{600}	Model 2 for k_{600}	Model 3 for k_{600}	$Sc_O{}^2$(T)	*m*(T)	$Sc_O{}^2$(T, S)	Model 1 for *k* (cm/h)	Model 2 for *k* (cm/h)	Model 3 for *k* (cm/h)	Model 1 for *k* (m/h)	Model 2 for *k* (m/h)	Model 3 for *k* (m/h)
10.63	3.71	4.53	6.298	1.200	5.365	894.084	0.00282	895.245	5.156	0.982	4.392	0.052	0.010	0.044
10.64	3.71	4.53	6.298	1.200	5.365	893.526	0.00282	894.686	5.158	0.983	4.393	0.052	0.010	0.044
10.57	3.71	4.53	6.298	1.200	5.365	897.442	0.00282	898.632	5.147	0.981	4.384	0.051	0.010	0.044
10.56	3.71	4.53	6.298	1.200	5.365	898.004	0.00282	899.194	5.145	0.980	4.382	0.051	0.010	0.044
10.56	3.71	4.53	6.298	1.200	5.365	898.004	0.00282	899.194	5.145	0.980	4.382	0.051	0.010	0.044
10.53	3.71	4.53	6.298	1.200	5.365	899.690	0.00282	900.883	5.140	0.979	4.378	0.051	0.010	0.044
10.43	2.60	3.17	2.284	0.891	1.000	905.342	0.00282	906.541	1.858	0.725	0.814	0.019	0.007	0.008
10.45	3.53	4.31	5.348	1.150	4.236	904.208	0.00282	905.380	4.353	0.936	3.448	0.044	0.009	0.034
10.38	4.27	5.21	9.257	1.356	8.876	908.186	0.00282	909.387	7.519	1.101	7.210	0.075	0.011	0.072
10.38	4.45	5.43	10.208	1.406	10.005	908.186	0.00282	909.362	8.291	1.142	8.127	0.083	0.011	0.081
10.43	4.45	5.43	10.208	1.406	10.005	905.342	0.00282	906.541	8.304	1.144	8.140	0.083	0.011	0.081
10.44	5.01	6.11	13.166	1.562	13.517	904.775	0.00282	905.973	10.714	1.271	11.000	0.107	0.013	0.110
10.46	3.15	3.84	3.340	1.044	1.853	903.642	0.00282	904.839	2.720	0.850	1.509	0.027	0.009	0.015
10.44	3.34	4.07	4.344	1.097	3.044	904.775	0.00282	905.948	3.535	0.893	2.478	0.035	0.009	0.025
10.51	5.20	6.34	14.170	1.614	14.708	900.817	0.00282	901.985	11.557	1.317	11.996	0.116	0.013	0.120
10.53	2.78	3.39	2.442	0.941	1.000	899.690	0.00282	900.858	1.993	0.768	0.816	0.020	0.008	0.008
10.6	1.30	1.59	1.142	0.530	1.000	895.761	0.00282	896.924	0.934	0.433	0.818	0.009	0.004	0.008
10.66	4.08	4.98	8.253	1.303	7.685	892.411	0.00282	893.595	6.763	1.068	6.297	0.068	0.011	0.063
10.71	4.08	4.98	8.253	1.303	7.685	889.631	0.00283	890.813	6.773	1.069	6.307	0.068	0.011	0.063
10.76	4.64	5.66	11.211	1.459	11.197	886.863	0.00283	888.017	9.216	1.199	9.203	0.092	0.012	0.092
10.82	4.64	5.66	11.211	1.459	11.197	883.556	0.00283	884.731	9.233	1.201	9.220	0.092	0.012	0.092
10.91	3.34	4.07	4.344	1.097	3.044	878.626	0.00283	879.796	3.587	0.906	2.514	0.036	0.009	0.025
10.97	4.64	5.66	11.211	1.459	11.197	875.359	0.00283	876.525	9.276	1.207	9.264	0.093	0.012	0.093
11.06	5.01	6.11	13.166	1.562	13.517	870.489	0.00284	871.649	10.923	1.296	11.214	0.109	0.013	0.112
11.12	3.34	4.07	4.344	1.097	3.044	867.261	0.00284	868.394	3.611	0.912	2.531	0.036	0.009	0.025
11.21	5.94	7.25	18.079	1.820	19.349	862.450	0.00284	863.578	15.069	1.517	16.128	0.151	0.015	0.161
11.31	3.15	3.84	3.340	1.044	1.853	857.146	0.00285	858.268	2.793	0.873	1.549	0.028	0.009	0.015
11.43	4.27	5.21	9.257	1.356	8.876	850.838	0.00285	851.954	7.768	1.138	7.449	0.078	0.011	0.074
11.52	4.82	5.88	12.162	1.509	12.325	846.148	0.00285	847.258	10.235	1.270	10.372	0.102	0.013	0.104
11.61	3.90	4.76	7.302	1.253	6.556	841.492	0.00286	842.598	6.162	1.057	5.532	0.062	0.011	0.055
11.72	4.82	5.88	12.162	1.509	12.325	835.849	0.00286	836.948	10.298	1.277	10.436	0.103	0.013	0.104
11.82	3.15	3.84	3.340	1.044	1.853	830.762	0.00286	831.856	2.837	0.887	1.574	0.028	0.009	0.016
11.96	4.27	5.21	9.257	1.356	8.876	823.712	0.00287	824.798	7.895	1.156	7.571	0.079	0.012	0.076
12.04	4.82	5.88	12.162	1.509	12.325	819.720	0.00287	820.802	10.398	1.290	10.538	0.104	0.013	0.105
12.14	4.64	5.66	11.211	1.459	11.197	814.766	0.00287	815.843	9.615	1.251	9.602	0.096	0.013	0.096
12.25	4.82	5.88	12.162	1.509	12.325	809.365	0.00288	810.436	10.465	1.298	10.605	0.105	0.013	0.106
12.37	3.90	4.76	7.302	1.253	6.556	803.529	0.00288	804.594	6.306	1.082	5.662	0.063	0.011	0.057
12.47	3.34	4.07	4.344	1.097	3.044	798.710	0.00288	799.769	3.762	0.950	2.637	0.038	0.010	0.026
12.55	5.20	6.34	14.170	1.614	14.708	794.883	0.00289	795.939	12.302	1.402	12.770	0.123	0.014	0.128
12.62	4.45	5.43	10.208	1.406	10.005	791.556	0.00289	792.608	8.881	1.223	8.705	0.089	0.012	0.087
12.7	4.08	4.98	8.253	1.303	7.685	785.897	0.00289	786.943	7.206	1.138	6.710	0.072	0.011	0.067
12.74	5.57	6.80	16.124	1.717	17.028	783.089	0.00289	784.132	14.104	1.502	14.895	0.141	0.015	0.149
12.8	6.31	7.70	20.033	1.923	21.669	780.759	0.00290	781.800	17.550	1.685	18.983	0.176	0.017	0.190
12.85	6.12	7.47	19.030	1.870	20.477	778.903	0.00290	779.941	16.691	1.640	17.960	0.167	0.016	0.180
12.89	4.27	5.21	9.257	1.356	8.876	776.130	0.00290	777.165	8.133	1.191	7.799	0.081	0.012	0.078
12.95	4.45	5.43	10.208	1.406	10.005	774.748	0.00290	775.782	8.977	1.236	8.799	0.090	0.012	0.088
12.98	4.82	5.88	12.162	1.509	12.325	773.371	0.00290	774.403	10.705	1.328	10.849	0.107	0.013	0.108
13.01	5.57	6.80	16.124	1.717	17.028	773.829	0.00290	774.862	14.189	1.511	14.984	0.142	0.015	0.150
13	3.71	4.53	6.298	1.200	5.365	772.912	0.00290	773.944	5.546	1.057	4.723	0.055	0.011	0.047
13.02	4.82	5.88	12.162	1.509	12.325	772.912	0.00290	773.944	10.709	1.328	10.852	0.107	0.013	0.109
13.02	6.49	7.92	20.984	1.973	22.797	773.829	0.00290	774.862	18.465	1.736	20.061	0.185	0.017	0.201
13	4.08	4.98	8.253	1.303	7.685	774.289	0.00290	775.322	7.260	1.146	6.760	0.073	0.011	0.068
12.99	2.41	2.94	2.117	0.838	1.000	774.748	0.00290	775.782	1.862	0.737	0.879	0.019	0.007	0.009
12.98	3.71	4.53	6.298	1.200	5.365	776.591	0.00290	777.627	5.533	1.054	4.712	0.055	0.011	0.047
12.94	3.53	4.31	5.348	1.150	4.236	776.130	0.00290	777.165	4.699	1.010	3.722	0.047	0.010	0.037

12.95	3.15	3.84	3.340	1.044	1.853	777.977	0.00290	779.014	2.931	0.916	1.626	0.029	0.009	0.016
12.91	0.00	0.00	0.000	0.168	1.000	779.830	0.00290	780.870		0.141	0.839		0.001	0.008
12.87	1.30	1.59	1.142	0.530	1.000	780.295	0.00290	781.334	0.958	0.444	0.839	0.010	0.004	0.008
12.86	1.67	2.04	1.467	0.633	1.000	781.690	0.00290	782.731	1.229	0.530	0.838	0.012	0.005	0.008
12.83	0.74	0.90	0.650	0.374	1.000	783.089	0.00289	784.132	0.544	0.313	0.837	0.005	0.003	0.008
12.8	0.74	0.90	0.650	0.374	1.000	784.959	0.00289	786.004	0.543	0.312	0.835	0.005	0.003	0.008
12.76	0.00	0.00	0.000	0.168	1.000	786.836	0.00289	787.883		0.140	0.834		0.001	0.008
12.72	0.00	0.00	0.000	0.168	1.000	787.777	0.00289	788.825		0.140	0.833		0.001	0.008
12.7	0.00	0.00	0.000	0.168	1.000	790.609	0.00289	791.660		0.140	0.831		0.001	0.008
12.64	0.00	0.00	0.000	0.168	1.000	791.556	0.00289	792.608		0.140	0.831		0.001	0.008
12.62	0.00	0.00	0.000	0.168	1.000	792.505	0.00289	793.558		0.139	0.830		0.001	0.008
12.6	0.00	0.00	0.000	0.168	1.000	795.360	0.00289	796.416		0.139	0.828		0.001	0.008
12.54	0.00	0.00	0.000	0.168	1.000	797.751	0.00288	798.809		0.139	0.826		0.001	0.008
12.49	0.00	0.00	0.000	0.168	1.000	799.190	0.00288	800.250		0.139	0.825		0.001	0.008
12.46	0.00	0.00	0.000	0.168	1.000	800.633	0.00288	801.694		0.138	0.824		0.001	0.008
12.43	0.00	0.00	0.000	0.168	1.000	802.079	0.00288	803.142		0.138	0.823		0.001	0.008
12.4	0.00	0.00	0.000	0.168	1.000	804.013	0.00288	805.078		0.138	0.822		0.001	0.008
12.36	0.00	0.00	0.000	0.168	1.000	805.468	0.00288	806.535		0.138	0.821		0.001	0.008
12.33	0.00	0.00	0.000	0.168	1.000	806.440	0.00288	807.508		0.138	0.820		0.001	0.008
12.31	0.00	0.00	0.000	0.168	1.000	807.413	0.00288	808.482		0.138	0.820		0.001	0.008
12.29	0.00	0.00	0.000	0.168	1.000	807.413	0.00288	808.482		0.138	0.820		0.001	0.008
12.29	0.00	0.00	0.000	0.168	1.000	811.814	0.00287	812.888		0.137	0.817		0.001	0.008
12.2	0.00	0.00	0.000	0.168	1.000	811.814	0.00287	812.888		0.137	0.817		0.001	0.008
12.2	0.00	0.00	0.000	0.168	1.000	813.781	0.00287	814.856		0.137	0.815		0.001	0.008
12.16	0.00	0.00	0.000	0.168	1.000	815.754	0.00287	816.832		0.137	0.814		0.001	0.008
12.12	0.19	0.23	0.167	0.221	1.000	816.743	0.00287	817.822	0.136	0.180	0.813	0.001	0.002	0.008
12.1	0.37	0.45	0.325	0.271	1.000	816.248	0.00287	817.326	0.264	0.220	0.814	0.003	0.002	0.008
12.11	0.37	0.45	0.325	0.271	1.000	818.229	0.00287	819.310	0.264	0.220	0.812	0.003	0.002	0.008
12.07	0.93	1.13	0.817	0.427	1.000	818.229	0.00287	819.310	0.664	0.347	0.812	0.007	0.003	0.008
12.07	1.11	1.35	0.975	0.477	1.000	820.217	0.00287	821.300	0.791	0.387	0.811	0.008	0.004	0.008
12.03	0.74	0.90	0.650	0.374	1.000	822.212	0.00287	823.297	0.526	0.303	0.810	0.005	0.003	0.008
11.99	0.74	0.90	0.650	0.374	1.000	823.712	0.00287	824.798	0.526	0.302	0.809	0.005	0.003	0.008
11.96	0.74	0.90	0.650	0.374	1.000	826.724	0.00287	827.813	0.524	0.302	0.807	0.005	0.003	0.008
11.9	0.56	0.68	0.492	0.324	1.000	828.740	0.00286	829.831	0.396	0.261	0.806	0.004	0.003	0.008
11.86	1.11	1.35	0.975	0.477	1.000	828.740	0.00286	829.831	0.785	0.384	0.806	0.008	0.004	0.008
11.86	0.74	0.90	0.650	0.374	1.000	830.256	0.00286	831.349	0.523	0.301	0.805	0.005	0.003	0.008
11.83	0.00	0.00	0.000	0.168	1.000	831.269	0.00286	832.364		0.135	0.804		0.001	0.008
11.81	0.37	0.45	0.325	0.271	1.000	832.792	0.00286	833.888	0.261	0.218	0.803	0.003	0.002	0.008
11.78	0.93	1.13	0.817	0.427	1.000	835.338	0.00286	836.437	0.655	0.342	0.801	0.007	0.003	0.008
11.73	0.56	0.68	0.492	0.324	1.000	836.360	0.00286	837.460	0.394	0.259	0.801	0.004	0.003	0.008
11.71	0.00	0.00	0.000	0.168	1.000	837.895	0.00286	838.996		0.134	0.800		0.001	0.008
Average									5.88505	0.74870	4.66057	**0.05885***	**0.00749***	0.04661

*k range

Table J.2. Parameters used to calculate the range of gas transfer velocity (*k*) used in PorGy for May 28, 2010. Temperature (T), wind speed at 1m (U_1), wind speed at 10m (U_{10}), the transfer velocity adjusted to Schmidt number (*Sc*) 600 (k_{600}) for models 1, 2 and 3, Sc adjusted to temperature (Sc_O^2 (T)), Sc adjusted to temperature and salinity (Sc_O^2 (T,S)), the linear function of water temperature (*m*) and gas transfer velocity (*k*) for model 1, 2 and 3 are presented.

Temp. (T) (°C)	Wind speed (U_1) (m/s)	Wind speed (U_{10}) (m/s)	Model 1 for k_{600}	Model 2 for k_{600}	Model 3 for k_{600}	Sc_O^2(T)	*m*(T)	Sc_O^2(T, S)	Model 1 for *k* (cm/h)	Model 2 for *k* (cm/h)	Model 3 for *k* (cm/h)	Model 1 for *k* (m/h)	Model 2 for *k* (m/h)	Model 3 for *k* (m/h)
22.43	0.00	0.00	0.0000	0.1680	1.0000	472.160	0.0032	472.903	0.0000	0.1892	1.1264		0.0019	0.0113
22.32	0.00	0.00	0.0000	0.1680	1.0000	474.620	0.0032	475.305	0.0000	0.1888	1.1235		0.0019	0.0112
22.26	0.00	0.00	0.0000	0.1680	1.0000	475.968	0.0032	476.655	0.0000	0.1885	1.1220		0.0019	0.0112
22.17	0.00	0.00	0.0000	0.1680	1.0000	477.999	0.0032	478.672	0.0000	0.1881	1.1196		0.0019	0.0112
22.06	0.00	0.00	0.0000	0.1680	1.0000	480.494	0.0032	481.155	0.0000	0.1876	1.1167		0.0019	0.0112
21.99	0.00	0.00	0.0000	0.1680	1.0000	482.090	0.0032	482.752	0.0000	0.1873	1.1148		0.0019	0.0111
21.9	0.19	0.23	0.1669	0.2209	1.0000	484.150	0.0032	484.815	0.1857	0.2457	1.1125	0.0019	0.0025	0.0111
21.86	1.11	1.35	0.9750	0.4768	1.0000	485.070	0.0032	485.720	1.0837	0.5299	1.1114	0.0108	0.0053	0.0111
21.79	1.11	1.35	0.9750	0.4768	1.0000	486.684	0.0032	487.351	1.0819	0.5290	1.1096	0.0108	0.0053	0.0111
21.77	1.48	1.81	1.3000	0.5797	1.0000	487.146	0.0032	487.814	1.4418	0.6429	1.1090	0.0144	0.0064	0.0111
21.71	1.30	1.59	1.1419	0.5296	1.0000	488.536	0.0032	489.190	1.2647	0.5865	1.1075	0.0126	0.0059	0.0111
21.67	1.30	1.59	1.1419	0.5296	1.0000	489.466	0.0032	490.121	1.2635	0.5860	1.1064	0.0126	0.0059	0.0111
21.68	2.04	2.49	1.7919	0.7354	1.0000	489.233	0.0032	489.919	1.9831	0.8139	1.1067	0.0198	0.0081	0.0111
21.57	1.48	1.81	1.3000	0.5797	1.0000	491.799	0.0032	492.457	1.4350	0.6398	1.1038	0.0143	0.0064	0.0110
21.54	2.41	2.94	2.1169	0.8384	1.0000	492.502	0.0032	493.160	2.3350	0.9247	1.1030	0.0234	0.0092	0.0110
21.5	1.11	1.35	0.9750	0.4768	1.0000	493.441	0.0032	494.100	1.0744	0.5254	1.1020	0.0107	0.0053	0.0110
21.46	1.67	2.04	1.4669	0.6325	1.0000	494.382	0.0032	495.042	1.6150	0.6964	1.1009	0.0161	0.0070	0.0110
21.44	1.67	2.04	1.4669	0.6325	1.0000	494.854	0.0032	495.514	1.6142	0.6960	1.1004	0.0161	0.0070	0.0110
21.41	1.67	2.04	1.4669	0.6325	1.0000	495.562	0.0032	496.223	1.6130	0.6955	1.0996	0.0161	0.0070	0.0110
21.41	1.30	1.59	1.1419	0.5296	1.0000	495.562	0.0032	496.223	1.2557	0.5824	1.0996	0.0126	0.0058	0.0110
21.4	2.60	3.17	2.2838	0.8912	1.0000	495.798	0.0032	496.460	2.5107	0.9798	1.0993	0.0251	0.0098	0.0110
21.42	3.15	3.84	2.7670	1.0442	1.0000	495.326	0.0032	495.987	3.0433	1.1485	1.0999	0.0304	0.0115	0.0110
21.4	1.67	2.04	1.4669	0.6325	1.0000	495.798	0.0032	496.460	1.6127	0.6954	1.0993	0.0161	0.0070	0.0110
21.46	0.74	0.90	0.6500	0.3738	1.0000	494.382	0.0032	495.042	0.7156	0.4116	1.1009	0.0072	0.0041	0.0110
21.18	1.48	1.81	1.3000	0.5797	1.0000	501.036	0.0032	501.894	1.4214	0.6338	1.0934	0.0142	0.0063	0.0109
21.58	1.67	2.04	1.4669	0.6325	1.0000	491.565	0.0032	492.207	1.6196	0.6984	1.1041	0.0162	0.0070	0.0110
21.73	1.11	1.35	0.9750	0.4768	1.0000	488.072	0.0032	488.710	1.0804	0.5283	1.1080	0.0108	0.0053	0.0111
21.78	1.48	1.81	1.3000	0.5797	1.0000	486.915	0.0032	487.552	1.4422	0.6431	1.1093	0.0144	0.0064	0.0111
21.88	1.30	1.59	1.1419	0.5296	1.0000	484.610	0.0032	485.244	1.2698	0.5889	1.1120	0.0127	0.0059	0.0111
21.99	1.48	1.81	1.3000	0.5797	1.0000	482.090	0.0032	482.721	1.4494	0.6463	1.1149	0.0145	0.0065	0.0111
22.05	1.48	1.81	1.3000	0.5797	1.0000	480.721	0.0032	481.352	1.4514	0.6472	1.1165	0.0145	0.0065	0.0112
22.15	0.37	0.45	0.3250	0.2709	1.0000	478.451	0.0032	479.079	0.3637	0.3032	1.1191	0.0036	0.0030	0.0112
22.2	2.23	2.72	1.9588	0.7883	1.0000	477.321	0.0032	477.948	2.1947	0.8832	1.1204	0.0219	0.0088	0.0112
22.28	0.00	0.00	0.0000	0.1680	1.0000	475.519	0.0032	476.144	0.0000	0.1886	1.1226		0.0019	0.0112
22.42	0.19	0.23	0.1669	0.2209	1.0000	472.383	0.0032	473.005	0.1880	0.2487	1.1263	0.0019	0.0025	0.0113
22.48	1.30	1.59	1.1419	0.5296	1.0000	471.046	0.0032	471.667	1.2879	0.5973	1.1279	0.0129	0.0060	0.0113
22.51	0.19	0.23	0.1669	0.2209	1.0000	470.379	0.0032	470.999	0.1884	0.2493	1.1287	0.0019	0.0025	0.0113
22.66	1.11	1.35	0.9750	0.4768	1.0000	467.060	0.0032	467.676	1.1044	0.5400	1.1327	0.0110	0.0054	0.0113
22.66	1.30	1.59	1.1419	0.5296	1.0000	467.060	0.0032	467.676	1.2934	0.5999	1.1327	0.0129	0.0060	0.0113
22.73	0.37	0.45	0.3250	0.2709	1.0000	465.519	0.0032	466.134	0.3687	0.3074	1.1345	0.0037	0.0031	0.0113
22.86	2.04		0.0000	0.1680	1.0000	462.672	0.0032	463.284	0.0000	0.1912	1.1380		0.0019	0.0114
22.94	2.23	2.72	1.9588	0.7883	1.0000	460.929	0.0032	461.539	2.2334	0.8988	1.1402	0.0223	0.0090	0.0114
23.01	1.48	1.81	1.3000	0.5797	1.0000	459.409	0.0032	460.032	1.4847	0.6620	1.1420	0.0148	0.0066	0.0114
23.07	1.30	1.59	1.1419	0.5296	1.0000	458.110	0.0032	458.732	1.3060	0.6057	1.1437	0.0131	0.0061	0.0114
22.99	0.56	0.68	0.4919	0.3238	1.0000	459.843	0.0032	460.481	0.5615	0.3696	1.1415	0.0056	0.0037	0.0114
23.12	1.11	1.35	0.9750	0.4768	1.0000	457.030	0.0032	457.636	1.1164	0.5459	1.1450	0.0112	0.0055	0.0115
23.17	0.74	0.90	0.6500	0.3738	1.0000	455.952	0.0032	456.557	0.7452	0.4286	1.1464	0.0075	0.0043	0.0115
23.23	0.56	0.68	0.4919	0.3238	1.0000	454.662	0.0032	455.266	0.5647	0.3717	1.1480	0.0056	0.0037	0.0115
23.21	1.48	1.81	1.3000	0.5797	1.0000	455.092	0.0032	455.696	1.4917	0.6652	1.1475	0.0149	0.0067	0.0115
23.37	1.11	1.35	0.9750	0.4768	1.0000	451.666	0.0032	452.295	1.1230	0.5491	1.1518	0.0112	0.0055	0.0115
23.4	2.60	3.17	2.2838	0.8912	1.0000	451.026	0.0032	451.669	2.6323	1.0272	1.1526	0.0263	0.0103	0.0115
23.45	1.86	2.27	1.6338	0.6854	1.0000	449.961	0.0032	450.603	1.8853	0.7909	1.1539	0.0189	0.0079	0.0115
23.36	1.11	1.35	0.9750	0.4768	1.0000	451.879	0.0032	452.494	1.1228	0.5490	1.1515	0.0112	0.0055	0.0115
23.4	2.04	2.49	1.7919	0.7354	1.0000	451.026	0.0032	451.640	2.0654	0.8477	1.1526	0.0207	0.0085	0.0115

23.41	1.30	1.59	1.1419	0.5296	1.0000	450.813	0.0032	451.427	1.3165	0.6106	1.1529	0.0132	0.0061	0.0115
23.42	1.67	2.04	1.4669	0.6325	1.0000	450.600	0.0032	451.228	1.6916	0.7294	1.1531	0.0169	0.0073	0.0115
23.53	1.11	1.35	0.9750	0.4768	1.0000	448.262	0.0032	448.888	1.1273	0.5512	1.1561	0.0113	0.0055	0.0116
23.54	0.93	1.13	0.8169	0.4267	1.0000	448.050	0.0032	448.676	0.9447	0.4934	1.1564	0.0094	0.0049	0.0116
23.55	0.74	0.90	0.6500	0.3738	1.0000	447.838	0.0032	448.478	0.7518	0.4324	1.1567	0.0075	0.0043	0.0116
23.56	1.11	1.35	0.9750	0.4768	1.0000	447.626	0.0032	448.266	1.1280	0.5516	1.1569	0.0113	0.0055	0.0116
23.41	0.74	0.90	0.6500	0.3738	1.0000	450.813	0.0032	451.441	0.7494	0.4310	1.1529	0.0075	0.0043	0.0115
23.52	0.93	1.13	0.8169	0.4267	1.0000	448.474	0.0032	449.100	0.9442	0.4932	1.1559	0.0094	0.0049	0.0116
23.48	0.37	0.45	0.3250	0.2709	1.0000	449.323	0.0032	449.950	0.3753	0.3128	1.1548	0.0038	0.0031	0.0115
23.47	0.00	0.00	0.0000	0.1680	1.0000	449.536	0.0032	450.163	0.0000	0.1940	1.1545		0.0019	0.0115
23.25	0.93	1.13	0.8169	0.4267	1.0000	454.233	0.0032	454.866	0.9382	0.4901	1.1485	0.0094	0.0049	0.0115
23.47	0.00	0.00	0.0000	0.1680	1.0000	449.536	0.0032	450.163	0.0000	0.1940	1.1545		0.0019	0.0115
23.46	1.30	1.59	1.1419	0.5296	1.0000	449.748	0.0032	450.376	1.3180	0.6113	1.1542	0.0132	0.0061	0.0115
23.45	1.11	1.35	0.9750	0.4768	1.0000	449.961	0.0032	450.589	1.1251	0.5502	1.1539	0.0113	0.0055	0.0115
23.39	1.11	1.35	0.9750	0.4768	1.0000	451.239	0.0032	451.868	1.1235	0.5494	1.1523	0.0112	0.0055	0.0115
23.37	0.37	0.45	0.3250	0.2709	1.0000	451.666	0.0032	452.295	0.3743	0.3120	1.1518	0.0037	0.0031	0.0115
23.33	0.56	0.68	0.4919	0.3238	1.0000	452.520	0.0032	453.151	0.5660	0.3726	1.1507	0.0057	0.0037	0.0115
23.29	1.11	1.35	0.9750	0.4768	1.0000	453.376	0.0032	454.007	1.1209	0.5481	1.1496	0.0112	0.0055	0.0115
23.15	0.00	0.00	0.0000	0.1680	1.0000	456.383	0.0032	457.018	0.0000	0.1925	1.1458		0.0019	0.0115
23.14	0.00	0.00	0.0000	0.1680	1.0000	456.599	0.0032	457.234	0.0000	0.1924	1.1455		0.0019	0.0115
23.11	0.00	0.00	0.0000	0.1680	1.0000	457.246	0.0032	457.881	0.0000	0.1923	1.1447		0.0019	0.0114
23.08	0.93	1.13	0.8169	0.4267	1.0000	457.894	0.0032	458.530	0.9345	0.4881	1.1439	0.0093	0.0049	0.0114
22.91	0.93	1.13	0.8169	0.4267	1.0000	461.582	0.0032	462.222	0.9307	0.4861	1.1393	0.0093	0.0049	0.0114
22.96	0.00	0.00	0.0000	0.1680	1.0000	460.494	0.0032	461.133	0.0000	0.1916	1.1407		0.0019	0.0114
22.91	2.04	2.49	1.7919	0.7354	1.0000	461.582	0.0032	462.222	2.0416	0.8379	1.1393	0.0204	0.0084	0.0114
22.88	1.48	1.81	1.3000	0.5797	1.0000	462.236	0.0032	462.877	1.4801	0.6600	1.1385	0.0148	0.0066	0.0114
22.76	2.23	2.72	1.9588	0.7883	1.0000	464.861	0.0032	465.520	2.2238	0.8949	1.1353	0.0222	0.0089	0.0114
22.66	0.37	0.45	0.3250	0.2709	1.0000	467.060	0.0032	467.721	0.3681	0.3068	1.1326	0.0037	0.0031	0.0113
22.58	1.48	1.81	1.3000	0.5797	1.0000	468.827	0.0032	469.491	1.4697	0.6553	1.1305	0.0147	0.0066	0.0113
22.53	0.00	0.00	0.0000	0.1680	1.0000	469.935	0.0032	470.600	0.0000	0.1897	1.1291		0.0019	0.0113
22.36	0.74	0.90	0.6500	0.3738	1.0000	473.724	0.0032	474.393	0.7310	0.4204	1.1246	0.0073	0.0042	0.0112
22.89	0.00	0.00	0.0000	0.1680	1.0000	462.018	0.0032	462.644	0.0000	0.1913	1.1388		0.0019	0.0114
22.4	0.00	0.00	0.0000	0.1680	1.0000	472.829	0.0032	473.482	0.0000	0.1891	1.1257		0.0019	0.0113
22.43	0.00	0.00	0.0000	0.1680	1.0000	472.160	0.0032	472.797	0.0000	0.1893	1.1265		0.0019	0.0113
22.4	0.56	0.68	0.4919	0.3238	1.0000	472.829	0.0032	473.467	0.5537	0.3645	1.1257	0.0055	0.0036	0.0113
22.29	0.00	0.00	0.0000	0.1680	1.0000	475.294	0.0032	475.949	0.0000	0.1886	1.1228		0.0019	0.0112
22.31	0.00	0.00	0.0000	0.1680	1.0000	474.845	0.0032	475.500	0.0000	0.1887	1.1233		0.0019	0.0112
22.33	1.11	1.35	0.9750	0.4768	1.0000	474.396	0.0032	475.035	1.0958	0.5358	1.1239	0.0110	0.0054	0.0112
22.26	0.56	0.68	0.4919	0.3238	1.0000	475.968	0.0032	476.624	0.5519	0.3633	1.1220	0.0055	0.0036	0.0112
22.23	0.19	0.23	0.1669	0.2209	1.0000	476.644	0.0032	477.301	0.1871	0.2476	1.1212	0.0019	0.0025	0.0112
22.2	0.56	0.68	0.4919	0.3238	1.0000	477.321	0.0032	477.948	0.5511	0.3628	1.1204	0.0055	0.0036	0.0112
22.1	0.00	0.00	0.0000	0.1680	1.0000	479.585	0.0032	480.229	0.0000	0.1878	1.1178		0.0019	0.0112
22.08	0.37	0.45	0.3250	0.2709	1.0000	480.039	0.0032	480.684	0.3631	0.3027	1.1172	0.0036	0.0030	0.0112
22.15	0.93	1.13	0.8169	0.4267	1.0000	478.451	0.0032	479.095	0.9142	0.4775	1.1191	0.0091	0.0048	0.0112
Average									0.9406	0.4876	1.1297	0.0120	**0.0049***	**0.0113***

***** *k* range

Table J.3 Parameters used to calculate the range of gas transfer velocity (k used in PorGy for July 05, 2010. Temperature (T), wind speed at 1m (U_1), wind speed at 10m (U_{10}), the transfer velocity adjusted to Schmidt number (Sc) 600 (k_{600}) for models 1, 2 and 3, Sc adjusted to temperature (Sc_O^2 (T)), Sc adjusted to temperature and salinity (Sc_O^2 (T,S)), the linear function of water temperature (m) and gas transfer velocity (k) for model 1, 2 and 3 are presented.

Temp. (T) (°C)	Wind speed (U_1) (m/s)	Wind speed (U_{10}) (m/s)	Model 1 for k_{600}	Model 2 for k_{600}	Model 3 for k_{600}	Sc_O^2(T)	m(T)	Sc_O^2(T, S)	Model 1 for k (cm/h)	Model 2 for k (cm/h)	Model 3 for k (cm/h)	Model 1 for k (m/h)	Model 2 for k (m/h)	Model 3 for k (m/h)
21.27		0.00	0.0000	0.1680	1.0000	498.8848	0.0032	499.5338						
21.01		0.00	0.0000	0.1680	1.0000	505.1337	0.0032	505.7891						
21.09		0.00	0.0000	0.1680	1.0000	503.1999	0.0032	503.8374						
20.91		0.00	0.0000	0.1680	1.0000	507.5650	0.0032	508.2388						
20.88		0.00	0.0000	0.1680	1.0000	508.2974	0.0032	508.9560						
20.97		0.00	0.0000	0.1680	1.0000	506.1043	0.0032	506.7927						
20.94	0.19	0.23	0.1635	0.2198	1.0000	506.8339	0.0032	507.5231	0.1828	0.2457	1.1181	0.0018	0.0025	0.0112
21.13	0.74	0.90	0.6515	0.3743	1.0000	502.2368	0.0032	502.9210	0.7328	0.4210	1.1249	0.0073	0.0042	0.0112
20.99	1.11	1.36	0.9784	0.4778	1.0000	505.6187	0.0032	506.2745	1.0957	0.5351	1.1199	0.0110	0.0054	0.0112
20.9	1.67	2.04	1.4664	0.6324	1.0000	507.8090	0.0032	508.4991	1.6375	0.7061	1.1166	0.0164	0.0071	0.0112
21.03	1.67	2.04	1.4664	0.6324	1.0000	504.6493	0.0032	505.3361	1.6443	0.7091	1.1213	0.0164	0.0071	0.0112
20.73	2.04	2.49	1.7934	0.7359	1.0000	511.9815	0.0032	512.7085	1.9916	0.8172	1.1105	0.0199	0.0082	0.0111
20.86	1.30	1.59	1.1419	0.5296	1.0000	508.7865	0.0032	509.5099	1.2734	0.5906	1.1151	0.0127	0.0059	0.0112
20.95	2.78	3.40	2.4449	0.9422	1.0000	506.5906	0.0032	507.2955	2.7343	1.0538	1.1184	0.0273	0.0105	0.0112
21	2.04	2.49	1.7934	0.7359	1.0000	505.3761	0.0032	506.0637	2.0090	0.8244	1.1202	0.0201	0.0082	0.0112
20.95	2.23	2.72	1.9569	0.7877	1.0000	506.5906	0.0032	507.2794	2.1886	0.8810	1.1184	0.0219	0.0088	0.0112
22.01	1.48	1.81	1.3030	0.5806	1.0000	481.6330	0.0032	482.1720	1.5074	0.6717	1.1569	0.0151	0.0067	0.0116
21.69	3.15	3.85	3.3549	1.0450	1.8704	489.0007	0.0032	489.5772	3.7140	1.1568	2.0707	0.0371	0.0116	0.0207
20.99	2.97	3.62	2.6084	0.9940	1.0000	505.6187	0.0032	506.2745	2.9211	1.1132	1.1199	0.0292	0.0111	0.0112
20.93	2.97	3.62	2.6084	0.9940	1.0000	507.0774	0.0032	507.7508	2.9154	1.1110	1.1177	0.0292	0.0111	0.0112
21.18	2.97	3.62	2.6084	0.9940	1.0000	501.0362	0.0032	501.6874	2.9389	1.1199	1.1267	0.0294	0.0112	0.0113
21.04	3.15	3.85	3.3549	1.0450	1.8704	504.4074	0.0032	505.0939	3.6565	1.1389	2.0386	0.0366	0.0114	0.0204
21.03	2.97	3.62	2.6084	0.9940	1.0000	504.6493	0.0032	505.3202	2.9248	1.1146	1.1213	0.0292	0.0111	0.0112
21.18	3.15	3.85	3.3549	1.0450	1.8704	501.0362	0.0032	501.6715	3.6689	1.1428	2.0455	0.0367	0.0114	0.0205
21.49	4.27	5.21	9.2391	1.3548	8.8554	493.6760	0.0032	494.2726	10.1794	1.4927	9.7567	0.1018	0.0149	0.0976
21.63	3.15	3.85	3.3549	1.0450	1.8704	490.3974	0.0032	490.9909	3.7086	1.1552	2.0677	0.0371	0.0116	0.0207
21.59	3.53	4.30	5.3212	1.1485	4.2046	491.3313	0.0032	491.9257	5.8767	1.2684	4.6435	0.0588	0.0127	0.0464
21.63	3.90	4.75	7.2875	1.2521	6.5387	490.3974	0.0032	490.9909	8.0559	1.3841	7.2282	0.0806	0.0138	0.0723
21.56	4.45	5.43	10.2222	1.4066	10.0225	492.0333	0.0032	492.6440	11.2812	1.5523	11.0607	0.1128	0.0155	0.1106
21.46	3.71	4.53	6.3043	1.2003	5.3716	494.3822	0.0032	494.9951	6.9409	1.3215	5.9140	0.0694	0.0132	0.0591
21.48	4.08	4.98	8.2559	1.3030	7.6883	493.9112	0.0032	494.5395	9.0937	1.4353	8.4685	0.0909	0.0144	0.0847
21.5	4.83	5.89	12.1885	1.5101	12.3566	493.4409	0.0032	494.0530	13.4320	1.6642	13.6172	0.1343	0.0166	0.1362
21.68	4.27	5.21	9.2391	1.3548	8.8554	489.2331	0.0032	489.8567	10.2252	1.4994	9.8005	0.1023	0.0150	0.0980
21.36	3.90	4.75	7.2875	1.2521	6.5387	496.7454	0.0032	497.3922	8.0039	1.3751	7.1815	0.0800	0.0138	0.0718
21.44	4.64	5.66	11.2054	1.4584	11.1895	494.8536	0.0032	495.4985	12.3305	1.6048	12.3131	0.1233	0.0160	0.1231
21.51	2.97	3.62	2.6084	0.9940	1.0000	493.2059	0.0032	493.8491	2.9699	1.1317	1.1386	0.0297	0.0113	0.0114
21.38	4.45	5.43	10.2222	1.4066	10.0225	496.2716	0.0032	496.9179	11.2326	1.5456	11.0131	0.1123	0.0155	0.1101
21.72	4.45	5.43	10.2222	1.4066	10.0225	488.3041	0.0032	488.9423	11.3238	1.5582	11.1025	0.1132	0.0156	0.1110
21.72	3.71	4.53	6.3043	1.2003	5.3716	488.3041	0.0032	488.9423	6.9837	1.3296	5.9505	0.0698	0.0133	0.0595
21.75	3.71	4.53	6.3043	1.2003	5.3716	487.6088	0.0032	488.2463	6.9887	1.3306	5.9547	0.0699	0.0133	0.0595
21.87	2.23	2.72	1.9569	0.7877	1.0000	484.8397	0.0032	485.4744	2.2537	0.9071	1.1517	0.0225	0.0091	0.0115
21.7	2.78	3.40	2.4449	0.9422	1.0000	488.7684	0.0032	489.4226	2.8005	1.0793	1.1455	0.0280	0.0108	0.0115
21.84	4.45	5.43	10.2222	1.4066	10.0225	485.5302	0.0032	486.1966	11.3558	1.5626	11.1338	0.1136	0.0156	0.1113
21.75	4.08	4.98	8.2559	1.3030	7.6883	487.6088	0.0032	488.2774	9.1519	1.4444	8.5227	0.0915	0.0144	0.0852
21.85	4.27	5.21	9.2391	1.3548	8.8554	485.2999	0.0032	485.9505	10.2662	1.5054	9.8398	0.1027	0.0151	0.0984
21.85	3.34	4.07	4.3380	1.0967	3.0375	485.2999	0.0032	485.9505	4.8203	1.2187	3.3752	0.0482	0.0122	0.0338
21.96	3.90	4.75	7.2875	1.2521	6.5387	482.7753	0.0032	483.4079	8.1189	1.3949	7.2847	0.0812	0.0139	0.0728
22.03	5.19	6.34	14.1402	1.6129	14.6733	481.1770	0.0032	481.8232	15.7793	1.7998	16.3742	0.1578	0.0180	0.1637
22.16	2.04	2.49	1.7934	0.7359	1.0000	478.2250	0.0032	478.8528	2.0844	0.8553	1.1622	0.0208	0.0086	0.0116

22.25	2.41	2.94	2.1179	0.8387	1.0000	476.1935	0.0032	476.8193	2.4685	0.9775	1.1656	0.0247	0.0098	0.0117
22.32	1.11	1.36	0.9784	0.4778	1.0000	474.6203	0.0032	475.2292	1.1430	0.5582	1.1682	0.0114	0.0056	0.0117
22.19	3.53	4.30	5.3212	1.1485	4.2046	477.5467	0.0032	478.1739	5.9606	1.2865	4.7098	0.0596	0.0129	0.0471
22.55	3.71	4.53	6.3043	1.2003	5.3716	469.4916	0.0032	470.0652	7.1225	1.3561	6.0688	0.0712	0.0136	0.0607
22.06	3.90	4.75	7.2875	1.2521	6.5387	480.4939	0.0032	481.1240	8.1381	1.3982	7.3019	0.0814	0.0140	0.0730
22.47	4.83	5.89	12.1885	1.5101	12.3566	471.2686	0.0032	471.8590	13.7443	1.7029	13.9338	0.1374	0.0170	0.1393
22.32	2.78	3.40	2.4449	0.9422	1.0000	474.6203	0.0032	475.2292	2.8560	1.1006	1.1682	0.0286	0.0110	0.0117
22.72	4.08	4.98	8.2559	1.3030	7.6883	465.7392	0.0032	466.3691	9.3643	1.4780	8.7205	0.0936	0.0148	0.0872
22.23	5.19	6.34	14.1402	1.6129	14.6733	476.6441	0.0032	477.2704	15.8543	1.8084	16.4521	0.1585	0.0181	0.1645
22.3	2.78	3.40	2.4449	0.9422	1.0000	475.0692	0.0032	475.6938	2.8541	1.0999	1.1674	0.0285	0.0110	0.0117
22.33	3.71	4.53	6.3043	1.2003	5.3716	474.3961	0.0032	475.0200	7.0853	1.3490	6.0371	0.0709	0.0135	0.0604
22.2	4.27	5.21	9.2391	1.3548	8.8554	477.3209	0.0032	477.9478	10.3518	1.5180	9.9219	0.1035	0.0152	0.0992
22.39	2.41	2.94	2.1179	0.8387	1.0000	473.0529	0.0032	473.6754	2.4795	0.9818	1.1707	0.0248	0.0098	0.0117
22.41	2.23	2.72	1.9569	0.7877	1.0000	472.6061	0.0032	473.2282	2.2924	0.9227	1.1714	0.0229	0.0092	0.0117
22.44	2.97	3.62	2.6084	0.9940	1.0000	471.9369	0.0032	472.5582	3.0584	1.1655	1.1725	0.0306	0.0117	0.0117
22.21	1.86	2.26	1.6299	0.6841	1.0000	477.0952	0.0032	477.7219	1.8974	0.7964	1.1641	0.0190	0.0080	0.0116
22.26	0.93	1.13	0.8150	0.4261	1.0000	475.9684	0.0032	476.5940	0.9502	0.4968	1.1659	0.0095	0.0050	0.0117
22.61	0.74	0.90	0.6515	0.3743	1.0000	468.1636	0.0032	468.7660	0.7680	0.4413	1.1789	0.0077	0.0044	0.0118
22.62	0.37	0.45	0.3270	0.2715	1.0000	467.9426	0.0032	468.5298	0.3856	0.3202	1.1793	0.0039	0.0032	0.0118
22.68		0.00	0.0000	0.1680	1.0000	466.6193	0.0032	467.2051		0.1985	1.1815		0.0020	0.0118
22.71		0.00	0.0000	0.1680	1.0000	465.9590	0.0032	466.5442		0.1987	1.1826		0.0020	0.0118
22.64	1.48	1.81	1.3030	0.5806	1.0000	467.5011	0.0032	468.0878	1.5375	0.6851	1.1800	0.0154	0.0069	0.0118
22.7	0.93	1.13	0.8150	0.4261	1.0000	466.1790	0.0032	466.7644	0.9635	0.5037	1.1822	0.0096	0.0050	0.0118
22.83	1.48	1.81	1.3030	0.5806	1.0000	463.3277	0.0032	463.8805	1.5468	0.6893	1.1871	0.0155	0.0069	0.0119
22.65	2.41	2.94	2.1179	0.8387	1.0000	467.2805	0.0032	467.8669	2.4999	0.9899	1.1804	0.0250	0.0099	0.0118
22.63	0.93	1.13	0.8150	0.4261	1.0000	467.7218	0.0032	468.3087	0.9614	0.5026	1.1796	0.0096	0.0050	0.0118
22.6	1.48	1.81	1.3030	0.5806	1.0000	468.3846	0.0032	468.9722	1.5356	0.6843	1.1785	0.0154	0.0068	0.0118
22.53	1.11	1.36	0.9784	0.4778	1.0000	469.9352	0.0032	470.5243	1.1506	0.5619	1.1759	0.0115	0.0056	0.0118
22.63	0.19	0.23	0.1635	0.2198	1.0000	467.7218	0.0032	468.3238	0.1928	0.2592	1.1796	0.0019	0.0026	0.0118
22.6	0.56	0.68	0.4880	0.3225	1.0000	468.3846	0.0032	468.9873	0.5751	0.3801	1.1785	0.0058	0.0038	0.0118
22.6	0.56	0.68	0.4880	0.3225	1.0000	468.3846	0.0032	468.9722	0.5751	0.3801	1.1785	0.0058	0.0038	0.0118
22.57	0.19	0.23	0.1635	0.2198	1.0000	469.0485	0.0032	469.6518	0.1925	0.2588	1.1774	0.0019	0.0026	0.0118
22.62	0.19	0.23	0.1635	0.2198	1.0000	467.9426	0.0032	468.5599	0.1928	0.2592	1.1792	0.0019	0.0026	0.0118
22.62		0.00	0.0000	0.1680	1.0000	467.9426	0.0032	468.5599		0.1981	1.1792		0.0020	0.0118
22.61		0.00	0.0000	0.1680	1.0000	468.1636	0.0032	468.7811		0.1980	1.1788		0.0020	0.0118
22.58		0.00	0.0000	0.1680	1.0000	468.8271	0.0032	469.4603		0.1979	1.1777		0.0020	0.0118
22.55		0.00	0.0000	0.1680	1.0000	469.4916	0.0032	470.1256		0.1977	1.1766		0.0020	0.0118
22.55		0.00	0.0000	0.1680	1.0000	469.4916	0.0032	470.1256		0.1977	1.1766		0.0020	0.0118
22.55		0.00	0.0000	0.1680	1.0000	469.4916	0.0032	470.1407		0.1977	1.1766		0.0020	0.0118
22.55		0.00	0.0000	0.1680	1.0000	469.4916	0.0032	470.1557		0.1977	1.1765		0.0020	0.0118
22.57		0.00	0.0000	0.1680	1.0000	469.0485	0.0032	469.7423		0.1978	1.1772		0.0020	0.0118
22.57		0.00	0.0000	0.1680	1.0000	469.0485	0.0032	469.7423		0.1978	1.1772		0.0020	0.0118
22.49		0.00	0.0000	0.1680	1.0000	470.8237	0.0032	471.5347		0.1973	1.1742		0.0020	0.0117
22.56		0.00	0.0000	0.1680	1.0000	469.2700	0.0032	469.9792		0.1977	1.1768		0.0020	0.0118
22.71		0.00	0.0000	0.1680	1.0000	465.9590	0.0032	466.6643		0.1986	1.1824		0.0020	0.0118
22.63		0.00	0.0000	0.1680	1.0000	467.7218	0.0032	468.4291		0.1981	1.1794		0.0020	0.0118
22.69		0.00	0.0000	0.1680	1.0000	466.3991	0.0032	467.1048		0.1985	1.1817		0.0020	0.0118
22.63		0.00	0.0000	0.1680	1.0000	467.7218	0.0032	468.4442	0.0000	0.1981	1.1794		0.0020	0.0118
Average									4.74256	0.87964	3.6307	**0.048***	**0.0088***	0.0363

***** *k* range

Appendix K – Bottle Incubation measurements for 24h-diurnal experiments

Table K.1. Bottle incubation measurements for Stonebridge pond in April 29, 2010. Incubation time for light BOD bottles was 3.5 hrs.

Light levels	PAR (µE/m/s)	O_2(mg/L)	T (°C)	Avg. PAR (µE/m/s)	Avg. O_2(mg/L)	Avg. HNP (mg O_2/L/hr)	Avg. HNP (mg C/m_3/hr)
O_2 initial	O_2 initial	14.96	14.1		14.82*		
O_2 initial	O_2 initial	14.9	14.1				
O_2 initial	O_2 initial	15.08	14.1				
O_2 initial	O_2 initial	15.08	14				
1	339.6	15.2	13.5	338.55	15.31	0.1400	52.50
1	337.5	15.42	13.2				
2	266.3	15.57	13.2	266.30	15.57	0.2143	80.36
3	172.18	15.26	14	148.37	15.18	0.1029	38.57
3	128.07	15.1	14.3				
3	144.87	15.18	14.9				
4	75.81	14.88	13.5	70.95	14.93	0.0324	12.14
4	61.43	14.89	14				
4	75.6	15.03	14.4				
5	69.8	15.03	13.4	58.96	14.94	0.0343	12.86
5	54.8	14.89	14.2				
5	52.29	14.9	14.6				
6	35.09	14.85	13.2	31.89	14.84	0.0067	2.50
6	31.96	14.84	13.7				
6	28.61	14.84	14.4				
7	26.54	14.78	13.6	27.37	14.72	-0.0300	-11.25
7	28.2	14.65	14.9				
Dark (48 hrs)[a]	0	11.68	14.6	0.00	11.91	-0.0607	-22.77
Dark (48 hrs)[a]	0	12.13	14.2				
Dark (3.5 hrs)[a]	0	14.49	13.6	0.00	14.61	-0.0600	-22.50
Dark (3.5 hrs)[a]	0	14.73	13.6				

PAR, photosynthetic available radiation
NPP, Net primary production
* Average O_2 calculated using the intercept of O_2 measured in dark bottles at 3.5 hrs and 48 hrs
[a] Dark bottle incubation time

Table K.2 Bottle incubation measurements for Stonebridge pond in May 28, 2010. Incubation time for light BOD bottles was 4 hrs.

Light levels	PAR (μE/m/s)	O_2 (mg/L)	T (°C)	Avg. PAR (μE/m/s)	Avg.O_2 (mg/L)	Avg. HNP (mg O_2/L/hr)	Avg. HNP (mg C/m_3/hr)
O_2 initial	O_2 initial	10.75	21.5		10.284*		
O_2 initial	O_2 initial		21.5				
O_2 initial	O_2 initial	10.89	21.5				
O_2 initial	O_2 initial	10.84	21.5				
O_2 initial	O_2 initial	10.65	21.5				
O_2 initial	O_2 initial	10.66	21.5				
1	339.6	10.84	22.6	338.55	10.83	0.1365	51.19
1	337.5	10.86	22.6				
1	337.5	10.79	22.4				
2	266.3	10.85	22.5	266.00	10.85	0.1415	53.06
3	172.18	10.44	22.5	148.37	10.42	0.0348	13.06
3	128.07	10.43	22.5				
3	144.87	10.4	22.4				
4	75.81	10.41	22.4	70.95	10.36	0.0190	7.12
4	61.43	10.31	22.4				
5	69.8	10.38	22.3	62.30	10.30	0.0040	1.50
5	54.8	10.22	22.3				
5		10.08	22.3				
6	35.09	10.29	22.3	33.53	10.26	-0.0073	-2.72
6	31.96	10.22	22.3				
Dark (70hrs)[a]	0	6.65	22.4	0.00	6.71	-0.0511	-19.15
Dark (70hrs)[a]	0	6.77	22.4				
Dark (4 hrs)[a]	0	10.09	22.5	0.00	10.08	-0.0510	-19.13
Dark (4hrs)[a]	0	10.07	22.3				

PAR, photosynthetic available radiation
NPP, Net primary production
* Average O_2 calculated using the intercept of O_2 measured in dark bottles at 3.5 hrs and 48 hrs
[a] Dark bottle incubation time

Table K.3 Bottle incubation measurements for Stonebridge pond in July 05, 2010. Incubation time for light BOD bottles was 4 hrs.

Light levels	PAR (µE/m/s)	O_2 (mg/L)	T (°C)	Avg. PAR (µE/m/s)	Avg. O_2(mg/L)	Avg. HNP (mg O_2/L/hr)	Avg. HNP (mg C/m3/hr)
O_2 initial	O_2 initial	9.79	24.7		9.47		
O_2 initial	O_2 initial	9.65	24.7				
O_2 initial	O_2 initial	9.53	24.8				
O_2 initial	O_2 initial	9.53	24.8				
1	339.6	10.07	23.5	338.55	10.05	0.1458	54.66
1	337.5	10.03	23.4				
2	266.3	10.07	23.4	226.30	10.07	0.1508	56.53
3	172.18	9.94	23.4	148.37	9.88	0.1020	38.25
3	128.07	9.83	23.4				
3	144.87	9.91	23.3				
3		9.82	23.3				
4	75.81	9.76	23.3	70.95	9.68	0.0532	19.97
4	61.43	9.64	23.4				
4	75.6	9.64	23.3				
5	69.8	9.61	23.3	58.96	9.59	0.0316	11.84
5	54.8	9.65	23.3				
5	52.29	9.52	23.3				
6	35.09	9.56	23.3	31.89	9.56	0.0220	8.25
6	31.96	9.55	23.3				
7	26.54	9.41	23.3	27.37	9.48	0.0020	0.75
7	28.2	9.54	23.3				
Dark (49.5 hrs)[a]	0	7.64	24.3	0.00	7.65	-0.0260	-9.76
Dark (49.5 hrs)[a]	0	7.65	24.3				
Dark (4 hrs)[a]	0	9.32	23.3	0.00	9.32	-0.0368	-13.78
Dark (4 hrs)[a]	0	9.32	23.3				

PAR, photosynthetic available radiation
NPP, Net primary production
* Average O_2 calculated using the intercept of O_2 measured in dark bottles at 3.5 hrs and 48 hrs
[a] Dark bottle incubation time

Appendix L – Fee computer program PSPARMS results

Table L. Fee computer program PSPARMS (Version 4.0, Fee 1998) results for bottle incubations of April 29, May 28 and July 05, 2010. Chlorophyll *a*, The chlorophyll-dependent rate of photosynthesis at optimal PAR (P^B_m) and the chlorophyll dependent slope of the photosynthesis versus PAR curve at low irradiance levels (α^B) are shown.

Date	Chlorophyll *a* (*B*) (mg Ch/m^3)	P^B_{max} (mg C/mg Chl *a*/m^2)	α^B (mg C/mg Chl *a*/hr)	Sum of Squares
April 29	294.56	0.16	0.18	0.00
May 28	266.20	0.22	0.22	0.01
July 05	173.00	0.33	0.56	0.00

Appendix M – Nutrient concentrations at the beginning and at the end of diurnal experiments.

Table M. Nutrient concentrations (mg/L) at the beginning (t_o) and at the end (t_{24}) of diurnal experiments on April 29, May 28 and July 05, 2010. Samples were taken at the inlet, outlet and at the pond subsurface (in pond). Reactive phosphorus (RP), nitrate (NO^-_3), ammonium (NH^+_4), total phosphorus (TP), total kjeldahl nitrogen (TKN) dissolved organic carbon (DOC) and total dissolved phosphorus (TDP) are presented.

Date	Source	RP (mg/L)		NO^-_3 (mg/L)		NH^+_4 (mg/L)		TP (mg/L)		TKN (mg/L)		DOC (mg/L)		TDP (mg/L)	
		t_o	t_{24}	t_o	t_{24}	t_o	t_{24}	t_o	t_{24}	t_o	t_{24}	t_o	t_{24}	t_o	t_{24}
Apr-29	In pond	0.003	0.002	0.06	0.031	0.036	0.019	0.030	0.033	0.59	0.69	2.00	2.67	0.015	0.014
	Inlet	0.001	0.003	1.033	0.68	0.004	0.009	0.022	0.026	0.39	0.58	2.04	2.39	0.012	0.020
	Outlet	0.003	0.004	0.034	0.017	0.017	0.033	0.032	0.038	0.58	0.68	2.49	2.30	0.008	0.011
May-28	In pond	0.017	0.006	0.020	0.005	0.043	0.066	0.119	0.086	1.61	1.17	4.14	3.48	0.017	0.013
	Inlet	0.001	0.002	0.323	0.328	0.034	0.034	0.029	0.027	0.63	0.59	2.82	3.09	0.008	0.009
	Outlet	0.012	0.009	0.020	0.020	0.129	0.014	0.116	0.092	1.41	1.17	3.34	4.27	0.020	0.027
Jul-05	In pond	0.005	0.002	0.041	0.049	0.003	0.01	0.058	0.035	1.02	0.77	6.79	6.45	0.012	0.015
	Inlet	0.002	0.003	0.749	0.622	0.048	0.049	0.01	0.015	0.47	0.55	3.28	5.35	0.011	0.019
	Outlet	0.005	0.005	0.020	0.020	0.017	0.074	0.05	0.049	0.9	0.93	4.83	2.84	0.100	0.008

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