System and plankton metabolism in the lower Grand River, Ontario

By

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

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

Abstract

Currently our understanding of both system and phytoplankton metabolism in large rivers is somewhat limited. Knowledge of the metabolic balance in such systems is necessary not only for proper management of the river itself, but also for the lakes into which they discharge. The River Continuum Concept proposes that the deep, turbid waters of large rivers have a poor light climate which leads to heterotrophic conditions (respiration > photosynthesis) yet this idea has been challenged. Similarly, it has been predicted that phytoplankton growth in large rivers is limited to areas of unusually favourable light climate and water retention (e.g. margins, backwaters), but the evidence is limited. Through longitudinal and diel measurements of Chl *a*, nutrient concentrations, dissolved oxygen and stable oxygen isotopes it was shown in this study that the lower Grand River was autotrophic during the two successive summers but either balanced or heterotrophic in other seasons. This implies that large rivers such as the Grand can be a transition zone for nutrients and a phytoplankton source, depending on season.

Experimental incubations to measure oxygen production under varying irradiance demonstrated that phytoplankton could indeed grow (i.e., achieve positive net production) in the main river channel. Comparison of system and plankton metabolic rates further indicated that the phytoplankton were responsible for the major portion of the system production, but much less of the respiration. Sediment oxygen demand probably accounted for much of the additional respiration, but interactions with marginal and upstream habitats was probably an additional influence on both consumption and production of oxygen.

The results further showed that stable oxygen isotope dynamics did not conform to the steady state model commonly used to infer metabolic patterns from environmental isotope data. A non-steady model was more successful and largely supported independent assessments of metabolism.

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Table of Contents

List of Figures

List of Tables

1 - Introduction

Introduction and Objectives

In this thesis I explore the metabolic conditions in the southern Grand River. Traditionally, the River Continuum Concept (RCC) has predicted that the lower section of large rivers will experience a heterotrophic metabolic balance (Vannotte et al 1980). In other words respiration (R) will exceed photosynthesis (P). Although phytoplankton populations are observed, increasing river depth and turbidity are expected to suppress autochthonous primary production to the point that the dominant biological processes are expected to involve the respiration of organic materials transported from upstream, either produced in autotrophic mid-reach sections or from terrestrial sources (ie. allochthonous production). However, while investigations of the metabolic dynamics in large rivers are limited, previous work has illustrated the potential for net phytoplankton growth as well as their potential to alter the nutrient regimes in large rivers (Admiraal et al 1992, Descy and Gosselain 1994, Reynolds 1994, Kohler 1995, VanNieuwenhuyse 2007, Leland and Frey 2008). And while this may indicate the potential for autotrophic conditions, studies that have specifically investigated the metabolic balance through measurements of P and R are limited (Descy and Gosselain 1994).

Knowledge of the metabolic balance in the lower regions of large rivers is important for proper management of those ecosystems. The P:R ratio will have a direct influence on the oxygen regime. R dominated systems are more likely to have waters undersaturated with respect to oxygen and this creates a host of problems for a wide range of aquatic organisms. Furthermore, as previously mentioned, autochthonous production in large rivers has been shown to alter the nutrient regimes (ie. conversion of

soluble inorganics into particulate organic forms), which will not only impact the local river ecosystem but the near shore ecosystems of the lakes which they discharge into. Thus the Grand River specifically may act as a sink or source for different forms of nutrients to the near shore ecosystem in Lake Erie.

My first objective is to characterize the metabolic balance in the Southern Grand River. Measurements of phytoplankton concentrations as well as nutrient changes will provide qualitative evidence, while measurements of diel oxygen cycles and stable oxygen isotopes will be used to provide quantitative results. My null hypothesis is that during summer the Southern Grand River is autotrophic. These results will then be examined to determine if they can be applied to large rivers in general.

The traditional techniques for measuring metabolic rates in aquatic ecosystems have focused on measurements of oxygen (diel and incubation studies) and carbon (^{14}C). More recently stable oxygen isotopes have been used to infer metabolic balance in a variety of aquatic ecosystems, however they have yet to be used in an area of river such as the southern Grand. The initial methodology involved the assumption of steady state conditions (Quay et al 1995). While this assumption may be valid in less productive systems, it is violated in highly productive systems that experience significant diel oxygen cycles. In order to overcome this, variations of the steady state approach have been tested, though success has been modest (Tobias et al 2007). A possible solution for systems that violate the steady state assumption is the recently developed PoRGy model (Venkiteswaran et al 2007). PoRGy is a non steady state model, and as such is capable of producing measurements of P and R in productive systems.

My second objective is to determine if the stable oxygen isotope work agrees with the more traditional methods. This will include examining the effectiveness of the PoRGy model in predicting P and R in the Southern Grand River. This model has not been tested on in the lower section of a large, eutrophic river. Results obtained from this model will be compared to those from the oxygen concentrations alone, and any differences will be examined for possible explanations.

Though it is clear large rivers can support extensive phytoplankton populations, the question of how they survive in such turbid, well mixed waters is not completely understood. If the actual river depth is greater than the critical depth net positive growth of phytoplankton should not be possible, yet this has been observed (Cole et al 1992). Several hypothesis ranging from enhanced photosynthetic capabilities (Cole et al 1991, in Descy and Gosselain 1994), induction effects (Harris and Piccinin 1977, Loehr 1987), and importation from more favorable growing environments (Cole et al 1992, Reynolds 1994) have been proposed to explain this phenomenon. Yet *in situ* testing of these theories is limited.

My third objective is to determine if in fact positive growth of phytoplankton is predicted in the Southern Grand River. Oxygen light and dark bottle incubations will be used to derive water column rates of P and R and thus demonstrate if phytoplankton growth is expected throughout this stretch of river, or rather is limited to particular areas. My null hypothesis is that positive phytoplankton growth will be predicted throughout this stretch of river. Photosynthetic parameters will also be examined to look for evidence of photoacclimation to low light levels. Finally the P and R rates from the bottles shall be

compared to the entire systems rates in order to examine phytoplankton contribution to system metabolism.

Study Site

The Grand River is the largest Canadian tributary into eastern Lake Erie, with the largest watershed in Southern Ontario at 6800 km^2. The river begins near the town of Dundalk and empties into Lake Erie at the town of Port Maitland. The watershed is home to ~900 000 people with a majority located in the middle section of river. Throughout its course, the Grand is subject to strong anthropogenic influence including pollution and channel modifications. Pollution includes both point sources (26 sewage treatment plants plus industry) as well as non point source loading from agricultural activities within the drainage basin. The Grand was declared a Canadian Heritage river in 1982.

The section of river to be examined is an approximately 35km stretch at the Southern end of the river running from Cayuga to the mouth at Lake Erie. A majority of the land use along this stretch of river is agricultural. Two sewage treatment plants are located along this reach, one at the top in Cayuga and the other in Dunnville approximately 8km from the mouth. The river channel is modified in the town of Dunnville by a low head dam. This dam serves to create conditions which can be seen as an intermediate between a large river and a reservoir. The water residence time has been increased though there is still noticeable flow. Starting at approximately 5km above the dam, wetlands begin to surround the main channel. Below the dam, the wetlands become more extensive down to the river mouth. This section of river runs through a clay plain and is naturally very turbid.

As an order 7 river, the Grand fringes upon being a true large river but it still provides a reasonable system to test the outlined hypothesis. With an average summer discharge of approximately $30m^3/s$ and significant increases during runoff and precipitation events, the southern Grand maintains a significant ecosystem and undoubtedly impacts the near shore system in Lake Erie. Although smaller than other Great Lakes tributaries such as the Detroit or Niagara, it still possesses many of the characteristics of a large river and particularly those draining catchments with significant human influence. These characteristics include increasing depth and turbidity, high nutrient concentrations, a general lack of submersed macrophytes and a significant phytoplankton population. Furthermore since rivers of the Grand's size are much more common than truly large rivers, and provide the more immediate links between catchments and receiving waters, it is important that we understand the metabolic functioning of such systems. The influence of the dam is discussed further in chapter 2 but briefly, although the dam causes a deviation from the natural channel morphology such a modification is certainly not unique to the Grand. So although the presented measurements may not represent the situation that would exist in the absence of artificial channel modifications, it is nonetheless important that we understand how the river functions in its current state.

2 – Community metabolism in a turbid, eutrophic lowland river (Grand River, Ontario)

Overview

The River Continuum Concept suggests that high order streams should be heterotrophic (Respiration >Photosynthesis). Observations in eutrophic lowland rivers challenge this belief but are still limited in number. I measured nutrient, chlorophyll, and oxygen concentrations, as well as oxygen isotope composition, to test whether the turbid and nutrient enriched lower Grand River, ON, Canada (order 7) was in fact heterotrophic. Dissolved inorganic nutrients decreased while chlorophyll and particulate organic nutrients increased moving downstream during the summer. Dissolved oxygen and stable oxygen isotopic composition both show photosynthetic influence during the summer season, increasing downstream. Diel *in situ* DO variations demonstrated autotrophy (P>R). A non steady-state model, PoRGy, using dissolved oxygen stable isotope diel curves confirmed these observations but could not accurately reproduce the $\delta^{18}O_{DO}$ cycle. In spring and fall, dissolved inorganic nutrients were often high, chlorophyll low, and the DO and its isotopic composition implied either balanced or heterotrophic metabolism. The results imply that large rivers such as the Grand can be a transition zone for nutrients, and a source of phytoplankton, depending on season. The effect of impoundments on metabolic balance in large rivers is discussed, as is the importance of reliable gas exchange estimates for estimating P and R rates.

Introduction

According to the River Continuum Concept (RCC) large rivers are expected to support substantial phytoplankton populations but also to have poor light conditions resulting from increasing turbidity and depth (Vannotte et al 1980). Primary production is thus predicted to be suppressed while respiration is subsidized by downstream transport of organic matter, resulting in a heterotrophic metabolic balance (R>P). Previous work on large, eutrophic rivers has indicated this may not always be the case. Studies on the Rhine River (Admiraal et al 1992), Meuse River (Descy and Gosselain 1994), Spree River (Kohler 1995) and other systems (Reynolds 1994, VanNieuwenhuyse 2007, Leland and Frey 2008) have supported the expectation that phytoplankton populations can grow and consume inorganic nutrients in large rivers, and potentially support an autotrophic system metabolism, while some (Cole et al. 1992) have found that only limited areas of large rivers can support net growth of phytoplankton. Studies that have directly characterized the metabolic balance in large rivers through measurement of oxygen or carbon dynamics are by comparison relatively limited (Descy and Gosselain 1994). Even in systems where net phytoplankton growth is possible, dissolved oxygen may be predominantly below saturation, implying that system metabolism is heterotrophic (Kohler 1995). There is a need for additional studies that include measurements of system metabolism as well as phytoplankton and nutrient dynamics if we are to know whether the predictions of the RCC are generally accurate or not for large eutrophic rivers.

A complication in assessing metabolic balance in large rivers is the near-universal presence of channel modifications. Channel modifications that increase water retention time (WRT) would be expected to favor increased net production of phytoplankton and

more autotrophic metabolism (Söballe and Kimmel 1987, Reynolds 1994). WRT will usually still be short compared to most lakes, however, and the typical turbidity of rivers and downstream transport of organic matter may still maintain a heterotrophic metabolic balance.

The use of stable oxygen isotopes, specifically $\delta^{18}O_{DO}$, provides an additional oxygen budget and thus offers the potential to enhance our understanding of metabolic processes in aquatic systems. This technique has been used to infer P:R ratios in a variety of systems (Quay et al 1995, Wang and Veizer 2000, Russ et al 2004, Wang et al 2008). The most common approach has involved the use of a steady-state model (Quay et al 1995). However, P:R ratios have not always been consistent with dissolved oxygen and $\delta^{18}O_{DO}$ data when violation of the steady state assumption is suspected (Wang et al 2008). Variations of the steady-state approach (daily mean value) have been used in more productive water with positive results (Tobias et al 2007). However in highly productive systems that exhibit significant diel oxygen cycling, the use of a non steady state model is likely more applicable (Venkiteswaran et al 2007). This study represents the first time that stable oxygen isotopes have been used to assess metabolic balance in a large, eutrophic river system and provides the opportunity to test both a non steady-state and a modified steady state approach.

Understanding the metabolic functioning of large rivers is crucial as these in-river dynamics will significantly impact the functioning of near shore ecosystem of the lakes they discharge into. Nutrient loading via tributaries has been shown to account for a significant percent of total loading in Lake Erie (Fraser 1987), and due to their close association with terrestrial systems, rivers are expected to generally have high

concentrations of nutrients compared to the lakes they discharge into (Wetzel 2001, Kalff 2002). This is likely true to a larger extent in rivers whose watersheds are dominated by human activity. However large amounts of production have the ability to transform these nutrients into organic forms. Knowledge of river discharge is of particular interest for proper lake management. This is especially important in the Great Lakes where dreissenid mussels and benthic algae, such as *Cladophora,* are likely altering the functioning of the nearshore ecosystem (Hecky et al 2004).

The present study provides the opportunity to examine nutrients, phytoplankton and oxygen dynamics in order to understand the metabolic balance in the lower 30 kilometers of the Grand River. The application of stable oxygen isotopes allows the comparison of this relatively new method to more traditional methodology. As well, here I can specifically determine how nutrient cycling in the lower Grand River affects nutrient forms being discharged into Lake Erie, and, in a general sense, provide insight into whether tributaries of the Great Lakes can be seen as sources of inorganic or organic nutrients.

Material and Methods

Sampling Sites

Sampling was conducted at 10 mid-channel sites and 3 shore sites. The 3 shore sites are located in the towns of York, Cayuga and Dunnville. The Cayuga site is located less than 0.5km upstream of site 1, while the Dunnville shore site corresponds to mid channel site 6. As the Dunnville and Cayuga shore sites are very close to sites 1 and 6 respectively, they are referred to as such throughout this chapter. The location of all sites is shown in Figure 2.1. A low head dam is located in the town of Dunnville, between sites 6 and 7.

The 10 mid-channel sites were sampled during July and August, and sites 1 through 6 were sampled in June and October in 2006. In 2007 the 10 sites were sampled once a month from May to August and also in October. The mid-channel sites were sampled from a boat over the course of 2 consecutive days; sites 1 through 6 on the first day and the remaining sites the next. The shore sites were sampled approximately monthly starting after ice- out until the first mid-channel survey in 2006. During 2007 the shore sites were conducted approximately monthly from ice-out until August. In 2006 the shore sites were sampled by lowering instruments from bridges. Due to problems with this approach, in 2007 the shore sites were sampled by wading offshore to a depth of approximately 1m, or when possible from a boat dock.

The results from surveys conducted from May through August were considered to represent summer conditions. This is due to the fact that discharge levels are expected to remain relatively stable during this time (ie., large discharge events will not disrupt the system as frequently as other seasons), as well during this time day length > night length.

Samples prior to May are considered to represent spring, while samples after August represent fall. The results presented in this chapter generally represent summer average values and include only the mid-channel sites. However results from all mid-channel and shore surveys are presented in appendices 1 and 2 respectively.

Figure 2.1 This Figure outlines the location of the 10 sampling sites. Cayuga is located just upstream of site 1 while Dunnville is located between sites 6 and 7. A low-head dam is located between sites 6 and 7. Fringing wetlands begin around site 4, but become a prevalent feature of the system from site 7 down to Lake Erie.

Diel sampling

Sampling the same site over the course of 24h was done during both field seasons. In 2006 site 6 was sampled during July and August, while in 2007 sampling was at site 6 in May and June, and sites 1 and 6 in July and August. In all cases sampling was done from shore as explained above, and conducted the day before or in most cases the day after the 2 day mid-channel survey. Dissolved oxygen and $\delta^{18}O_{DO}$ were sampled at 3h intervals throughout the 24h period, with the exception of the early morning at site 6. At times sampling was less frequent at site 1. All diel oxygen measurements are presented in appendix 3.

River Flow

River discharge was provided by Tom Arsenault of the Environment Canada Water Survey. The discharge was measured at Brantford, Ont. and represents the most downstream site available along the Grand River. Between Brantford and the study reach a few small tributaries empty into the Grand, and that may slightly affect the final discharge values along the study reach. However the discharge from these tributaries is relatively minor compared the river and so the discharge pattern observed at Brantford will accurately reflect changing water conditions along the study reach.

Depth measurements

Depth at each site was measure using a Hummingbird fish finder. At each mid-channel site the depth was measured at 5 points of approximately equal distance across

the river. These values were then averaged to provide a reasonable estimate of the river depth at each site.

PAR measurements

PAR measurements were taken using a Li-Cor cosine underwater quantum sensor. An initial reading was taken at the surface followed by readings at 0.25 meter intervals down to 1.5 meters or until light was less than 1% of the surface value. The attenuation coefficient (K) was estimated as the slope of the regression of ln (PAR) on depth (z) (Kirk 1994). The euphotic depth was defined as the depth at which 1% of incident PAR remained and was determined using the formula:

$$z_{eu} = -\ln(0.01)/K$$

Oxygen Measurements

Dissolved oxygen concentrations, conductivity and temperature were measured using a YSI 600XLM oxygen meter (Yellow Springs Instruments). Calibration was done according to the manufacturers instructions. Briefly, the conductivity calibration was done the day before sampling using a known standard. The meter was calibrated for oxygen each day prior to sampling the first station. With a damp towel wrapped around the sensor to create an air saturated environment the meter was calibrated according to local air pressure as measured with a barometer. At the end of each sampling day the meter was recalibrated to ensure no drift greater than 3% had occurred. The oxygen sensor membrane was changed prior to each mid-channel survey trip. The membrane was

changed at least 24hrs prior to using the meter to ensure it had completely settled prior to calibration.

Prior to profiling, the meter was lowered to a depth of approximately 1m and left for a minimum of 5 min to stabilize. It was then slowly lowered through the water column. After completion, the profile was uploaded and viewed to ensure the meter had run properly. The profiles were then exported as excel files to allow interpretation of the profiles. First any unreasonable values were removed. This generally occurred during the initial recordings as the meter was stabilizing. The values recorded between depths of 0.5m – 1.5m were then averaged and this value is presented in the results. This was done because the water chemistry and Chl *a* samples were sampled in this depth range. In the event of possible water column stratification this would ensure all values reported represent the same section of water.

Oxygen isotopes

Samples for $\delta^{18}O_{DO}$ were collected in 160 ml bottles that had been pre-evacuated. Prior to evacuation, 300mg of sodium azide was put in the bottles to prevent any biological activity. When sampling from shore, syringes were held underwater and tapped to remove air bubbles, then inserted into the evacuated bottles, which were kept underwater until full. When sampling the mid-channel sites samples were collected in Niskin bottles. A piece of clean tubing was attached to the outflow of the bottles and a syringe was then secured to the tubing. Water was allowed to flow through for at least 30s to remove any air bubbles before the bottle was filled.

$\delta^{18}O_{DO}$ samples were analyzed according to the methods outlined in Wassenar and Koehler (1999), on a Micromass Isochrom μG mass spectrometer.

Phytoplankton community

The phytoplankton composition analysis was conducted by Farrah Chan, a 4th year biology undergraduate student for her honors thesis. Briefly; the water column was vertically profiled using a Fluoroprobe (BBE). The Fluoroprobe emits 5 different wavelengths of light which correspond to the dominant algal pigments in the major groups of freshwater phytoplankton. By measuring the resulting fluorescence, the instrument is able to determine the group composition. Phytoplankton samples were also collected during water chemistry sampling and preserved with a solution of Lugol's Iodine. Selected preserved samples were analyzed using a compound microscope to ensure accuracy of the Fluoroprobe.

Water Chemistry and Chl *a*

Water samples were collected from the mid-channel sites using a Niskin bottle lowered to a depth of 1m. Samples were kept in a dark cooler until they could be processed. In all cases, samples were processed within 10h after collection. Water was passed through 200μm nylon screen to remove large particles prior to filtration. Three replicate samples were collected from each site which were then averaged. Chlorophyll *a* (Chl *a*) was determined by filtration on GFF filters, which were immediately frozen until analysis. Chl *a* was passively extracted for 20-24 hrs in a 90:10 acetone-water mixture.

Samples were then measured on a 10-AU-005 Fluorometer (Turner Designs) before and after the addition of 3 drops of 1N HCL.

Samples for TSS were collected on GFF filters that were combusted at 500^{o}C for 4h and then pre-weighed. Prior to re-weighing the filters, they were allowed to dry at 60^{o}C for at least 24h.

Particulate organic carbon (POC) and particulate organic nitrogen (PON) were collected on pre-combusted GFF filters. Analysis was done by combustion on a CE-440 Elemental Analyzer (Exeter Analytical Inc.)

Dissolved organic carbon (DOC) samples were passed through pre-combusted GFF filters and 30ml was collected in acid-cleaned, pre-combusted vials. 0.3ml of 50% phosphoric acid was added to the samples. Samples were then analyzed on a Dohrmann DC-190 (Rosemount Analytical) using high temperature combustion.

Soluble reactive phosphorous (SRP) samples were passed through 0.2µm polycarbonate filters into acid-cleaned polycarbonate containers. SRP was measured using the spectrophotometric molybdate blue method (APHA 1998). Analysis was preformed on an Ultrospec 3100 pro spectrometer. Total phosphorous (TP) analyses were preformed on whole water samples. Analysis was preformed by digestion with potassium persulfate for 30min in an autoclave. Analysis then followed the same protocol as SRP (APHA 1998).

Nitrate and nitrite were measure on whole water samples. Nitrate was measured by ion chromatography on a Dionex ICS 2500 equipped with an anion separator column AS22 with an AG22 guard column. Nitrite was analyzed by the addition of sulphanilamide and NNED and run on an Ultrospec 3100 pro spectrophotometer.

POC – Chl *a* relationship

The methodology briefly explained here was taken from Descy and Gosselain (1994), and is used to estimate the contribution of algal biomass to POC. When a regression of POC on Chl *a* is produced the slope represents the C:Chl *a* ratio. The Chl *a* concentrations at each site are then multiplied by the ratio to estimate the algal POC. The difference between the algal POC and total POC is simply referred to as non-algal POC. The Y-intercept of the regression approximates the initial non algal carbon entering from the upstream region.

In order for this approach to work a reasonably large range in Chl *a* concentrations is required. For this reason all summer values from both years were pooled together to produce the regression. The reason that summer values were used was that discharge levels are relatively constant and thus allochthonous input, and corresponding non algal inputs, are expected to be relatively equal. Including spring or fall values would likely violate this assumption.

Diel curve analysis - Diel DO method

The 4 factors that control the rate of change in oxygen concentrations can be presented in the mass balance equation:

$$\text{Equation 1: } d[O_2]/dt = (G/Z)\,([O_2]_s - [O_2]_w) - R + P + A$$

where $d[O_2]/dt$ is the measured change in oxygen concentration per hour (mg/l), G is the gas exchange coefficient, Z is the average depth, $[O_2]_s$ is the oxygen concentration at saturation, $[O_2]_w$ is the measured oxygen concentration, R is oxygen lost due to respiration, P is oxygen gained due to photosynthesis, A is the accrual of oxygen from

other sources. In this section of the lower Grand River accrual is assumed to be negligible.

Estimation of gas exchange coefficients was done using the method outlined in Parker et al (2005) and will briefly be explained here. If we take the above equation and consider samples taken during dark hours, we can assume that P is zero and thus remove it from the equation. Then rearrangement of the equation allows the G/Z to be determined from the slope of a plot of $d[O_2]/dt$ vs. $([O_2]_s - [O_2]_w)$. Knowing G/Z, it can be subbed into the mass balance equation which can then be rearranged to allow estimation of R using the night time data when P is zero. As R is assumed to be constant, multiplying this value by 24h will give the daily R.

These estimates of G/Z and R can then be substituted back into the equation and this will allow the determination of P according to the measured changes in $d[O_2]/dt$. This value of P is then multiplied by dt to provide an estimate of P occurring over each sampling interval (usually 3 hrs). Addition of the P estimates from each interval will then produce estimates of P over 24hr. This value is then used in conjunction with the 24hr R estimate to determine daily P:R ratios.

Oxygen isotopes modeling

Oxygen isotopes were modeled using the non steady-state model PoRGy (Venkiteswaran et al 2007) with the help of Jason Venkiteswaran. As the model randomly chooses a starting point from a range of acceptable values, each run can provide a different answer. In order to deal with this each diel cycle was run 10 times and the average values are presented here.

A modified steady-state model, using daily mean values (dmv), is outlined in Tobias et al (2007) and was also used to estimate P:R from the isotope data. Briefly this approach involves calculating time weighted daily average values for both dissolved oxygen and $\delta^{18}O_{DO}$ and using the steady state model to solve for the P:R ratio, independent of gas exchange.

Results

River flow

Seasonal river flow measured in Brantford from 2006 and 2007 is presented in Figure 2.2. 2006 had several large discharge events during the spring, while 2007 had fewer, smaller such events. By approximately the end of April river flow appears to become relatively stable and reach a summer base flow. The most obvious divergence in the hydrograph between the 2 years occurred during the fall. The fall of 2006 was dominated by frequent, large discharge events, but during 2007 the flow remained at summer levels throughout most of the fall. The observed spikes in river flow in the spring were likely the result of a combination of snow melt and rainfall, while spikes throughout the rest of the year were attributable to rainfall. There were more and larger summer discharge events in 2006 (Fig 2.3). The average flow was significantly greater in 2006 than in 2007. (34.8 vs. 25.9m^3/s)

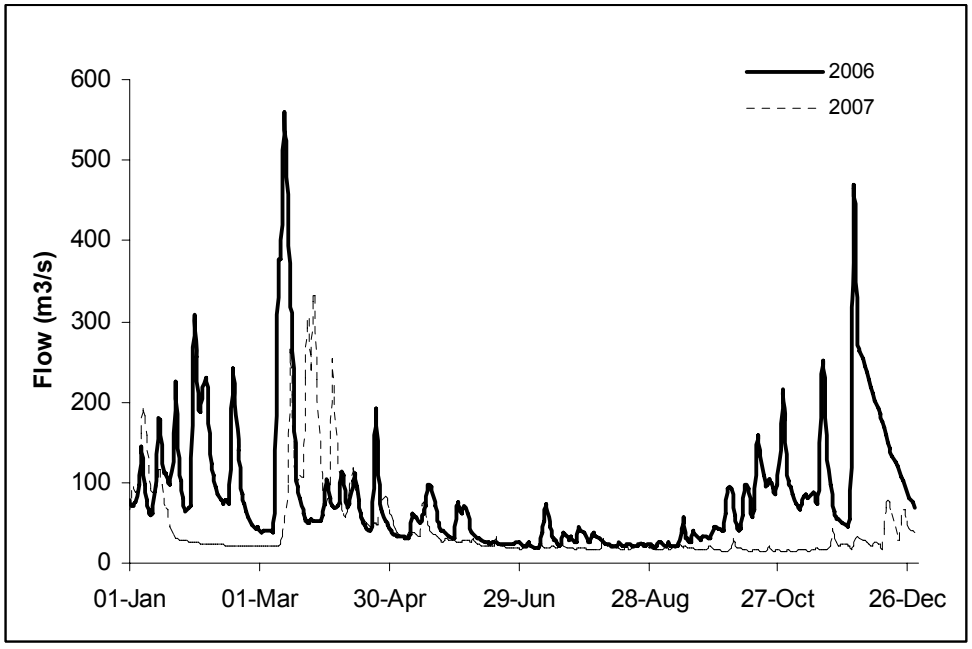


Figure 2.2 Grand River discharge at Brantford over the course of both sampling seasons.

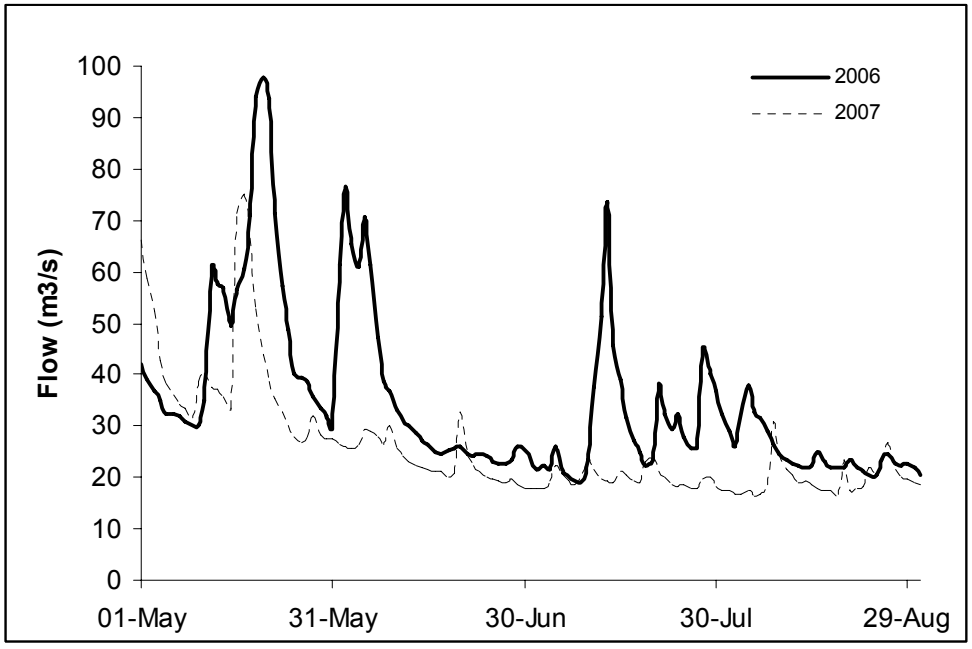


Figure 2.3 Discharge during the summer months from both sampling seasons at Brantford.

Turbidity and Light

During summer TSS values were lowest at the upstream sites (Fig 2.4). TSS was highest around the dam where the values increased 3-4 fold. In this area the river is much shallower and wider than any of the upstream sections. Moving downstream, TSS decreased but never reached values as low as upstream. Occasionally, very low concentrations were observed at the furthest downstream sites which reflect surges of much clearer lake water, as evident by large changes in conductivity. TSS was generally lower during the much drier summer of 2007 than in 2006. Note the TSS values in the fall of 2006 were highly elevated. It should be noted that this survey occurred after a significant rainfall. Light attenuation patterns along this stretch of river correspond quite well with the TSS patterns (Figure 2.5).

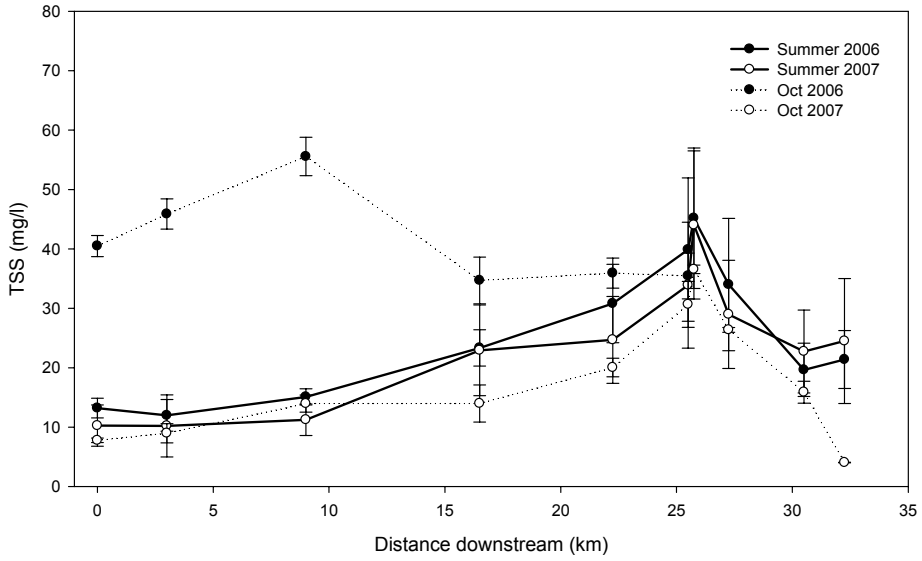


Figure 2.4 TSS from site 1 (0 on the x-axis) downstream towards Lake Erie. The symbols represent average values, and error bars the stand deviation at each site. The summer results represent all surveys conducted between May and August during the respective year.

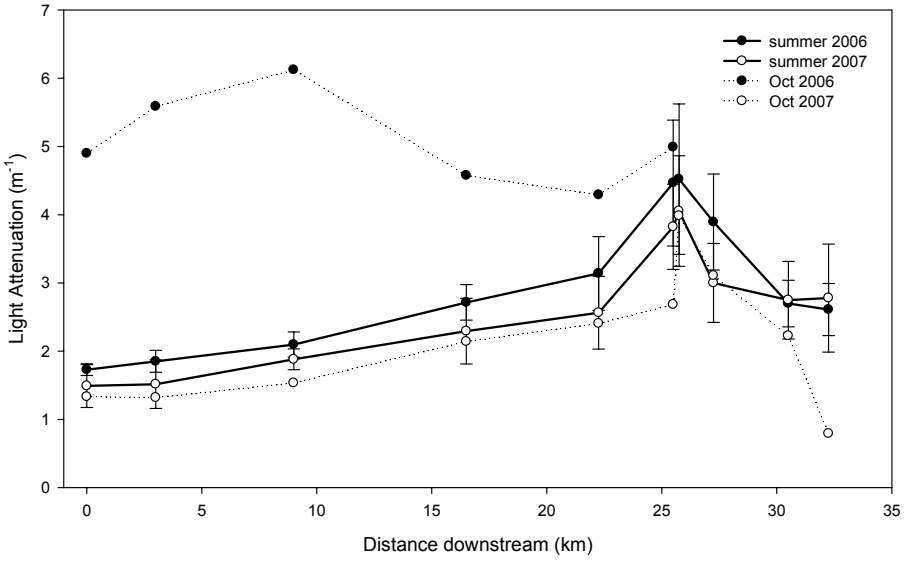


Figure 2.5 Light attenuation moving from site 1 (0 on the x-axis) downstream towards Lake Erie. The symbols represent average values, the error bars represent the standard deviation at each site. The summer results represent surveys conducted from May to August, while the October results are from a single survey.

Light attenuation values, while informative, are not enough to completely understand the light climate. The ratio of the euphotic depth to the average site depth provides information about the light environment in the water column. A ratio of 1 or greater would indicate the entire water column is in the euphotic zone. The entire water column is within the euphotic zone only in the upper 5km of the study reach (Figure 2.6). Below this point the combination of decreasing light penetration and increasing depth leads to light being attenuated well before the bottom. The low ratio at site 7 immediately below the dam is a function of a localized deep spot and does not accurately represent the rest of the section of river between the dam and the lake. The results from October of 2006 are much lower than any other survey and are a clear reflection of the increased light attenuation at that time.

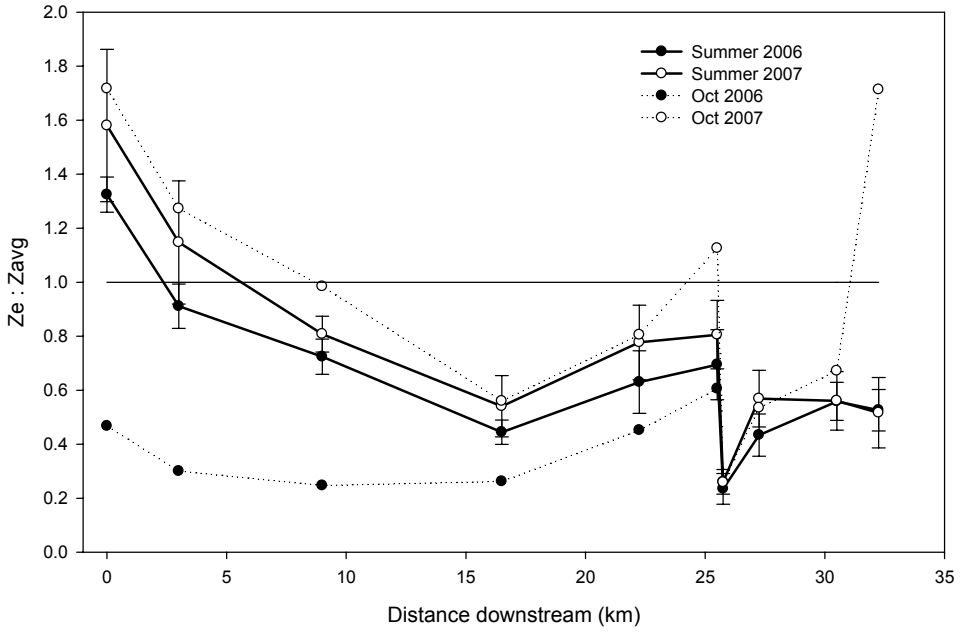


Figure 2.6 The ratio of euphotic depth to the average site depth. The symbols represent the site averages while the error bars represent standard deviation.

Phytoplankton

Despite the rapid attenuation of light, the Lower Grand River is capable of developing a significant phytoplankton population (Fig 2.7). Phytoplankton biomass as indicated by Chl *a* was lowest at the most upstream sites and increased downstream with peak values occurring above the dam. Values above the dam in excess of 100 µg/l were observed. Values during October were lower in both years but much more so in 2006. Site average Chl *a* concentrations were notably higher in 2007 than 2006. The higher error bars in 2007 resulted from elevated concentrations in July, when values above 100 µg/l were observed.

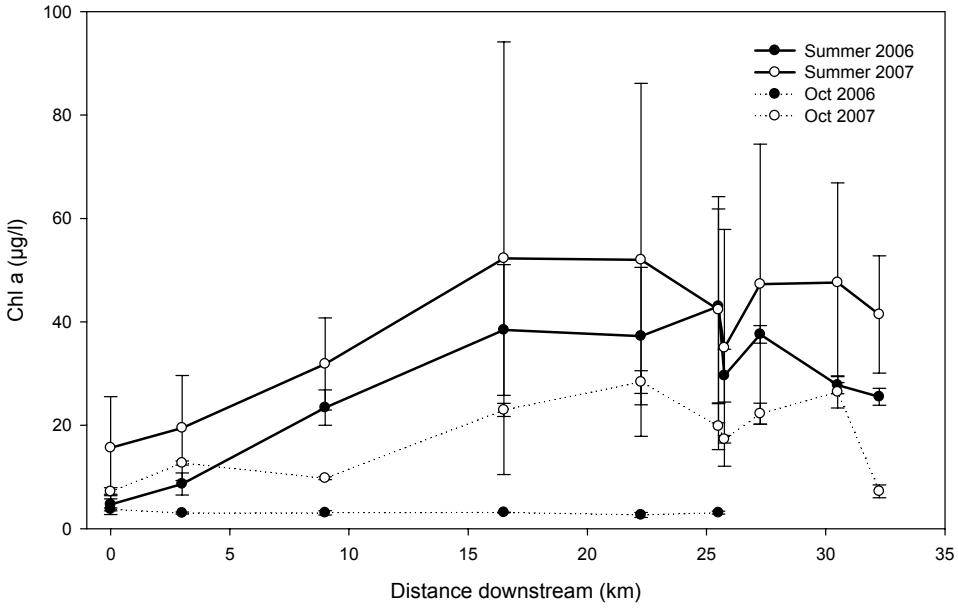


Figure 2.7 Chl *a* concentrations along the study reach. The symbols represent the average site values while the error bars represent standard deviation.

A better view of the seasonal Chl *a* pattern can be observed in Figure 2.8. A clear increase in phytoplankton can be observed during the summer in both years at the downstream site. During the summer the phytoplankton bloom may reach as far upstream as site 1, although the observed Chl *a* at this site can be variable.

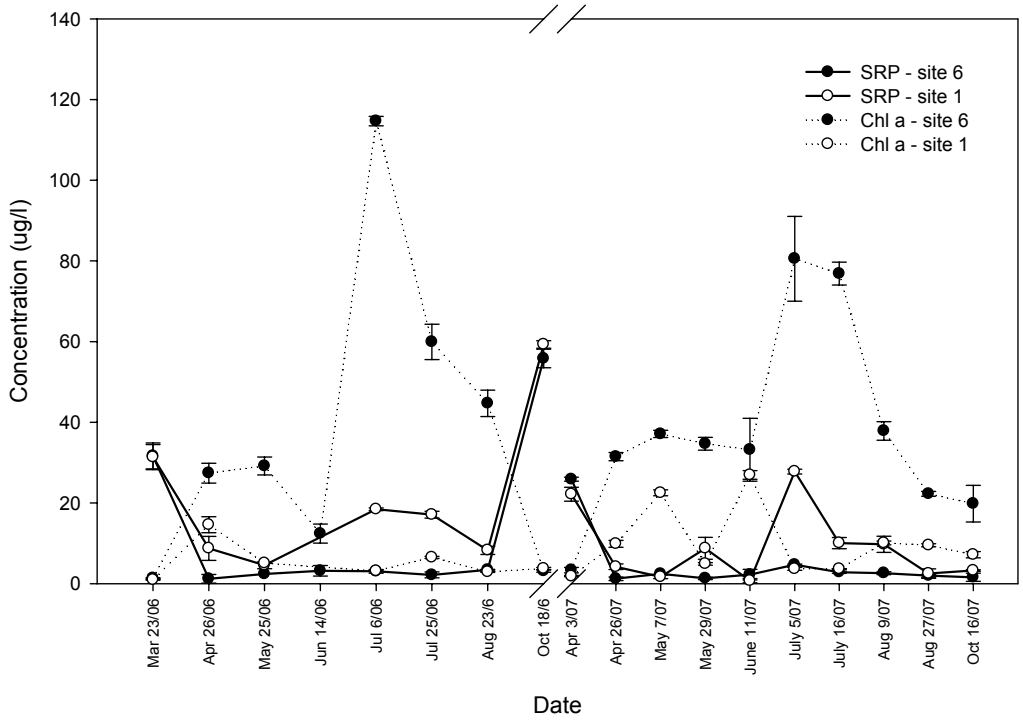


Figure 2.8 Changes in Chl *a* and SRP from spring to fall at 2 sites during both sampling seasons. The symbols represent average values for the particular day while the error bars represent standard deviation.

Fluoroprobe profiles demonstrated that while the dominant algal groups varied seasonally, Bacillariophyceae (diatoms) and Chlorophyceae (greens) were consistently the dominant groups (Table 2.1). Cyanobacteria were rarely observed, with the only exception being during the August survey when they made up approximately 5% of the population. While a seasonal shift was observed, there was little change from site to site.

Table 2.1 Changes in the dominant groups of phytoplankton during the spatial surveys conducted in 2007. The mixed group was generally dominated by Chryptophytes, but also includes Cyanobacteria.

Month	Bacillariophyceae	Chlorophyceae	Mixed
May	60%	30%	10%
June	25%	50%	25%
July	33%	33%	33%
August	35%	40%	15%
October	45%	30%	25%

Microscopic examination of selected samples confirmed the Fluoroprobe profiles were accurate at identifying the algal groups present, with R^2 values between the fluoroprobe concentrations and microscope counts of 0.61 for the diatom group, 0.54 for the green group and 0.92 for the mixed group (Chan 2008). The microscope work also determined an overwhelming majority (~70%) of the algal cells present were in the nanoplankton size range (2-20μm) (Chan 2008).

Nutrients

During the summer surveys a consistent downstream drawdown of SRP occurs at the upstream sites in 2006 (Figure 2.9). At certain times the upstream values were higher, and hence the drawdown was greater, as evident by the large standard deviations for these sites. However, no matter the upstream concentration, SRP was diminished by site 3 and remained in low concentrations down to the lake. The low range of standard deviation indicates that SRP was always low from this point down. This pattern was fairly consistent for all summer surveys in 2006. However, in 2007 this pattern was only

observed during the survey in July. During the other summer surveys SRP concentrations were very low to begin with and thus no drawdown effect could be observed. SRP also exhibits a seasonal drawdown during the summer as well (Fig 2.8).

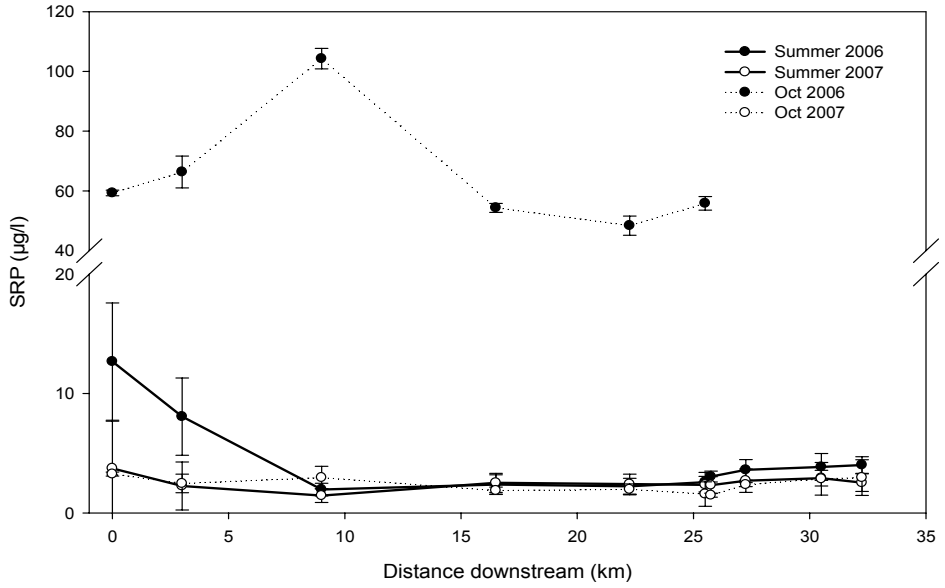


Figure 2.9 Spatial changes in SRP. The symbols represent the average values while the error bars represent the standard deviation at each site. Note the break on the concentration axis to show the much higher values in the fall.

In the spring of both years the upstream and downstream sites have very similar SRP levels. During both years we see a decline in SRP as the Chl *a* concentration increases. As expected from the above results the decline is much greater at the downstream site compared to the upstream site. In fact at times the SRP concentration at the upstream site can approach spring levels for short periods of time. In the fall of 2006 a dramatic return to high SRP levels is observed. This is in contrast to 2007 when SRP levels remained at summer lows throughout the fall sampling season.

TP concentrations show a different trend than SRP (Figure 2.10). Concentrations gradually increase up to a maximum around the dam. Following this, concentrations generally decline. Similar to SRP the concentrations of TP were higher in 2006 than 2007, with the October survey showing extremely high values. The October 2007 results are interesting as they show a spike at site 4 then a considerable decline that was not observed in the SRP concentrations. This pattern is unusual and was not observed during any other survey.

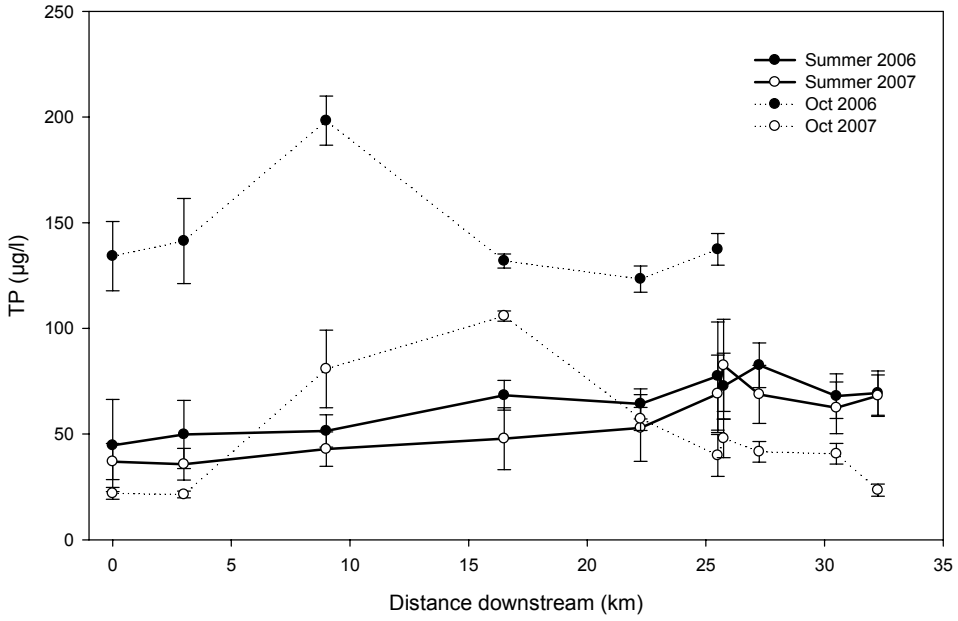
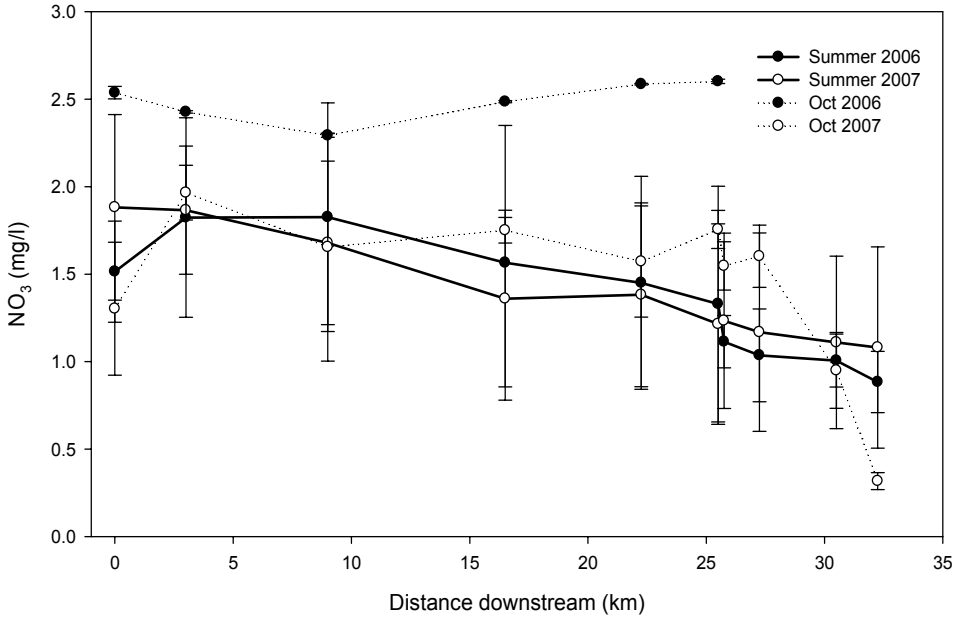


Figure 2.10 Spatial changes in TP. The symbols represent the average values while the error bars represent the standard deviation at each site.

Nitrate concentrations showed a declining trend moving downstream (Figure 2.11a), while conversely nitrite concentrations increased consistently moving downstream (Figure 2.11b). During the summer of 2006, nitrate values are typically higher than 2007 for the sites above the dam, and we observe a distinct loss of nitrate immediately below the dam. These trends are the result of elevated nitrate values observed in June 2006, which were almost double those observed in the July and August surveys of that year. As the June survey only sampled sites 2-6 the concentrations for these 5 sites were impacted while the other were not. If the results from that June survey are not averaged in with the summer surveys, the 2006 trend would appear similar to that of 2007 in shape and the concentrations would be slightly lower. Interestingly this problem is not evident in the nitrite results. Both nitrate and nitrite are elevated during the fall surveys. As well there is no distinct drawdown of nitrate during the fall.

Concentrations of PON generally follow the same spatial pattern that was apparent for phytoplankton (Figure 2.12). However while Chl *a* was consistently higher in 2007 this was not observed with PON, as in the middle reach values were higher in 2006 likely indicating terrestrial input is an important source. While the inorganic nitrogen concentrations were elevated in the fall, PON values in the fall are generally lower than those observed during the summer, with the exception of the upstream sites in 2006. This is understandably a reflection of lower phytoplankton values at this time of year.



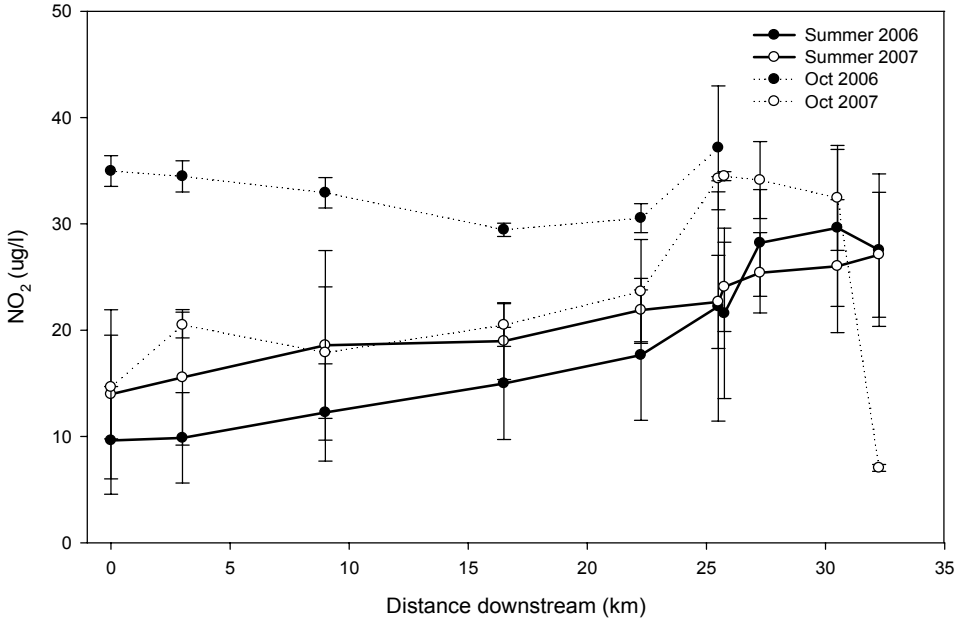


Figure 2.11 a) Spatial changes in NO_3. The symbols represent the average values while the error bars represent the standard deviation at each site. B) Spatial changes in NO_2.

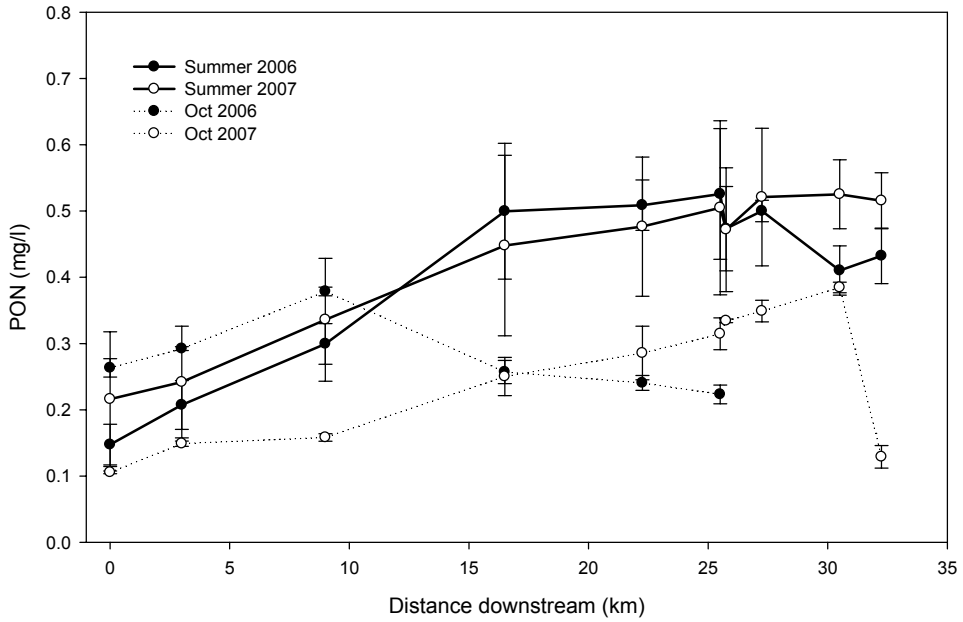


Figure 2.12 Spatial changes in PON. The symbols represent the average values while the error bars represent the standard deviation at each site. Note these trends are similar to those observed in Chl *a*.

Carbon

Unlike the previously discussed nutrients, there is no apparent spatial trend for DOC during the summer, as DOC remains fairly constant over this stretch of the river (Figure 2.13). Concentrations were highly elevated during the fall surveys, particularly in 2006, when the survey occurred after a significant rainfall. Both summer and fall results from 2007 appeared to show a variation among sites that was not evident in 2006. Some of the 2007 results (August) also had values more than 5 times higher than any previously reported and were not included in calculating the summer average. The oscillating pattern seen in 2007 may, therefore, not represent any biological or physical processes in the river, but rather be due to analytical error. POC on the other hand demonstrated distinct spatial trends (Fig 2.14). Generally the POC concentrations followed the same

pattern as Chl *a* and PON. However unlike PON, during the summer values were consistently higher in 2007.

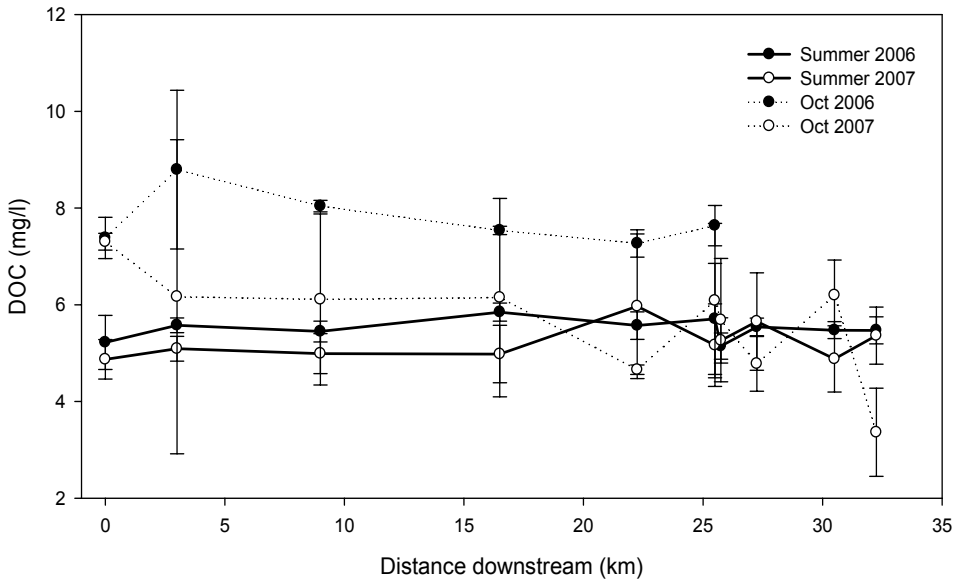


Figure 2.13 Spatial changes in DOC. The symbols represent the average values while the error bars represent the standard deviation at each site.

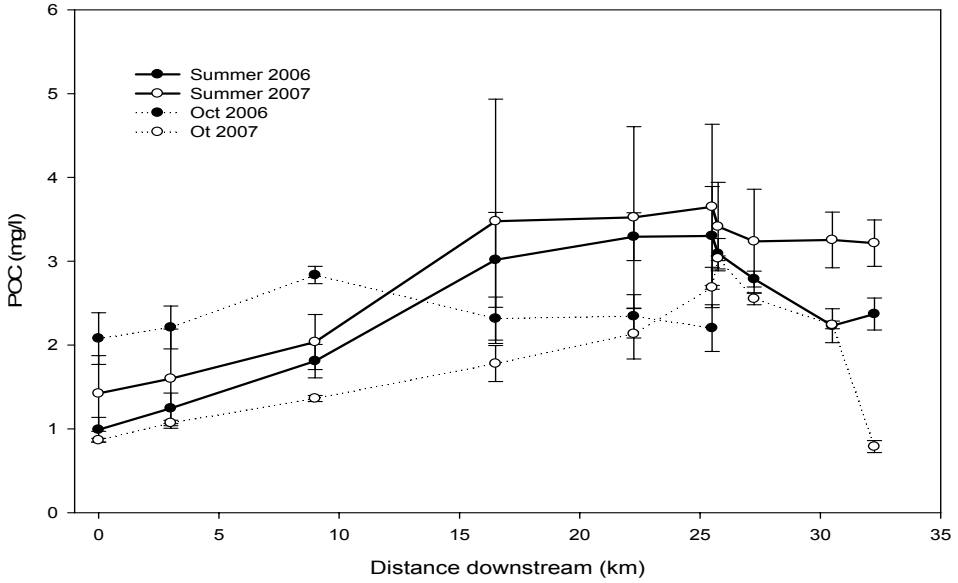


Figure 2.14 Spatial changes in POC. The symbols represent the average values while the error bars represent the standard deviation at each site. Note the POC trends are very similar to those of Chl *a*.

As expected based on the trends explained above, there is a significant relationship between POC and Chl *a* (Fig 2.15, $R^2 = 0.68$). Using this value the percentage of algal C within the total POC was determined. The intercept of the regression also indicated that approximately 1.4 mg/l of POC, averaged over the reach and the summer period, is not algal and is mostly likely due to loading from upstream reaches. At the upstream stations the algal C content makes up anywhere from 10 to just under 60% (average ~ 30%) of the POC (Fig 2.16). As we move downstream this increases to a range of 25 to 75% (average ~ 50%) of the POC. The average % algal C values peak at site 3, and then either hold relatively steady (2006) or decline (2007). Either way this peak occurs upstream of the POC and Chl *a* maxima. The percentage of algal C in the river is generally similar during the summers of 2006 and 2007, with the exception of the upstream sites in which the percentage of algal carbon is twice as high in 2007 as 2006.

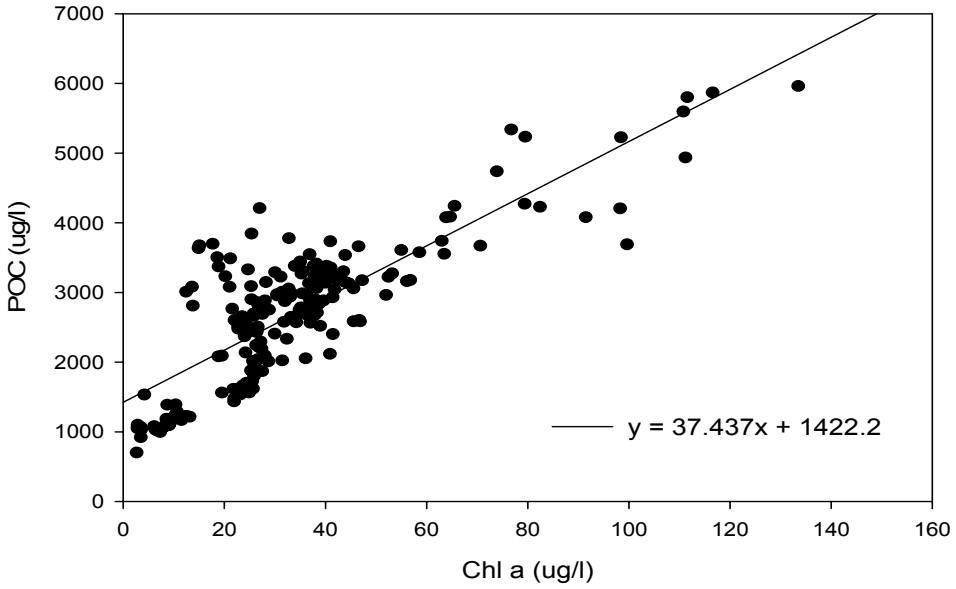


Figure 2.15 The relationship between POC vs. Chl *a* (R2= 0.68).

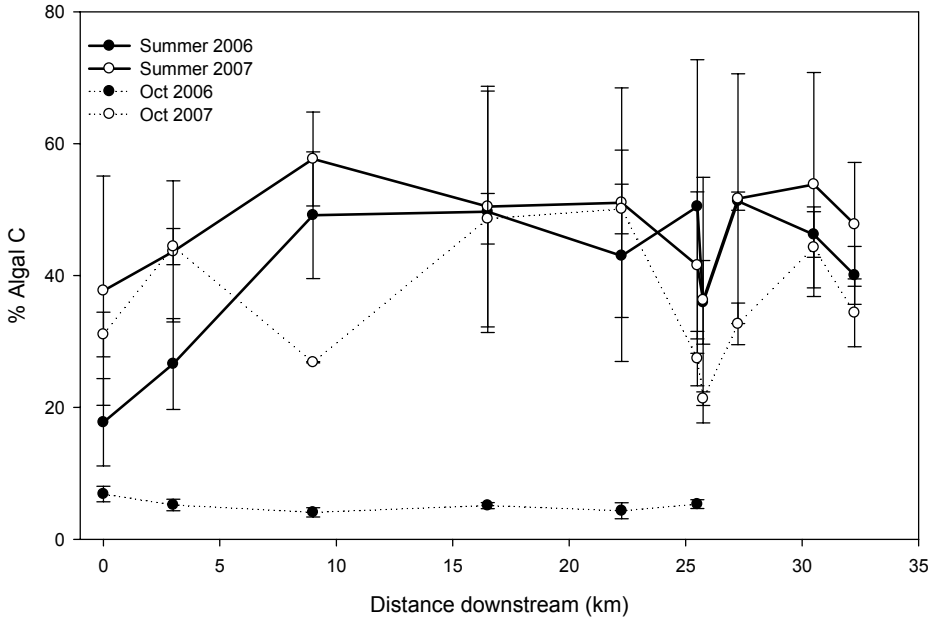


Figure 2.16 Spatial changes in % algal carbon. The symbols represent the average values while the error bars represent the standard deviation at each site.

Dissolved Oxygen and Isotopes

The seasonal and spatial distribution of dissolved oxygen and $\delta^{18}O_{DO}$ (Fig 2.17) shows that both are close to atmospheric equilibrium early in both years and at both upstream and downstream sites. In summer a dramatic increase in the dissolved oxygen percent saturation occurs at the downstream site with values generally well above the atmospheric equilibrium value of 100%. However at the upstream site dissolved oxygen is often below, and at some times, well below saturation

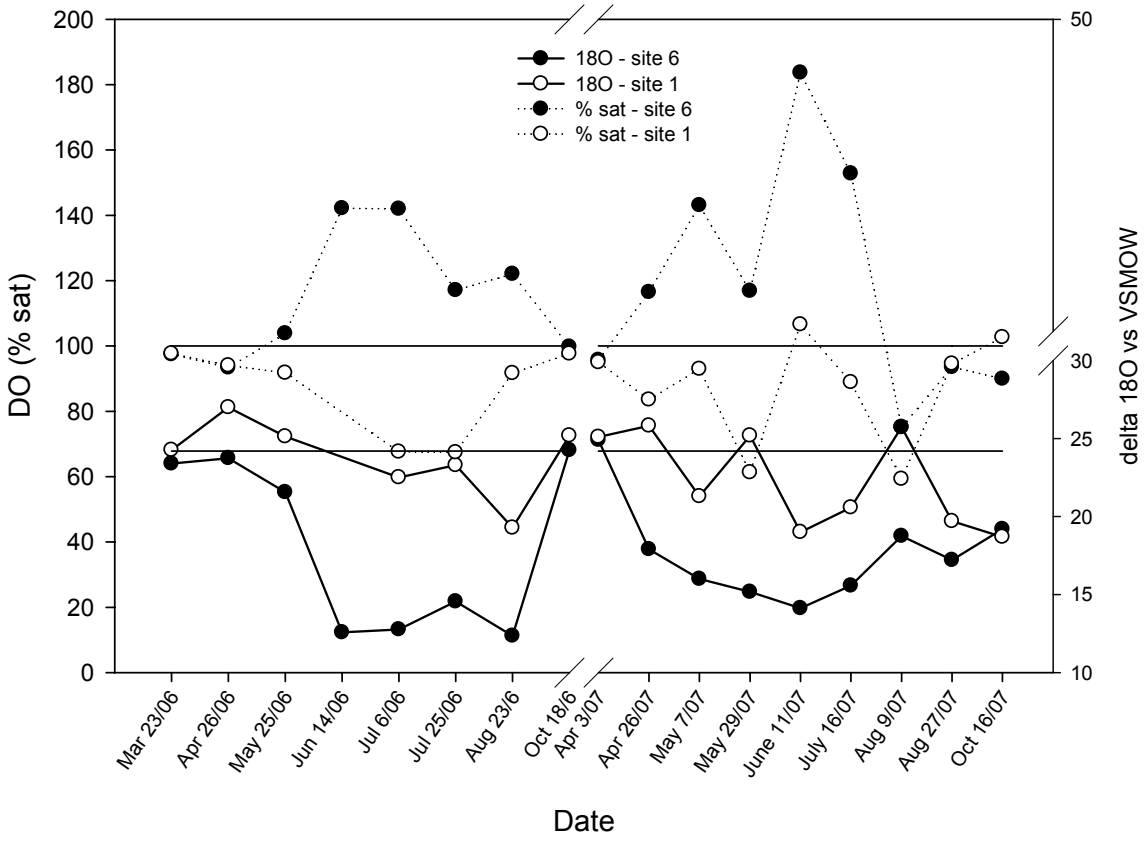


Figure 2.17 Changes in dissolved oxygen and $\delta^{18}O_{DO}$ from spring to fall at 2 sites during both sampling seasons. The symbols represent values for the particular day. The straight lines represent the atmospheric equilibrium points for both dissolved oxygen and $\delta^{18}O_{DO}$.

The $\delta^{18}O_{DO}$ values in summer also show a photosynthetic influence at the downstream site, with values dropping well below the atmospheric equilibrium. This is not observed at the upstream site, as values fluctuate between equilibrium values and those that show a slight photosynthetic influence. So, while both years behave similarly in spring and summer, a difference is seen in the fall. In 2006 both dissolved oxygen and oxygen isotope values return to the equilibrium points. In 2007 dissolved oxygen

concentrations drop back to values close to 100%, however $\delta^{18}O_{DO}$ values continued to show photosynthetic inputs.

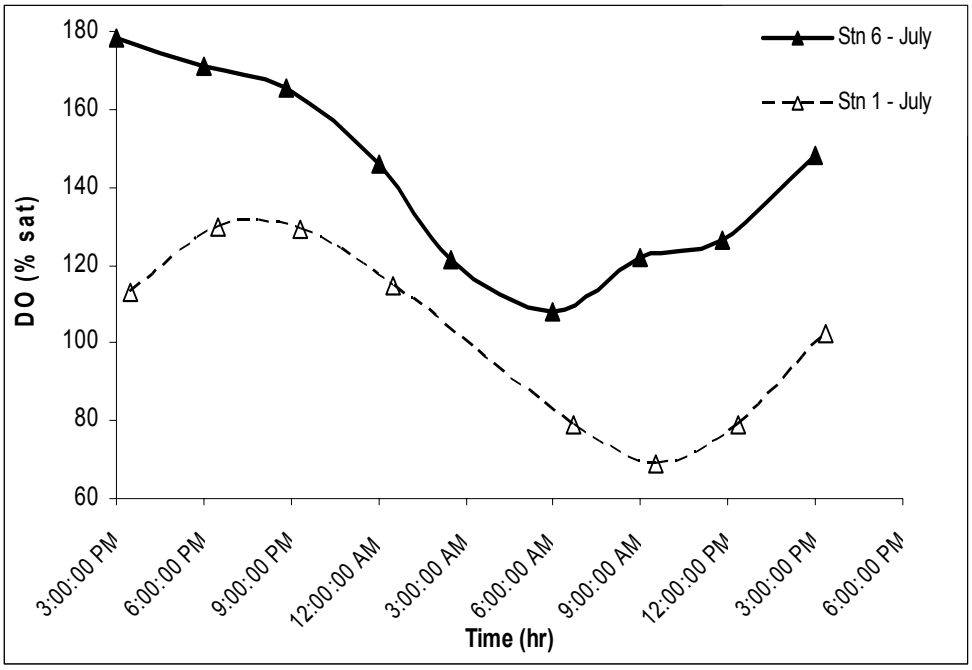


Figure 2.18 The diel oxygen cycle at both diel sites during July of 2007. Note that at site 1 concentrations are generally balance around 100% saturation while at site 6 they are almost consistently above. This Figure shows an example of the diel measurements at both sites. All diel sampling results are presented in appendix 3.

Diel oxygen observations give a more direct measure of metabolic processes occurring at individual sites. A significant diel cycle was observed over 24h at both upstream and downstream sites (Fig 2.18) and confirmed that higher levels of dissolved oxygen, usually above atmospheric equilibrium, occurred at the downstream site. Of the 6 diel cycles measured at the downstream site, 5 of them had DO averaging above equilibrium through the cycle and two (May and July 2007) had DO above equilibrium

at all observation times. Another set of diels conducted in August 2007 had dissolved oxygen levels roughly equal at both the upstream and downstream site. Dissolved oxygen concentration was also generally higher in 2007 than 2006. This occurred during both August (Figure 2.19) and July. As diel sampling was not conducted at site 1 in 2006 I cannot compare the upstream site between the years.

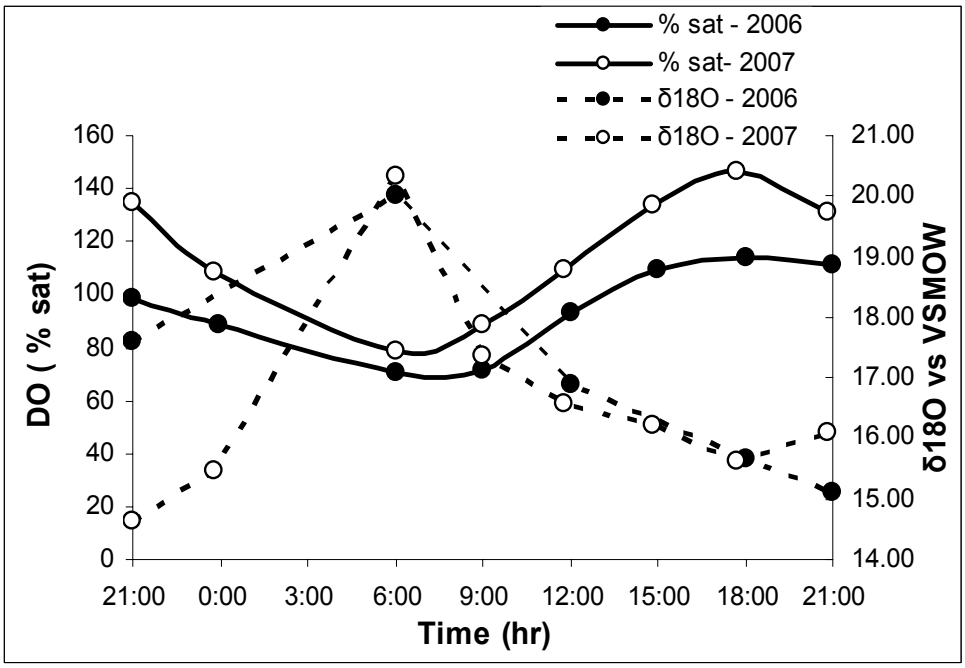


Figure 2.19 Dissolved oxygen and $\delta^{18}O_{DO}$ diel cycles at site 6 during August of both 2006 and 2007. Both oxygen balances show a stronger influence of photosynthetically derived oxygen in 2007.

The $\delta^{18}O_{DO}$ also exhibited a diel cycle which is evident in Figure 2.19, with photosynthetically produced oxygen lowering the values during the day and respiration, along with gas exchange, raising them at night. When comparing the diel cycles at the upstream and downstream sites, the downstream site generally had lower $\delta^{18}O_{DO}$ values, consistent with the dissolved oxygen results while the upstream site experienced a greater

diel cycle. The $\delta^{18}O_{DO}$ approached but did not attain the atmospheric equilibrium value of 24.2‰ in the early morning hours at both sites. In fact values >20‰ were common at the upstream site during early morning but were rarely observed at the downstream site. As seen in Figure 2.19, $\delta^{18}O_{DO}$ was slightly lower in 2007 than in 2006 during August, and this difference was observed in July as well.

Diel Curve Analysis

The analysis of the night time DO data was used to quantitatively estimate G. Of the six diels at the downstream site, 2 of them provided reliable estimates of G. The unreliable estimates were either nonsensical (i.e. negative values), provided unreasonable estimates of G, or in 1 case provided a positive intercept value. Such a value indicates a source other than gas exchange was adding a significant amount of dissolved oxygen to the system at night which clearly violates the assumptions. The diels that provided reliable estimates were those with dissolved oxygen concentrations that were generally closer to atmospheric saturation values as opposed to those that deviated far from saturation, especially during the night time. Aeration coefficients (G/Z) of 0.319 h^{-1} in July of 2006 and 0.121 h^{-1} in August of 2007 were obtained. Considering an average river depth of 1.52m at the downstream site, gas transfer velocities of 0.183 m/hr and 0.485 m/hr were calculated. From this average, values of .220 h^{-1} and 0.334 m/hr for the aeration coefficient and gas transfer velocity, respectively, were adopted for the downstream site. The average hourly areal rates of both P and R determined using this value are presented in table 2.2, with the resulting P:R ratios presented in table 2.4. This method produced an erroneous estimate for R (negative value, indicating that R was

adding oxygen) during the May 2007 survey and so no estimates of the actual P, R or P:R ratios could be made. The absolute rates of P and R were higher when estimated from the diel DO estimates alone than when using PoRGy to incorporate information from the isotopic composition (Table 2.3). Both methods suggested that rates of P and R could vary widely over time during the summer season and between years. Times of higher P (June and July, 2007) were associated with higher values of P:R as well.

Table 2.2 Average hourly P and R rates as estimated using the diel DO estimate method and the non steady-state isotope model PoRGy for the diels conducted at site 6.

Date	Dissolved oxygen curve		PoRGy	
	P (mgO2/m2/hr)	R (mgO2/m2/hr)	P (mgO2/m2/hr)	R (mgO2/m2/hr)
July 2006	680	540	448	366
Aug 2006	758	959	545	652
May 2007	/	/	/	/
June 2007	1632	433	956	375
July 2007	1283	399	764	594
Aug 2007	1179	975	637	482

A closer look at the PoRGy results is displayed in table 2.3. It appears that gas exchange rates estimated at site 6 are generally higher than those at site 1, and the α_r values show less isotopic discrimination at site 1, though I cannot make any strong conclusions due to limited results at site 1. PoRGy was consistently successful at fitting the dissolved oxygen concentrations as indicated by the R^2 values and Fig. 20, with the exception of June 2007. The model had difficulty fitting the $\delta^{18}O_{DO}$ cycles at site 6, but was much more successful at site 1 (e.g. Figure 2.20). This is especially apparent in July 2007 and may account for the odd estimates of G and α_r at site 6. It appeared difficult for

PoRGy to explain the often relatively small diel cycle in $\delta^{18}O_{DO}$ compared to the larger dissolved oxygen cycle.

Table 2.3 Estimated P:R ratios, α_r values, and gas exchange coefficients along with the R^2 values for the dissolved oxygen and $\delta^{18}O_{DO}$ as estimated by PoRGy. The May 2007 survey did not provide reasonable values and so is not included here. These values represent the average of 10 separate model runs. All results are from site 6 unless noted.

Date	P:R	G (m/hr)	α_r	R^2 DO	R^2 $\delta^{18}O_{DO}$
July 2006	1.21	0.275	0.991	0.886	0.470
Aug 2006	0.82	0.167	0.989	0.869	0.741
June 2007	2.62	0.179	0.996	0.485	0.411
July 2007	1.29	0.064	0.975	0.884	0.198
Aug 2007	1.32	0.160	0.998	0.926	0.524
Site 1 July 2007	0.94	0.080	0.981	0.696	0.834
Site 1 Aug 2007	1.15	0.083	0.984	0.927	0.938

The dmv method, which uses diel-average values of DO and $\delta^{18}O_{DO}$ to estimate P:R from a steady-state flux model, provided results consistent with those obtained by the diel DO estimates in five of the eight diel cycles. The result from June 2007 was much lower than other estimates, however, while estimates for May and July of 2007 were clearly erroneous (negative; Table 2.4). The P:R ratios derived from PoRGy were otherwise consistent with those derived from the diel DO estimates except in July 2007, when the PoRGy ratio was almost 50% lower. PoRGy was nonetheless unable to fit the cycle observed in May 2007.

Table 2.4 P:R ratios from the diels at site 6 during the summers of 2006 and 2007 using the 3 methods of evaluation. Also included are the minimum and maximum % saturation values observed to provide an idea of the magnitude of the oxygen cycle. The ratios in brackets are results from site 1. Lack of night time observations prevented the use of the dissolved oxygen diel curve method.

Date	Max % sat	Min % sat	P:R - DO	P:R - dmv	P:R – PoRGy
July 2006	123	88	1.26	1.09	1.21
Aug 2006	114	70	0.79	0.93	0.82
May 2007	130	113	N/A	-1.47	N/A
June 2007	170	88	3.71	1.31	2.62
July 2007	178	108	3.22	-0.09 (1.02)	1.29 (0.94)
Aug 2007	146	79	1.22	1.22 (1.22)	1.32 (1.15)

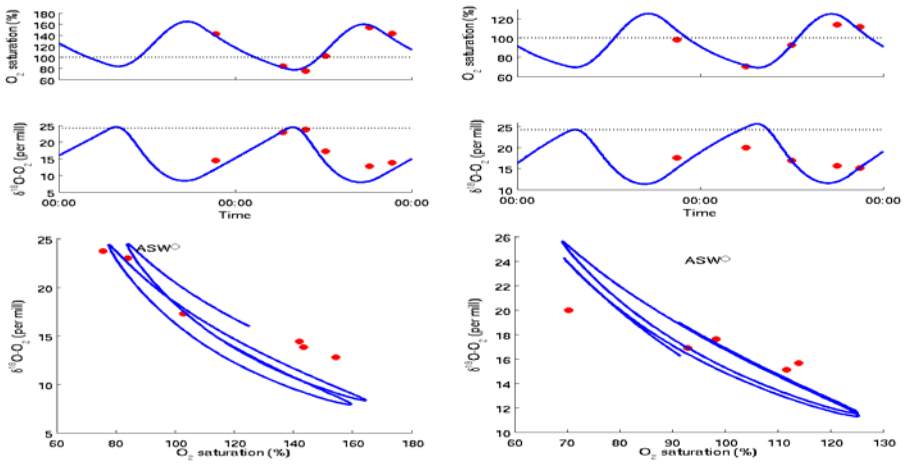


Figure 2.20 PoRGy's attempt to fit dual oxygen curves during Aug 2007. The curve on the left is from site 1 while the right is site 6. The upper curve is the dissolved oxygen, the second $\delta^{18}O_{DO}$, while the lower plot is $\delta^{18}O_{DO}$ vs. dissolved oxygen. The R2 for the $\delta^{18}O_{DO}$, at site 6 is 0.524 and this represents one of the better isotope fits at this site.

Discussion

The lower Grand River is capable of generating a significant phytoplankton population during the summer months. The observed species composition is quite similar to what was observed in the Meuse River, a large eutrophic river (Descy et al 1987). The phytoplankton was dominated by smaller cells in the nanoplankton size range. This agrees with the work of Chételat et al (2006) who found that smaller plankton will dominate in river systems regardless of the nutrient concentrations or water residence times (WRT). However, the average Chl *a* concentration from the rivers in their study was quite low (< 7µg/L). The results presented here demonstrate that this concept may hold true for rivers with larger phytoplankton biomasses as well. Smaller cells generally have greater photosynthetic efficiency, and faster growth rates, and are therefore better suited to the lower light and short WRTs that are common in rivers (Reynolds 1994). These smaller sized phytoplankton are optimal size as prey for zooplankton (Kalff 2001), and this autochthonous production is an important source in river food webs (Thorpe and Delong 2002). This is probably the case in the Grand River, although the high turbidity levels may interfere with zooplankton feeding (Wofsy 1983). It is also important to note that cyanobacteria are relatively rare along this section of river. Cyanobacteria are common in eutrophic lakes and are associated with a variety of problems including water fouling and toxic effects on various organisms (Kalff 2001) but these observations in the Grand River suggest they are less prominent in eutrophic rivers, perhaps because of greater turbulence and mixing energy (Reynolds 1994).

Consumption of inorganic nutrients, coupled with increases in particulate organic matter and phytoplankton abundance, was clearly evident from spring to summer and

with distance downstream in the lower section of the Grand River during the summer. This evidence supports the theory that *in situ* growth of phytoplankton is capable of significantly modifying nutrients in the lower reaches of large, eutrophic rivers (Admiraal et al 1992). NO_3 exhibited a decreasing trend along most of the study reach, while SRP concentrations declined over a short distance, coincident with the rise of phytoplankton concentrations. Diel dynamics could have contributed to the longitudinal patterns of SRP, as upstream sites were sampled earlier in the day, but measurements conducted every 4 hours during the diel survey in July 2007 revealed no significant diel variations of SRP so the longitudinal trend was most likely related to the accompanying increase of phytoplankton. The more continuous pattern of NO_3 decrease along the reach may partly reflect the abundance of this form of nitrogen relative to phytoplankton needs but may also reflect additional processes peculiar to the nitrogen cycle. The increase of nitrite along the study reach suggested that denitrification or other microaerobic processes may be important. For both SRP and nitrate, however, the drawdown of concentrations was strongly dependent on season. In non-summer conditions (e.g. March and October 2006) I observed relatively low Chl *a* and little or no inorganic nutrient drawdown, consistent with limitation of phytoplankton growth by lower solar radiation and increased discharge and turbidity. Similar seasonality has been previously observed in the Meuse River (Admiraal et al 1992). The observation of relatively high Chl *a* levels coupled with low inorganic nutrient values in the very dry fall of 2007 demonstrates the importance of discharge to phytoplankton dynamics. The continuation of low, summer-like, discharge levels permitted conditions favorable to autochthonous production to continue into the fall despite the seasonal decrease of incident solar radiation.

A strong correlation between Chl *a* and POC was observed. The C:Chl *a* ratio of 37.437 is very similar to what Descy and Gosselain (1994) observed in the Meuse River, and is within the expected C:Chl *a* values in such systems (Riemann et al, 1989). Over the course of both summers algal carbon accounted for an estimated 45% of the total POC throughout the entire study reach. This value compares favorably to values obtained for several other large eutrophic rives such as the R. Rhine (15-65%), R. St. Laurent and R. Ebro (55%), R. Meuse (58%), and 50% for the R. Loire (Descy and Gosselain, 1994), as well as 15-65% for the Meuse River (Admiraal et al 1992). Using the values calculated for algal C, and assuming phytoplankton nutrient composition follows the Redfield ratio, approximately half of the TP exported out of this reach, on average, may be contained within the phytoplankton during summer months. Furthermore, at certain times almost all of the TP may have been algal. It therefore seems clear that the Grand and other large eutrophic rivers can develop large phytoplankton populations that play a major role in the particulate and dissolved nutrient properties. Such results suggest, but do not establish, that the system metabolic balance may contradict the expectations of the RCC that P should be less than R.

Both the dissolved oxygen and stable oxygen isotope results imply P>R during the summer, shifting to P≤R throughout the rest of the year. It is hard to envision a scenario in which dissolved oxygen is consistently above saturation during a full diel cycle, yet daily production is less than respiration. The quantitative estimates support the idea that P>R. Thus I agree with the notion put forth by Descy and Gosselain (1994) that large rivers, although assumed to be heterotrophic by the RCC, can in fact be autotrophic for at least part of their course and for part of the year. However the metabolic balance

certainly exhibits a seasonal trend. An autotrophic metabolic balance likely begins during the late spring and shifts to a balanced or heterotrophic metabolism during the fall. It should be noted that even though the lower Grand is autotrophic the cyclical nature of dissolved oxygen presents the potential for occasional periods of spatial and temporal anoxia. Such problems have previously been recorded at select areas along this stretch of river (MacDougall 2007).

Clearly the near shore ecosystem in Lake Erie, in the case of the Grand River, will be strongly impacted by metabolism in the river. Like many lakes, Erie and the other Laurentian Great Lakes are managed and modeled on the assumption that rivers provide inorganic nutrients that subsequently fuel in-lake phytoplankton production, which in turn supports higher trophic level production but can also drive a variety of water quality problems (e.g. Lam et al. 1987; Jeppesen et al. 2005). For much of the year this assumption may be reasonable, but when loading is in fact largely in particulate organic form then the implications for in-lake processes are quite different. For example, Erie is one of the many lakes that now support large populations of filter-feeding dreissenid mussels, and the mussel-dominated nearshore benthic system is well-placed to retain, or at least detain, particulate nutrients from tributaries (e.g. Nicholls et al. 2001). Such nutrient retention may be linked to growth of nuisance algae, specifically *Cladophora*, and other challenges for nearshore lake management (Hecky et al 2004), even if available inorganic nutrient concentrations are relatively low.

The diel DO estimates produced plausible estimates of P, R and P:R ratios but did pose problems insofar as only two of the six diels provided reasonable estimates of G, though the gas transfer velocity used in the diel DO estimates falls in the range of values

that covers moderate – G environments (Venkiteswaran et al 2008), which the Lower Grand River can be expected to generally behave as. This may reflect uncertainties surrounding G in large rivers, compounded by sparse sampling density. Estimates of G in the literature vary significantly depending on the formulas used (Raymond and Cole 2001, Jha et at 2004). Estimates specific to the system and period of interest are therefore desirable, even if an indirect estimation must be used (Parker et al, 2005). The night time data method (Parker et al 2005) requires the assumption of a constant G. However, large rivers, which can experience a wide range of gas exchange rates (Raymond and Cole 2001), are likely to be strongly influenced by wind conditions which typically vary over the diel period and drive corresponding variations in G (Crusius and Wanninkhof 2003). Wind speed values measured by Environment Canada in Hamilton, Ontario (approximately 30km NNE of Dunnville) support the idea that changing wind conditions were at least partly responsible for some of the unreliable G estimates. Hourly measures during the diel periods are presented in appendix 4 and attest to the variability in wind speed. During the diels that produced reliable results the absolute differences in wind speed during the night time period (9:00pm – 6:00am) were 3 and 5 km/h. During the 4 diels that produced unreliable estimates the absolute differences were 3, 7, 11 and 22 km/h. As the night time data points are limited, if even one is altered as a result of changing G rates, the method may give incorrect results. This is especially problematic in the Southern Grand River, or potentially any system in which the dissolved oxygen levels deviate so far from the atmospheric equilibrium point. As dissolved oxygen concentrations move further away from atmospheric equilibrium they are subject to a stronger influence via gas exchange, and so if the assumption of a constant G is invalid

the results will suffer. Taking this into consideration it is not surprising that the two diels that provided reasonable estimates of G had dissolved oxygen concentrations that were generally closer to atmospheric equilibrium than those that provided unreasonable results.

To evaluate this uncertainty in gas exchange rates, a sensitivity analysis was performed, with the estimated gas exchange rate both increased and decreased by 50% to cover a wide range of possible rates. In all 5 cases in which an autotrophic balance (P>R) had been predicted, the P:R balance remained autotrophic under both increased and decreased G. I suspect this uncertainty in gas exchange may account for the inability to determine P and R values for the May 2007 survey. The small oxygen decline at night (130 – 113% saturation) indicates the average gas exchange rate of 0.22m/hr was certainly an overestimation. This in turn led to underestimating R to the point it was actually predicted to be adding oxygen. This reinforces the importance of understanding G in order to estimate P and R ratios.

Information on stable oxygen isotope composition allows the use of an additional oxygen budget to constrain P, R and P:R (Quay et al 2005, Venkiteswaran et al 2007). The first published applications of the dual isotope approach assumed a steady state model that makes knowledge of G unnecessary and supports estimates of P:R but not absolute rates of P and R (e.g., Quay et al. 1995). The pronounced diel cycles at my study sites clearly challenge the applicability of this approach. Like Tobias et al. (2007) I found that P:R ratios estimated with the steady state model from the DO and isotope data at individual times through the diel cycle (results not shown) varied widely and were often nonsensical (i.e., <0). Also like Tobias et al. (2007) I found that the daily mean value (dmv) modification of the steady state model approach still gave some unreasonable

results and cannot be considered a truly valid approach when such obvious diel cycling is apparent. When the dmv method gave plausible P:R results they were reasonably consistent with those from the diel DO analysis, but it is hard to know whether this agreement is merely fortuitous.

PoRGy (Venkiteswaran et al 2007) is a relatively realistic model for non-steady state oxygen isotope dynamics that assumes mass balance equations for each isotope that are essentially the same as specified in Quay et al. (1995) but allows for non-steady state fluxes, time-varying P and temperature-dependent R. Using iterative nonlinear regression PoRGy can estimate not only P:R ratios but also P, R, G and α_r. The estimates of G at site 6 ranged from 0.064 m/hr to 0.275 m/hr, supporting the idea that G can be highly variable at such sites. They also suggest that the sensitivity analysis of the diel DO estimates for P, R and P:R (above) used an appropriate range of G. The P:R ratios derived from PoRGy were consistent with those from the diel DO analysis and further supported the conclusion that, at least at site 6, the southern Grand did indeed have an autotrophic metabolic balance during the summer.

Increased wind exposure at site 6 mostly likely results in a higher and more variable rate of G versus site 1, though I cannot make strong conclusions due to limited data at site 1. At site 6 the river is significantly wider and more exposed than at the upstream site. The PoRGy estimates of respiratory isotopic fractionation (α_r) also differed between sites, with less fractionation occurring at the downstream site. This may be indicative of increased respiration in the sediments where oxygen concentrations may be lower than the water column (Hendry et al 2002) and respiratory isotope discrimination is expected to be relatively small (Brandes and Devol 1997). This explanation is plausible

because at site 6 the river is much wider than site 1 while the average depth is similar, allowing for a greater amount of exchange between the sediments and water column.

While the results generated with PoRGy appeared reasonable, the model did struggle to fit the measured $\delta^{18}O_{DO}$ cycle at site 6. The model generally predicted a larger diel cycle than observed. The model did quite accurately reproduce the measured dissolved oxygen cycle which was more pronounced. If the DO dynamics were dominant in determining the PoRGy results this may contribute to the good agreement of P:R between PoRGy and the diel DO analysis. The difficulty in reproducing the isotopic ratio dynamics appeared to be the reason the May 2007 diel experiment did not produce reliable results, and likely explains why the July 2007 estimates of G and α_r were much different from the others. The lower absolute estimates for P and R by PoRGy compared to the diel DO analysis may reflect the model's attempts to reconcile the larger DO cycle with the smaller $\delta^{18}O_{DO}$ cycle. The model was much better at reproducing the more pronounced $\delta^{18}O_{DO}$ cycle at the upstream site.

I propose two possibilities to explain the difficulties in modeling diel dynamics of $\delta^{18}O_{DO}$. The first involves differences in α_r, the isotopic fractionation during respiration. Changes in river depth and width will alter the sediment surface to water volume ratio, controlling the rate of exchange between the sediments and water column. This will undoubtedly affect the community α_r rate for a given area of river. If the section of river upstream of the sampling site experiences heterogeneity in this regard and the balance of water column vs sediment respiration changes during the diel cycle, then the effective value of α_r, assumed constant over the diel cycle in PoRGy, may vary. However when the model used low values of α_r the dampened diel cycle was still not reproduced, suggesting

additional processes were occurring. The PoRGy model assumes a constant rate of gas exchange over the diel cycle and this assumption may be invalid at the shallow and wind-exposed site 6. The upstream site is less exposed to wind and has higher current velocities, so more constant factors such as flow velocity and depth may be more important in controlling G (Raymond and Cole 2001, equations presented in Jha et al 2004). This possibly explains why the model explained the observed diel variations better at the upstream site. To my knowledge this is the first time stable oxygen isotopes have been used to infer metabolic balance in a large, eutrophic river ecosystem. Further studies are necessary to determine if the relatively muted diel cycle of δ^{18}_{DO} is typical of such systems and if so to understand the processes responsible. Additions or changes to the PoRGy model may be needed to fully account for processes in such large riverine systems.

Large lowland rivers are often, or even typically, modified by human structures, water usage and management practices and this can make it difficult to generalize about their behavior. In the Grand River, the presence of a low-head dam between sites 6 and 7 is one factor that alters the natural functioning of this system, partly by increasing the WRT time of the study reach from as little as 8h historically to almost 3 days currently (Gilbert et al 2004). Several investigations have linked plankton biomass to WRT (Descy et al 1987, Søballe and Kimmel 1987) and the effect of the dam on WRT should favor greater phytoplankton development, although evidence for links between WRT and phytoplankton in rivers is not entirely consistent (e.g. Chételat et al. 2006). However, summer turbidity in the reach may also be higher as the dam delays downstream transport of sediments and helps maintain a stock of fine sediments available for resuspension in

low discharge periods (i.e. summer), resulting in currently very high turbidity and impaired light availability for the phytoplankton. To predict the expected abundance of phytoplankton and the system metabolic balance in the absence of structures such as the dam requires information beyond that currently available including a good understanding of the expected morphometry of a free river channel, its hydrology, sediment transport and water clarity. In any case, the Grand River is probably more typical than otherwise in having such a control structure in its lower reaches and we may anticipate that many other rivers share its tendency towards a seasonal occurrence of autotrophic metabolism and the accompanying consequences for nutrient dynamics.

3 – Plankton metabolism in the lower Grand River, Ontario

Overview

Although large, eutrophic rivers often support significant phytoplankton populations, measurements of planktonic photosynthesis (P) and respiration (R) often fail to explain how they develop in such turbid, rapidly-flushed environments or to define the contribution of plankton to the system metabolism. This study used dissolved oxygen (DO) changes in bottles to estimate planktonic P and R in the southern Grand River (Ontario, Canada; stream order 7) to define the scope for positive phytoplankton growth in a turbid lowland river. Comparisons against previous *in situ* diel curve analysis provided estimates of the contribution of plankton to system metabolism. The response of P to irradiance in the experimental incubations showed that Grand River phytoplankton had very high light utilization efficiencies and light-saturated photosynthetic rates. Consistent with *in situ* metabolism, nutrient, and chlorophyll patterns in the study reach, the bottle experiments indicated that net phytoplankton growth should indeed be possible throughout most of the study reach in summer. System R, estimated from *in situ* measurements, was much greater than planktonic R as estimated in bottles, consistent with a major role for sediments, benthos, and fringing habitats in metabolism of the reach. Despite the poor light penetration and limited scope for benthic P in the main channel, the system P was also larger than planktonic P measured in bottles, suggesting that photo-autotrophs in the fringing habitats and spatial variations in plankton metabolism were important to system metabolism. While the depth of lowland river systems and their flushing rates are recognized as important factors, the choice of the

currency for measurement of P and R may also be important when comparing with previous investigations.

Introduction

Though it is clear that large rivers can support significant phytoplankton populations, exactly how they survive and grow in such systems is not fully understood. In order to support a growing phytoplankton population, the critical depth, the depth at which gross water column photosynthesis (P) by phytoplankton is equal to respiration (R), must be greater than the actual river depth (Falkowski and Raven 1997). In large river systems the combination of increasing depth and high turbidity, and the resulting poor light environment is expected to suppress production so that positive phytoplankton growth is not attainable. However, this is clearly contradictory to the observations of large plankton population in the Southern Grand River and has been previously discussed for several large rivers (Cole et al 1992, Descy and Gosselain 1994). Several theories have been developed to explain this apparent contradiction.

The production hypothesis proposes that physiological adaptation to low light promotes phytoplankton growth in such systems (Cole et al 1991, in Descy and Gosselain 1994). A somewhat similar idea involves enhanced photosynthesis of planktonic algae as vertical mixing carries them through changing light gradients. An initial induction period of raised photosynthetic rates has been observed upon dark to light transitions before rates leveled off to more sustainable values (Harris and Piccinin 1977). The implications of this induction period were modeled by Loehr (1987) who concluded that varying light intensities as a result of vertical mixing may increase productivity 2.2 fold versus rates measured in continuous light. The possibility of an unusual degree of physiological adaptation, compared to the known range for phytoplankton, was examined in Descy and Gosselain (1994) but the evidence was inconclusive.

The importation argument proposes that phytoplankton cannot in fact grow throughout much of a large river system. Net positive growth is limited to shallow areas and then imported into the rest of the river (Cole et al 1992). A very similar concept is that of "dead zones" which have a longer water residence time than the surrounding main channel and thus accommodate additional phytoplankton growth (Reynolds 1994). Such areas have been shown to be important plankton habitats (Walks 2007). Finally the removal hypothesis suggests that sedimentation of plankton is reduced in such systems as a result of turbulent mixing (Reynolds et al 1990). As well zooplankton grazing is also expected to be reduced in large rivers systems, as suspended solids interfere with feeding (Wofsy 1983).

In this study I address whether phytoplankton net growth is possible in the main channel of the Southern Grand River. Light and dark bottle oxygen incubations allow me to isolate the planktonic segment of the river and infer the metabolic balance. These incubations also allow us the opportunity to examine potential increases in photosynthetic efficiency which may explain how phytoplankton are capable of growing in such a light limited environment. Finally I will compare these P and R rates in the water column to those measured for the entire ecosystem to estimate the contribution of non-planktonic processes.

Materials and Methods

Study Site

The river stretch and sites sampled are the same as those described in chapter 1.

Oxygen Incubations

Oxygen incubations were conducted once per month during July and August of 2006 and from May to August in 2007 coinciding with the spatial surveys. Water for the oxygen incubations was collected from shore at site 6 following the 24 hour diel measurements. Water was collected in a dark 20L carboy and returned immediately to the laboratory at the University of Waterloo, where incubations began within 3 hours of sample collection. The sample was stirred to ensure there was no settling out of particulates. Acid cleaned 300ml B.O.D. in 2006 and 150ml bottles in 2007 were filled using tubing by allowing a volume roughly equal to three times the volume of the B.O.D. bottle to flow through to ensure that there was no air contamination. After the bottle stopper was in place, the bottle was checked to ensure no air bubbles were present and refilled if necessary. Once the bottles were filled 4-5 bottles were randomly selected and the oxygen concentrations were measured immediately, with the bottles saved and filtered for Chl *a*. Bottles were randomly selected and wrapped in aluminum foil for dark treatment (2 in 2006 and 4 in 2007). The remaining bottles were randomly divided up between 5 or 6 light levels, with (2007) or without (2006) mixing during the incubation. A temperature controlled water bath was used to keep the water temperature within $2^{o}C$ of river temperature. Light was provided by 2 500W halogen lights, with light intensities inside the incubator measured using a Li-Cor spherical underwater quantum sensor. Light

bottles were incubated for 4-5 hours while the dark bottles were left for 20-24 hours. Oxygen was measured using calibrated electrodes (Hach HQ40d in 2007, WTW MultiLine P4 meter with and Oxical-SL probe in July 2006) and, in August of 2006 using Winkler titrations according to Carignan et al (1998).

The rate of oxygen change in the dark bottles estimated R in $mgO_2/l/hr$. P ($mgO_2/l/hr$) was estimated by adding the R to the rate of change in the light bottles (net production), under the assumption the R rate is the same in the light and dark bottles (Carignan et al. 2000). Photosynthetic light parameters α^B (the initial slope representing efficiency of light utilization) and P^Bmax (max rate of photosynthesis) were estimated using the equations of Jasby and Platt (1976). Both parameters were normalized to phytoplankton biomass as measured by Chl *a*.

Assuming the photosynthetic parameters are representative of the study area, daily areal P ($mgO/m^2/d^1$) was estimated at each site during the spatial surveys (as outlined in chapter 1) using the phytoplankton production model as outlined in Fee (1990). Daily areal P was integrated to the average main channel depth as it was assumed the water column was well-mixed, and vertical temperature profiling suggested this was usually the case. The Chl *a* concentrations and light attenuation values used for estimation at each site were taken from the results of the spatial surveys presented in chapter 2. The cloud cover coefficient was left at the default value of 70%, while the atmospheric effect was determined using PAR values measured on a cloud free day. Daily areal respiration was estimated by multiplying the hourly R rate by the average river depth and 24 hours. The P:R shown represents the ratio of daily areal photosynthesis to daily areal respiration. The P:R values presented for each year represent the average values from the 2 incubations in

2006, and the 4 incubations in 2007. Entire system P, R and P:R ratios were taken from chapter 1 as estimated using the diel DO method.

Results

Oxygen Incubations

The estimated photosynthetic parameters for all 6 incubations are presented in Table 3.1. It appears that early in the summer (May and June) the photosynthetic parameters may be lower than later in the summer, though it is hard to make any strong conclusions based on so few incubations. Although there were methodological differences, the limited comparisons I can make between parameters for 2006 and 2007 did not indicate consistent differences; photosynthetic parameters in July and August were high in both years. The overall average (±SD) for both years for α^B was 31.21 ± 11.69 mgO/mgchla/mol/m^2 while the average P^Bmax was 26.10 ± 11.03 mgO/mgchla/hr. The R^2 values indicate that all P vs. I curves were relatively well described by the model. The P vs. I curves for August 2006 and June 2007 are shown in Figure 3.1 to illustrate the difference between the best and worst fit relationships. While the R^2 values are higher in 2006 they were only based on 10 bottles while in 2007 a total of 18 bottles were measured.

Table 3.1 Estimated photosynthetic parameters estimated from the P vs. I curves along with the resulting R^2 from the 6 incubations at site 6. The bottle estimates of R are also provided.

Date	α^B	P^Bmax	R^2	R^B (mgO/mgchla/m2/hr)
Jul 06	28.69	24.45	0.961	2.45
Aug 06	37.66	31.67	0.968	3.80
May 07	17.96	16.77	0.751	1.88
Jun 07	27.00	16.87	0.703	3.94
Jul 07	25.22	21.28	0.870	1.29
Aug 07	51.36	45.58	0.914	6.85

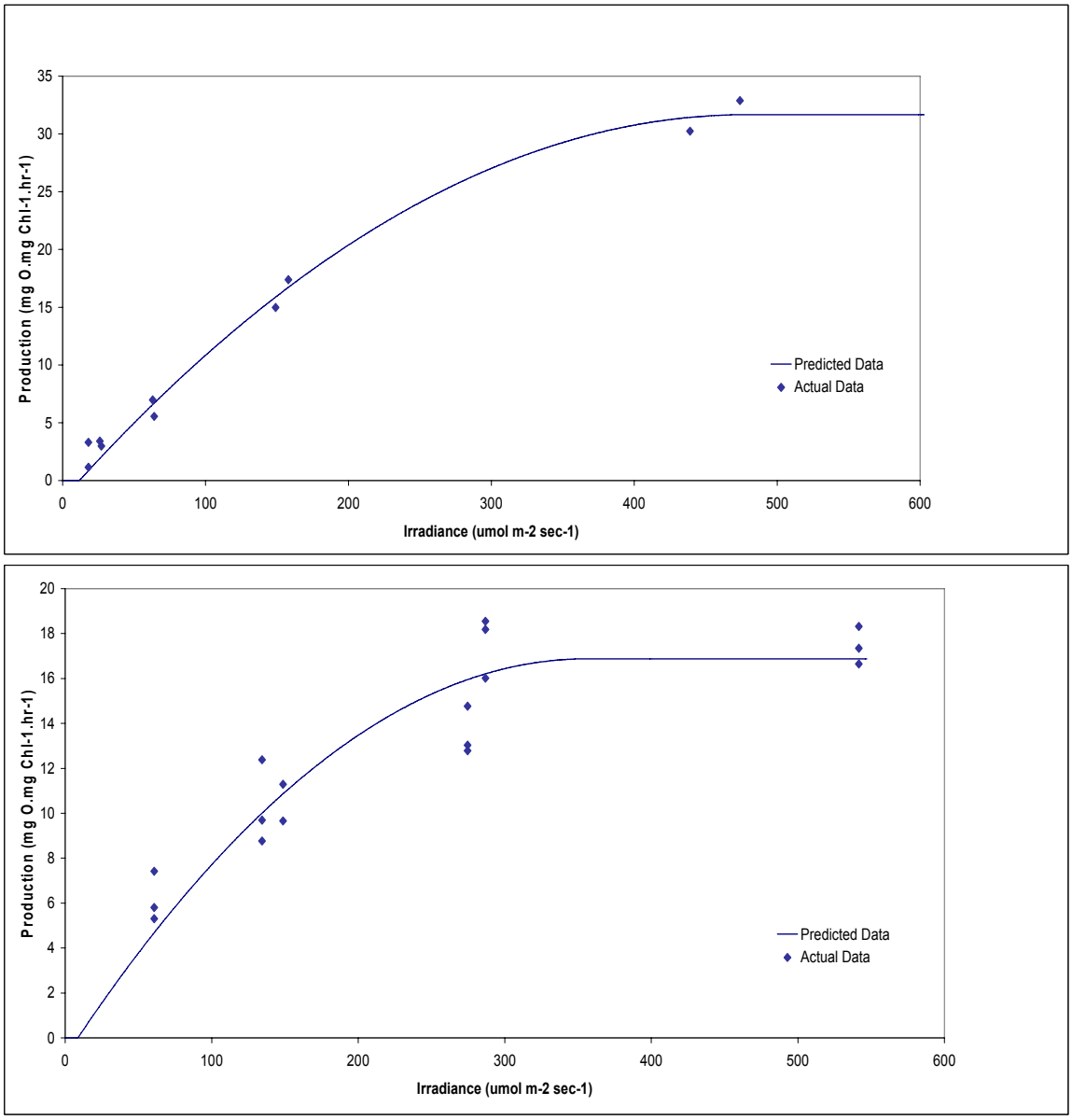


Figure 3.1 The P vs. I relationships from August 2006 (top) and June 2007 (bottom). These 2 curves show the best and worst fit data, with the other curves falling in between.

Table 3.2 Average values from all surveys conducted in the summers of 2006 and 2007.

Site	Chl *a* (µg/l)	k (m^{-1})	Depth (m)	Euphotic depth (m)
1	12.00	1.57	2.01	3.01
2	14.74	1.66	2.74	2.87
3	28.04	1.97	3.05	2.35
4	45.62	2.47	3.84	1.92
5	44.76	2.81	2.38	1.70
6	41.30	4.10	1.52	1.16
7	33.18	4.21	4.47	1.13
8	44.06	3.30	2.77	1.45
9	40.98	2.73	3.08	1.72
10	36.13	2.72	3.39	1.76

Phytoplankton biomass, light attenuation and depth data from the 10 sites along the study reach is shown in table 3.2. These represent average values from all summer surveys at each site, however during the phytoplankton production modeling the individual values from the corresponding spatial surveys were used. Nonetheless this presents a picture of the changing plankton biomass and physical conditions along the study stretch. The major difference in depth between sites 6 and 7 results from the dam, located between them, which serves to back up sediments above and re-suspends them below. As I have used the same photosynthetic parameters at all sites it is the differences in Chl *a* and light attenuation that will significantly influence P.

P and R rates

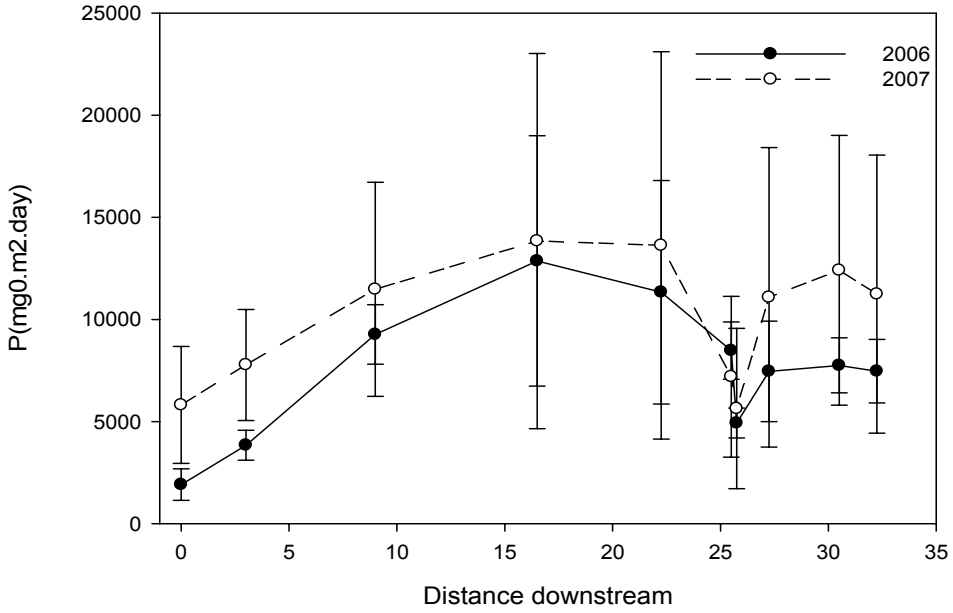


Figure 3.2 Average P in 2006 and 2007 from site 1 (0 on the x axis) downstream. The error bars represent the standard deviation. For comparison purposes with the *in situ* systems, site 6 is located at km 25.

The daily areal P calculated at the 10 sampling sites is presented in Figure 3.2. It is clear the highest levels of P occur upstream of the dam in Dunnville. P levels drop considerably at the sites directly above and below the dam due to increasing turbidity as evident in the increasing light attenuation. Following this drop we see a rise in P levels below the dam, though this increase is much more significant in 2007.

The average P:R ratios at each site for both 2006 and 2007 are shown in Figure 3.3. It's apparent throughout a majority of this river stretch that the plankton in the water column have an autotrophic balance, with P:R ratios above 3 being observed. It is also apparent that P:R ratios were consistently higher in 2007 than in 2006. P:R was low just above km25, immediately below the low head Dunnville dam. The dam overflow creates

a deep, highly turbid area which is inhospitable for phytoplankton. Only a short distance downstream, depth and turbidity was more moderate and P:R > 1 prevailed down to the river mouth despite relatively deep channel depths.

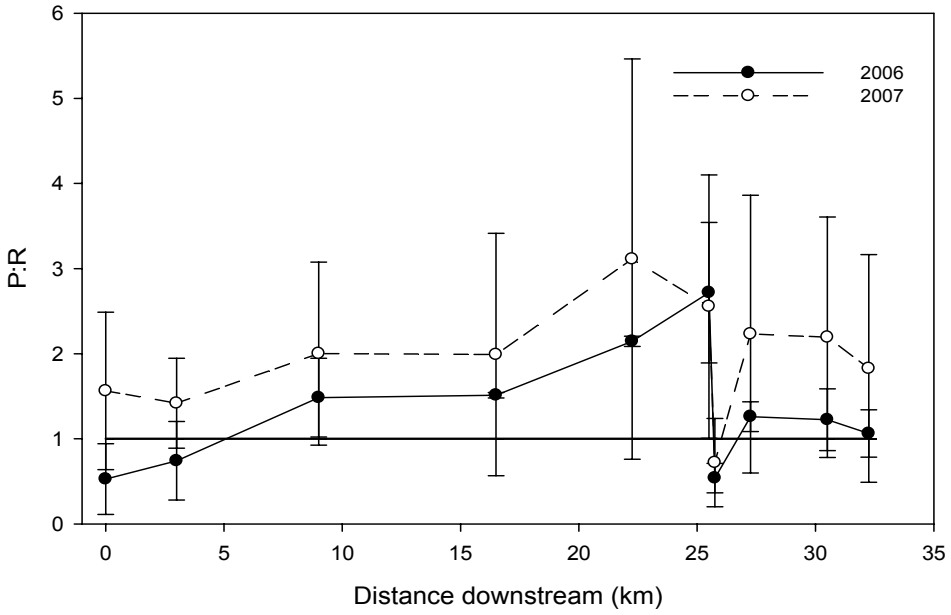


Figure 3.3 The average P:R ratios calculated using the Fee model from the 2 incubations in 2006 and 4 in 2007 are presented here, moving from site 1 (0 on the x-axis) downstream towards Lake Erie. The error bars represent standard deviation. The P:R = 1 line is put in for reference. Site 6 is located at km 25.

The absolute P and R values from the incubations are presented in Table 3.3, along with absolute values from the entire system as estimated from diel oxygen measurements (see Chapter 1). Both P and R values are significantly higher for the entire system than in the water column samples alone. However in all case with the exception of June 2007, the P:R ratio is significantly higher for the water column processes. This indicates the water column is actually more autotrophic than the entire system.

Table 3.3 P, R and P:R from the bottle incubations (Fee) representing only water column processes to the whole system values (DO) at site 6. Both P and R are daily areal values in units of $mgO_2/m^2/day$. The May 2007 survey is not included here as there were no diel DO estimates made at this time.

Date	**P (Fee)**	**P (DO)**	**R (Fee)**	**R (DO)**	**P:R (Fee)**	**P:R (DO)**
Jul 06	7478	16323	2265	12939	3.30	1.26
Aug 06	9465	18185	4436	23023	2.13	0.79
Jun 07	5987	39166	4823	10572	1.24	3.71
Jul 07	12760	30796	2714	9569	4.70	3.22
Aug 07	6538	28285	2477	23244	2.64	1.22

Discussion

Water column P:R ratios clearly indicate that throughout the summer the planktonic segment of the Southern Grand River is definitely autotrophic and capable of supporting a growing phytoplankton population. In other words the critical depth is greater the average channel depth. Although the P:R ratios are high, it seems unlikely that I have overestimated them. In fact the use of static incubations may potentially underestimate the productivity in well mixed systems in which phytoplankton experience constantly varying light levels (Loehr 1987, Kohler 1995). In a similar system, incubations involving rotating bottles through the water column yielded rates of primary productivity 15% higher on average, than static bottle incubations (Mallin and Paerl 1992). This increase was attributed to the reduced photoinhibition and mitigation of light limitation that can occur in high and low intensity exposed bottles respectively, in static incubations. The work of Harris and Piccinin (1977) on short term dynamics of P also suggests that the relatively long incubations may in fact underestimate Pmax.

I must also take into account issues with measuring phytoplankton respiration. The oxygen consumption in the dark bottles is not only resulting from phytoplankton respiration but also bacterial respiration. Bacterial respiration has been shown to account for a significant portion of pelagic respiration (Roberts and Howarth 2006). So even if the water column P<R it is still conceivable that net growth of phytoplankton is possible. To overcome this problem of using dark bottle rates other investigators have assumed phytoplankton respiration is related to the maximum photosynthetic rate but this relationship is not fully understood and literature values can vary greatly (see Cole et al 1992, Falkowski and Raven 1997). As well it is likely that the average channel depths I

used to model P and R were slightly overestimated. When selecting sites I specifically chose the deepest locations within a certain area of river. These specific sites were chosen with the idea that if stratification was present it would be most observable when profiling at the deepest spots. Any overestimation would likely have no impact on production estimates as light was attenuated quickly in the upper part of the water column. With the exception of the most upstream stretch the euphotic depth was never greater than the channel depth. However this would lead to an overestimation of daily areal respiration. So it appears that the assumptions I have made err on the side of underestimating P, while overestimating R, and thus underestimating the P:R ratios.

Unlike what Cole et al (1992) observed in the Hudson River, and Descy and Gosselain (1994) in the Meuse River, net positive growth is possible in the main channel of the Southern Grand River. Increased photosynthetic efficiency appears to be at least partly responsible for this. Using a standard photosynthetic quotient of 1.25 to convert their values from units of carbon to oxygen Cole et al (1992) reported an α^B of 3.5–5 mgO/mgChla/mol/m^2, while Descy and Gosselain (1994) reported a value of 15 mgO/mgchla/mol/m^2. When reviewing costal water and estuaries Keller (1998, in Cole et al, 1992) reported a range in α^B from ~10.5 to 21 mgO/mgChla/mol/m^2. These values all fall below our average α^B value of 31.21 mgO/mgchla/mol/m^2. As well our P^Bmax value of 26.10 mgO/mgchla/hr is well above the 7.5 mgO/mgchla/hr and 10 mgO/mgchla/hr reported by Cole et al (1992) and Descy and Gosselain (1994) respectively. These discrepancies may result from a variety of factors. They may reflect the use of photosynthetic quotients which can vary widely (Kalff 2002). These enhanced values may be reflective of high nutrient concentrations and/or high temperatures in the river

(Raven and Falkowski 1997). However these enhanced parameters may lend support to the production hypothesis. The enhanced α values indicate a potential low light adaptation that may help phytoplankton flourish in the Grand River.

When comparing my results to previous work I need to also consider methodological differences, specifically the use of ^{14}C measurements. The uncertainty in what ^{14}C is actually measuring can potentially lead to underestimation of P:R ratios as this method is not expected to provide a true estimate of P (Carignan et al 2000). The use of oxygen measures not only eliminates this issue, but allows the use a common currency for estimating both P and R. The removes the uncertainty associated with using a photosynthetic quotient.

The importation hypothesis holds that shallow areas are needed to support phytoplankton populations in large rivers. I can say this is not the case in the Grand River. However it must be pointed out that the average depth of the study reach was ~3m, less than the 3-6m for the Meuse (Descy and Gosselain 1994), and 9.4m for the Hudson (Cole et al 1992). As these rivers are significantly deeper, shallower sections may become more necessary to support plankton growth. If I increase the average depth in the model, I find that at 6m net positive growth is only possible at certain spatial and temporal intervals and at 9m net positive growth is never predicted. So while it is clear that river depth is an important control on phytoplankton growth, the requirement of shallower "nursery" zones is not applicable to all large rivers, though they may contribute to the larger larger value of P derived from the in situ DO method compared to the bottle method.

Absolute R rates for the entire system were higher than those measured by the bottle incubations. This observation is consistent with the idea that sediments and benthic metabolism are significant oxygen consumers in such systems. What is really interesting is that absolute P rates were also significantly higher for the entire system than in the bottle incubations. The River Continuum Concept (Vannotte et al 1980) predicts that increasing turbidity and depth will lead to a shift from macrophytes to phytoplankton as the dominant producers as river size increases from mid to large orders. Previous river sampling by the Ontario Ministry of Natural Resources indicated that submersed macrophytes were very rare along this stretch of the Grand (Tom MacDougall personal comm.). Visual observations confirmed this as macrophytes were only observed in isolated areas close to shore. As well the average river depth is greater than the euphotic depth throughout most of the river stretch indicating that light is consistently attenuated before reaching the bottom.

So if phytoplankton are indeed the dominant producers I must explain the excess production observed. Even if the methods are underestimating production as discussed above this would certainly not account for the entire difference, so I need to consider other factors. Algal production in the fringing habitats including the wetlands may contribute part of the extra production. A firmer understanding of the connectivity of these fringing areas with the main channel would help in understanding their influence on such river dynamics. The most likely explanation for the differing production rates lies in the spatial and temporal resolve of the light and dark bottle versus the diel DO method. The oxygen changes measured in the diel DO method were strongly influenced by processes that occurred both upstream and previously in time. So there is a higher spatial

and temporal influence involved with this methodology than the incubation method, which uses data specific to the site measured at one point in time. Put simply, production measured at site 6 using the diel method was influenced by preceding conditions as well as the actual conditions at that site. This is different from the incubation method which uses parameters (Chl *a*, attenuation) measured at site 6. So comparing results from both methods at site 6 is not reliable, instead we need to look at incubation estimates from further upstream. The P rates estimated from the upstream sites are consistently 1.5 to 2.5 those at site 6. These values are much closer to those predicted from the diel DO method. Taking this into account it appears that the production measured in the incubations represents a large portion of the total system production as would be expected in a large river system where phytoplankton are the dominant producers. The generally higher P:R ratios from the incubation method, versus the diel DO method, indicate the water column is more autotrophic than the entire system. This result agrees with idea of production dominated by the phytoplankton with respiration in the sediments contributing heavily to system metabolism.

4 - **Conclusions and future directions**

These investigations have demonstrated the autotrophic nature of the southern Grand River during the summer, with the river acting as a source of phytoplankton and converting inorganic nutrients into particulate form. The stable oxygen isotopes provided a second oxygen budget to work with and the results were in agreement with the more traditional measures. This study confirms the necessity of a non steady state model, such as PoRGy, in order to deal with the daily oxygen cycling observed. The results from the oxygen incubations demonstrate that phytoplankton are capable of surviving throughout the lower end of the river. Comparisons of P and R rates from bottle incubations with those from the entire system suggest that benthic activity dominates the oxygen consumption while the phytoplankton are the dominant oxygen producers. While solid evidence exists to back up the main conclusions there are several areas of uncertainty that came up throughout the study. The following issues provide areas for future work:

1. The seasonality is not well understood. The limited results from this study show low phytoplankton biomass, and significantly higher inorganic nutrients, outside of the summer months. This suggests that system metabolism is balanced or shifts toward heterotrophy from fall through to spring. This represents a time frame of approximately 8 months in which the metabolic functioning is poorly defined.

2. The influence of the dam is not fully understood. The increase in water residence time above the dam promotes the growth of a phytoplankton biomass that may be unattainable otherwise. This much seems certain, yet quantitatively determining the influence of the

dam is difficult with present information. This is not only an issue encountered in the Grand River, but rather is quite common in large rivers.

3. The stable oxygen isotope results were generally as expected for an autotrophic system, yet the daily cycling of $\delta^{18}O_{DO}$ appeared to be much less than expected considering the cycle in oxygen concentrations. Further diel studies with better temporal resolution and ancillary meteorological data could help determine if this dampened cycle is common in such systems and, if so, to identify the responsible processes.

4. The oxygen incubations indicate that phytoplankton may show some adaptations to low light environments compared to previous studies in such systems. However due to issues with converting carbon to oxygen values the evidence is not conclusive. Future work would be needed in order confirm these results.

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Appendix 1. Data from all mid-channel spatial surveys conducted in 2006 and 2007.

Values represent the average of 3 replicate samples taken at each site.

Site	Date	TP (µg/l)	SRP (µg/l)	NO_3 (mg/l)	NO_2 (µg/l)	Chl *a* (µg/l)	POC (mg/l)	PON (mg/l)	TSS (mg/l)
2	Jun 13/06	61.65	8.61	2.72	10.80	6.58	1.45	0.23	15.29
3	Jun 13/06	45.64	1.48	2.87	16.23	19.30	2.08	0.31	15.86
4	Jun 13/06	69.35	1.48	2.82	21.30	23.06	3.78	0.64	27.57
5	Jun 13/06	59.72	1.77	2.28	20.09	18.30	3.59	0.56	33.85
6	Jun 13/06	60.02	1.92	2.23	24.97	15.13	3.65	0.56	40.72
1	Jul 24/06	63.18	17.09	1.76	14.20	6.50	1.04	0.17	13.92
2	Jul 24/06	59.63	11.30	1.66	14.07	10.58	1.30	0.23	12.33
3	Jul 24/06	57.40	2.06	1.58	15.03	25.32	1.68	0.32	16.00
4	Jul 24/06	71.29	2.85	1.13	15.93	35.52	2.62	0.46	23.33
5	Jul 24/06	68.05	2.11	1.27	22.00	39.08	3.04	0.50	36.43
6	Jul 24/06	78.59	2.16	1.27	31.03	59.91	3.60	0.59	51.50
7	Jul 25/06	55.93	2.85	1.25	28.83	33.93	3.08	0.53	54.83
8	Jul 25/06	90.76	2.85	1.28	32.70	36.43	2.78	0.49	43.83
9	Jul 25/06	74.74	3.34	1.14	36.27	29.00	2.29	0.45	23.17
10	Jul 25/06	66.52	3.83	1.04	34.00	26.20	2.32	0.47	25.60
1	Aug 23/6	26.07	8.52	1.27	5.07	2.91	0.94	0.12	12.50
2	Aug 23/6	32.19	4.47	1.39	5.07	8.11	1.05	0.16	9.43
3	Aug 23/6	49.49	2.18	1.38	6.83	24.23	1.76	0.27	13.67
4	Aug 23/6	64.80	2.49	1.16	9.83	51.58	2.90	0.45	20.50
5	Aug 23/6	63.63	2.60	1.08	11.70	48.03	3.35	0.48	23.18
6	Aug 23/6	69.44	3.43	0.79	11.60	44.69	2.78	0.43	27.72
7	Aug 24/6	77.99	3.10	0.98	14.33	25.24	3.10	0.42	35.52
8	Aug 24/6	74.40	4.36	0.80	23.71	38.74	2.79	0.51	24.18
9	Aug 24/6	61.21	4.36	0.87	24.01	26.52	2.19	0.39	16.12
10	Aug 24/6	72.29	4.21	0.73	21.06	24.83	2.40	0.40	17.15
1	Oct 18/6	134.17	59.22	2.54	34.97	3.75	2.08	0.26	40.49
2	Oct 18/6	141.30	66.31	2.43	34.46	3.02	2.21	0.29	45.88
3	Oct 18/6	198.26	104.27	2.29	32.92	3.07	2.84	0.38	55.56
4	Oct 18/6	131.89	54.30	2.49	29.45	3.14	2.32	0.26	34.71
5	Oct 18/6	123.33	48.35	2.59	30.54	2.66	2.34	0.24	35.92
6	Oct 18/6	137.40	55.82	2.60	37.16	3.10	2.20	0.22	35.45
1	May 7/07	32.92	1.68	2.41	26.66	22.51	1.47	0.22	8.94
2	May 7/07	41.04	2.05	2.37	25.96	23.70	1.57	0.24	10.34
3	May 7/07	44.86	1.40	2.37	33.08	31.28	1.95	0.30	11.15
4	May 7/07	52.05	2.05	2.05	23.88	36.54	2.50	0.37	26.87
5	May 7/07	61.37	2.28	2.12	23.79	36.76	3.06	0.46	33.50
6	May 7/07	88.24	2.42	2.03	21.62	37.10	3.11	0.47	49.37
7	May 8/07	95.23	2.33	1.91	21.80	35.81	3.25	0.54	64.28
8	May 8/07	75.36	2.61	1.94	21.53	32.36	2.79	0.54	43.39
9	May 8/07	67.16	3.35	1.85	20.84	34.33	2.82	0.48	34.13
10	May 8/07	69.49	2.79	1.89	20.41	35.93	2.97	0.49	41.83

1	Jun 11/07	34.48	0.70	1.47	9.21	26.93	2.10	0.37	15.65
2	Jun 11/07	32.21	0.57	1.64	12.92	32.51	2.48	0.37	20.21
3	Jun 11/07	41.46	1.11	1.73	15.22	45.15	2.52	0.49	12.52
4	Jun 11/07	32.40	1.81	1.55	17.94	27.74	2.96	0.41	15.54
5	Jun 11/07	41.28	1.61	1.54	22.05	38.01	3.24	0.64	19.86
6	Jun 11/07	64.61	2.21	1.27	21.97	33.18	3.78	0.56	27.04
7	Jun 12/07	80.10	1.91	1.42	28.49	13.42	2.96	0.65	37.51
8	Jun 12/07	67.06	2.41	1.40	28.48	25.78	2.68	0.44	23.53
9	Jun 12/07	50.34	2.62	1.14	28.38	39.68	3.19	0.50	18.86
10	Jun 12/07	65.27	2.41	1.26	31.47	32.59	3.08	0.47	19.75
1	Jul 16/07	50.25	10.04	1.71	7.76	3.65	1.00	0.12	7.84
2	Jul 16/07	41.18	5.17	1.67	10.37	9.17	1.15	0.18	6.85
3	Jul 16/07	49.21	2.14	1.28	11.45	23.79	1.71	0.28	10.08
4	Jul 16/07	67.82	3.41	0.79	18.59	120.68	5.87	0.67	32.63
5	Jul 16/07	66.31	2.14	0.80	24.49	106.95	5.24	0.62	28.91
6	Jul 16/07	75.75	2.83	0.64	28.24	76.85	5.09	0.65	35.33
7	Jul 17/07	100.88	2.28	0.71	26.06	69.73	4.19	0.56	38.72
8	Jul 17/07	80.00	3.61	0.65	29.03	90.87	4.16	0.68	22.21
9	Jul 17/07	74.52	3.41	0.63	33.82	75.52	3.65	0.60	18.71
10	Jul 17/07	79.91	2.44	0.66	33.44	56.65	3.60	0.57	17.92
1	Aug 27/07	30.40	2.49	1.94	12.24	9.50	1.12	0.15	8.55
2	Aug 27/07	28.58	1.24	1.78	12.98	12.52	1.20	0.18	6.79
3	Aug 27/07	36.06	1.14	1.33	14.56	27.18	1.96	0.28	11.25
4	Aug 27/07	39.13	2.80	1.05	15.48	24.21	2.58	0.34	16.67
5	Aug 27/07	42.59	2.90	1.07	17.24	26.22	2.56	0.37	16.49
6	Aug 27/07	47.67	1.97	0.93	18.82	22.25	2.62	0.34	23.85
7	Aug 28/07	53.81	2.80	0.90	19.93	20.96	3.26	0.38	35.65
8	Aug 28/07	52.75	2.18	0.68	22.53	40.21	3.33	0.48	26.81
9	Aug 28/07	57.64	2.28	0.82	21.05	40.81	3.36	0.52	19.25
10	Aug 28/07	58.12	2.49	0.51	23.09	40.55	3.22	0.53	18.50
1	Oct 16/07	21.94	3.25	1.30	14.65	7.18	0.87	0.11	7.78
2	Oct 16/07	21.46	2.46	1.97	20.49	12.69	1.07	0.15	8.97
3	Oct 16/07	80.84	2.96	1.65	17.89	9.77	1.36	0.16	13.96
4	Oct 16/07	105.86	1.87	1.75	20.49	22.96	1.78	0.25	13.98
5	Oct 16/07	57.16	1.97	1.57	23.64	28.37	2.13	0.29	20.03
6	Oct 16/07	39.90	1.58	1.76	34.26	19.82	2.69	0.31	30.67
7	Oct 17/07	47.96	1.48	1.55	34.49	17.29	3.04	0.33	36.57
8	Oct 17/07	41.63	2.37	1.60	34.12	22.25	2.55	0.35	26.38
9	Oct 17/07	40.67	2.86	0.95	32.45	26.45	2.24	0.38	15.89
10	Oct 17/07	23.50	2.96	0.32	7.05	7.24	0.79	0.13	4.03

Appendix 2. Data from all shore surveys that were conducted in 2006 and 2007 at the York(Yor), Cayuga(Cay) and Dunnville(Dun) sites. Values represent the average of 2 or 3 replicate samples collected at each site.

Site	Date	TP (µg/l)	SRP (µg/l)	NO_3 (mg/l)	NO_2 (µg/l)	Chl *a* (µg/l)	POC (mg/l)	PON (mg/l)	TSS (mg/l)
Cay	Mar 23/06	59.87	31.36	2.89	21.64	0.95	0.96	0.11	12.75
Dun	Mar 23/06	62.64	31.66	2.44	15.24	1.34	1.06	0.12	15.72
Yor	Apr 26/06	44.75	10.27	3.36	41.10	14.22	3.10	0.29	33.69
Cay	Apr 26/06	63.28	7.59	2.77	36.75	15.72	3.42	0.36	39.94
Dun	Apr 26/06	57.60	1.19	1.81	39.11	27.40	3.57	0.39	41.20
Yor	May 25/06	24.11	5.66	3.00	20.66	4.65	0.91	0.12	11.92
Cay	May 25/06	31.52	4.56	2.85	18.99	5.06	1.27	0.14	12.42
Dun	May 25/06	62.34	2.38	3.89	29.60	29.17	4.38	0.43	68.14
Yor	Jul 6/06	40.11	16.08	1.71	10.66	4.54	1.20	0.16	15.33
Cay	Jul 6/06	37.25	18.44	1.66	1.73	3.15	1.20	0.16	16.77
Dun	Jul 6/06	73.36	3.04	1.24	21.50	114.70	4.98	0.79	49.84
Yor	Apr 3/07	47.76	21.32	2.70	30.57	1.70	0.87	0.11	16.47
Cay	Apr 3/07	56.71	22.16	2.74	31.26	1.85	1.11	0.14	21.32
Dun	Apr 3/07	70.23	25.88	2.60	29.96	3.34	2.08	0.24	46.04
Yor	Apr 26/07	32.09	3.96	2.63	31.69	11.19	0.83	0.14	9.05
Cay	Apr 26/07	39.92	4.19	2.64	27.61	9.88	1.15	0.17	16.54
Dun	Apr 26/07	66.78	1.21	2.55	22.45	31.48	2.71	0.41	53.96
Yor	May 29/07	61.49	10.77	2.85	n/a	5.18	1.05	0.15	18.89
Cay	May 29/07	119.95	8.75	2.79	n/a	4.89	1.08	0.16	13.00
Dun	May 29/07	113.34	1.31	2.19	n/a	34.67	3.34	0.56	30.81
Yor	Jul 5/07	34.36	24.07	1.29	13.86	3.68	1.22	0.12	13.37
Cay	Jul 5/07	31.57	27.78	1.08	10.11	3.66	4.98	0.26	46.45
Dun	Jul 5/07	26.37	4.68	0.42	29.03	80.55	5.24	0.80	42.58
Yor	Aug 9/07	46.33	12.54	1.04	14.19	10.85	2.58	0.24	11.76
Cay	Aug 9/07	35.20	9.74	0.86	12.89	10.08	1.37	0.18	27.94
Dun	Aug 9/07	74.24	2.59	0.36	27.54	37.87	4.33	0.62	43.28
Yor	Nov 28/07	17.36	3.35	2.95	n/a	2.38	0.94	0.11	7.37
Cay	Nov 28/07	17.74	2.82	2.44	n/a	2.01	1.19	0.14	9.40

Appendix 3. Dissolved oxygen and $\delta^{18}O_{DO}$ results from all diel samples collected during 2006 and 2007. Throughout this thesis diel cycles collected at Dunnville and Cayuga are referred to as site 6 and site 1 respectively, as they shore sites located close to the mid-channel sites.

Site	Date	Time	DO (% sat)	$\delta^{18}O_{DO}$
Dun	Jul 25/06	15:16	116	17.60
Dun	Jul 25/06	18:10	118	17.16
Dun	Jul 25/06	21:00	107	17.60
Dun	Jul 26/06	0:00	98	17.41
Dun	Jul 26/06	6:10	88	19.59
Dun	Jul 26/06	9:05	90	18.32
Dun	Jul 26/06	12:00	110	15.43
Dun	Jul 26/06	15:15	124	15.54
Dun	Aug 21/6	21:00	98	17.61
Dun	Aug 21/6	23:58	89	
Dun	Aug 22/6	6:00	70	19.99
Dun	Aug 22/6	9:00	70	
Dun	Aug 22/6	12:00	93	16.90
Dun	Aug 22/6	15:00	110	
Dun	Aug 22/6	18:00	115	15.65
Dun	Aug 22/6	21:00	113	15.12
Dun	May 8/07	6:00	118	20.55
Dun	May 8/07	8:50	120	19.66
Dun	May 8/07	12:30	125	17.76
Dun	May 8/07	15:15	128	17.69
Dun	May 8/07	18:00	130	19.57
Dun	May 8/07	21:00	127	19.96
Dun	May 9/07	0:15	118	20.49
Dun	May 9/07	6:00	113	19.92
Dun	May 9/07	10:00	130	17.54
Dun	Jun 13/07	18:00	168	10.68
Dun	Jun 13/07	20:50	169	11.86
Dun	Jun 13/07	23:45	141	13.44
Dun	Jun 14/07	5:45	91	16.96
Dun	Jun 14/07	7:00	98	
Dun	Jun 14/07	8:45	135	12.73
Dun	Jun 14/07	14:00	172	
Dun	Jun 14/07	18:30	160	15.43

Dun	Jul 18/07	15:00	179	16.28
Dun	Jul 18/07	18:00	171	16.85
Dun	Jul 18/07	20:50	166	16.99
Dun	Jul 19/07	0:00	146	20.09
Dun	Jul 19/07	2:30	122	15.63
Dun	Jul 19/07	6:00	108	17.54
Dun	Jul 19/07	9:00	123	17.09
Dun	Jul 19/07	11:50	127	15.22
Dun	Jul 19/07	15:00	149	17.14
Cay	Jul 18/07	15:30	114	14.09
Cay	Jul 18/07	18:30	130	13.98
Cay	Jul 18/07	21:20	130	14.48
Cay	Jul 19/07	0:30	115	16.83
Cay	Jul 19/07	6:40	79	22.21
Cay	Jul 19/07	9:30	68	23.67
Cay	Jul 19/07	12:20	79	19.75
Cay	Jul 19/07	15:20	102	14.20
Dun	Aug 28/07	21:00	135	14.61
Dun	Aug 28/07	23:50	108	15.48
Dun	Aug 29/07	6:00	81	20.35
Dun	Aug 29/07	9:00	89	17.36
Dun	Aug 29/07	11:50	109	16.57
Dun	Aug 29/07	14:50	135	16.21
Dun	Aug 29/07	17:45	147	15.62
Dun	Aug 29/07	20:50	133	16.09
Cay	Aug 28/07	21:25	142	14.45
Cay	Aug 29/07	6:35	84	23.01
Cay	Aug 29/07	9:40	75	23.76
Cay	Aug 29/07	12:20	103	17.29
Cay	Aug 29/07	18:15	155	12.80
Cay	Aug 29/07	21:20	144	13.82

Appendix 4. Wind speed data measured by Environment Canada at Hamilton, Ontario during the diel survey.

Jul 25/06	Wind Speed (km/h)	Aug 21/06	Wind Speed (km/h)	May 9/07	Wind Speed (km/h)
15:00	15	21:00	7	6:00	22
16:00	15	22:00	6	7:00	28
17:00	13	23:00	9	8:00	30
18:00	17	0:00	6	9:00	19
19:00	11	1:00	6	10:00	19
20:00	11	2:00	7	11:00	30
21:00	11	3:00	7	12:00	30
22:00	9	4:00	7	13:00	19
23:00	6	5:00	7	14:00	26
0:00	9	6:00	11	15:00	22
1:00	6	7:00	11	16:00	22
2:00	6	8:00	13	17:00	26
3:00	7	9:00	11	18:00	19
4:00	6	10:00	15	19:00	11
5:00	7	11:00	19	20:00	6
6:00	11	12:00	24	21:00	7
7:00	11	13:00	19	22:00	0
8:00	20	14:00	20	23:00	6
9:00	20	15:00	22	0:00	0
10:00	26	16:00	15	1:00	0
11:00	28	17:00	13	2:00	0
12:00	26	18:00	13	3:00	0
13:00	33	19:00	13	4:00	0
14:00	28	20:00	11	5:00	0
15:00	28	21:00	4	6:00	4

Jun 13/07	Wind Speed (km/h)	Jul 18/07	Wind Speed (km/h)	Aug 28/07	Wind Speed (km/h)
18:00	15	15:00	15	21:00	6
19:00	9	16:00	17	22:00	7
20:00	0	17:00	22	23:00	7
21:00	0	18:00	22	0:00	9
22:00	0	19:00	11	1:00	7
23:00	9	20:00	6	2:00	7
0:00	7	21:00	0	3:00	7
1:00	11	22:00	4	4:00	7
2:00	13	23:00	0	5:00	9
3:00	19	0:00	0	6:00	7
4:00	22	1:00	6	7:00	7
5:00	22	2:00	6	8:00	9
6:00	30	3:00	0	9:00	11
7:00	24	4:00	11	10:00	22
8:00	26	5:00	0	11:00	22
9:00	22	6:00	7	12:00	19
10:00	22	7:00	4	13:00	19
11:00	26	8:00	6	14:00	20
12:00	24	9:00	11	15:00	17
13:00	33	10:00	11	16:00	22
14:00	37	11:00	17	17:00	15
15:00	33	12:00	13	18:00	17
16:00	24	13:00	13	19:00	11
17:00	24	14:00	15	20:00	7
18:00	24	15:00	13	21:00	7