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Development of an Integrated Process Model for Algae Growth in a Photobioreactor

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by

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DEDICATION

This thesis is dedicated to my loving parents and sister. They have always been behind me and made many sacrifices for my well being; even during these two years that they have been far away from me.

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ABSTRACT

While understanding the kinetics of algae growth plays an important role in improving algae cultivation technology, none of the existing kinetic models are able to describe algae growth when more than three growth limiting factors are involved. A model was developed in this study to describe algae growth in a photobioreactor. Two expressions were proposed based on the Monod model to relate the specific growth rate of algae to the concentration of nitrogen, phosphorus, inorganic carbon and light intensity in the culture media. Algal biomass concentration as a function of time was calculated by solving mass and energy balances around the photobioreactor. Model simulations were compared with the experimental data from the cultivation of wild type algae in a semi-continuous culture of a completely mixed photobioreactor. There were no significant differences between the model results from using the two proposed expressions of the specific growth rate of algae. Biomass concentration simulated by the model followed the same pattern as the measured concentration. However, there was discrepancy between the model output and the experimental results. This is because environmental conditions varied a lot during the experiment and some environmental factors such as temperature were not considered in the model. Also, most of the model's parameters were either derived theoretically or obtained from literature instead of being measured directly. It was found through sensitivity analysis that the maximum biomass density predicted by the model is very sensitive to the maximum specific growth rate for carbon, maximum growth yield and higher heating value of algae. Results from running the model for a

continuous culture of the same photobioreactor, showed that the minimum hydraulic retention time for the growth of algae will be 30 days. Further investigations are needed to get more accurate data for sensitive parameters so algae growth can be predicted more accurately. Future work towards integrating other factors including temperature, pH, inhibition factors and decay rate in the kinetic expression, will lead to a better prediction of algae growth.

CHAPTER 1-INTRODUCTION

The evidence of climate change and environmental impacts due to excessive use of fossil fuels is accumulating. With the increasing demand in energy, fossil fuels as non-renewable resources will be depleted soon. Oil and natural gas storage on earth has been estimated to be depleted in 40 and 64 years, respectively (Xin et al., 2010). Carbon dioxide, a greenhouse gas emitted during the consumption of fossil fuels, is considered to be one of the main causes of global warming (Morais and Costa 2007). As a result, production of energy from renewable resources and development of CO_2 sequestration methods were identified as two grand engineering challenges by the National Academy of Sciences (NAE, 2008).

CO_2 can be sequestrated through physical (e.g., underground injection of CO_2 into reservoirs), chemical (e.g., neutralization of carbonic acid to form carbonates or bicarbonates) and biological (e.g., biomass sequestration) methods (Lackner, 2003). Biofixation and utilization of CO_2 by microalgae are among the most productive biological methods of treating industrial waste and CO_2 emissions. The yield of algae biomass per acre is three to fivefold greater than from typical crops (Chang and Yang, 2003). Maximum daily CO_2 biofixation was calculated to be 53.29% and 28.08% for *Scenedesmus obliquus* and *Spirulina (Arthrospira) sp*., respectively, at input CO_2 concentration of 6% (Morais and Costa, 2007). *Chlorella sp.* and *Spirulina platensis* showed 46% and 39% mean fixation efficiency, respectively, at input CO_2 concentration of 10% (Ramanan et al., 2010).

Algae are not only productive CO_2 utilizers, but also one of the most photosynthetically efficient plants at converting solar energy into chemical energy. A 1-ha algae farm on wasteland can produce over 10 to 100 times the amount of oil as compared to any other known oil crops (Demirbas, 2010). Algae store the chemical energy to produce lipids, carbohydrates and proteins. The lipids and carbohydrates within algae can be converted into a variety of fuels such as biodiesel, methane and other hydrocarbons. The advantages of these fuels to other alternative sources of energy (e.g., hydroelectric, nuclear, wave, and wind power) are that, they are renewable, biodegradable, produce fewer emissions and do not contribute to the increase in CO_2 in the atmosphere (Scragg et al., 2003).

In order to grow algae, a culture medium, light to drive photosynthesis, and a source of water is needed. The growth medium must contribute inorganic elements that help make up the algal cells such as nitrogen, phosphorus, iron, and sometimes silicon (Sasi et al., 2011)**.** With wastewater, two of the essential needs for algae growth would be met. Wastewater could be used for a culture medium as well as a source of water.

Secondary effluents from wastewater treatment plants contain a large amount of contaminants, such as NH_4^+, NO_3^- and PO_4^{3-} that need to be treated before discharging into water bodies. Microalgae have been proposed as an alternative biological treatment for removing nutrients due to the lower cost and sludge production of this technology (Ruiz-Marin et al., 2010). A simple cellular structure and a large surface to volume body ratio, give algae the ability to uptake nitrogen, phosphorus and carbon into algal cells.

Depending on the type of algae, different methods are used to cultivate them. Phototrophic algae are commonly grown in open ponds and photobioreactors. In contrast

to the open ponds that raise the issues of land use cost, water availability, and appropriate climatic conditions, photobioreactors offer a closed culture environment that is protected from direct fallout and so is safe from invading microorganisms (Demirbas, 2010). Convenient configuration and optimization of artificial light as well as higher water-use efficiency and improved harvesting efficiency, are other advantages of photobioreactors to open ponds (Ono and Cuello, 2007). However, this technology is relatively expensive compared to the open ponds because of the infrastructure costs. Therefore, it is critical to improve biomass productivity to make the use of photobioreactors feasible.

Understanding the mechanisms of algae growth, the utilization of nutrients and developing models in order to predict biomass formation are essential to enhance and use photobioreactors. Kinetic modeling of microalgae growth has become significant because an accurate model is a prerequisite for designing an efficient photobioreactor, predicting process performance, and optimizing operating conditions.

Mathematical models such as the Monod and Droop models have been traditionally used to predict algae specific growth rate in response to the substrate concentration in culture medium. Several experiments have been done on different species of algae in order to obtain the parameters in the mentioned models. In some studies the specific growth rate of algae, shown by either Droop or Monod model, has been considered as a function of one substrate (nitrogen, phosphorus or carbon) (Kapdan & Aslan, 2008; Torres, 2004; Sunda, 2009; Smit, 2002; Yao, 2011; Tang, 2011). A few of them have looked at the integrated form of the Monod model which considers the algae specific growth rate as a function of both nitrogen and phosphorus concentration (Xin et al., 2010). Some of the studies, however, focused solely on the effect of light

intensity on algae growth rate, which is also shown by the Monod model (Martinez, 1997; Ogbonna, 1995; Yeh, 2010).

Both the Monod and Droop model state that the growth rate of an organism maybe limited by a single resource once its availability becomes very low. In reality; however, two or more factors typically limit the growth (Richmond, 2004). Therefore, those models do not predict the algae specific growth rate accurately when more than one compound is limiting. On the other hand, the effect of light intensity on specific growth rate of phototrophic algae is undeniable and should be considered as another variable. Therefore, there is a need for a model that considers all effective variables on algae growth.

1.1 Goal and Objectives

The goal of this study is to develop a model that is able to predict algae growth in continuous culture in a photobioreactor. The kinetic expression of the specific growth rate of algae for this model incorporates all critical factors that affect the growth; such as light intensity and concentration of nitrogen, phosphorus and inorganic carbon. Thus, the model is able to simulate algae growth when multiple factors limit growth.

The objectives of this study are:

1) Developing an integrated process model for algae growth;
2) Validating the model with experimental data; and
3) Conducting sensitivity analysis to identify the most sensitive parameters.

CHAPTER 2-BACKGROUND

2.1 Algae Growth vs. Substrate Concentration

In general, algae growth can be described by five phases as explained below (Vaccari et al., 2006; Richmond, 2004):

1) A lag phase, where a delay in growth initially happens due to the presence of non-viable cells or spores in the inoculums or physiological adjustments to change in nutrient concentration or culture conditions;
2) An exponential phase, where cells grow and divide as an exponential function of time, as long as mineral substrates and light intensity are saturated;
3) A linear growth phase, where growth rate is linear as a function of time;
4) A stationary growth phase, where the growth rate remains constant. However, increase of nutrient concentration may lead to luxury storage of nutrients by algae during this phase; and
5) A decline or death phase, where the decrease in the concentration of nutrients and/or accumulation of toxic waste products leads to microorganisms' death.

These five phases are shown in the schematic growth rate curve in Figure 1.

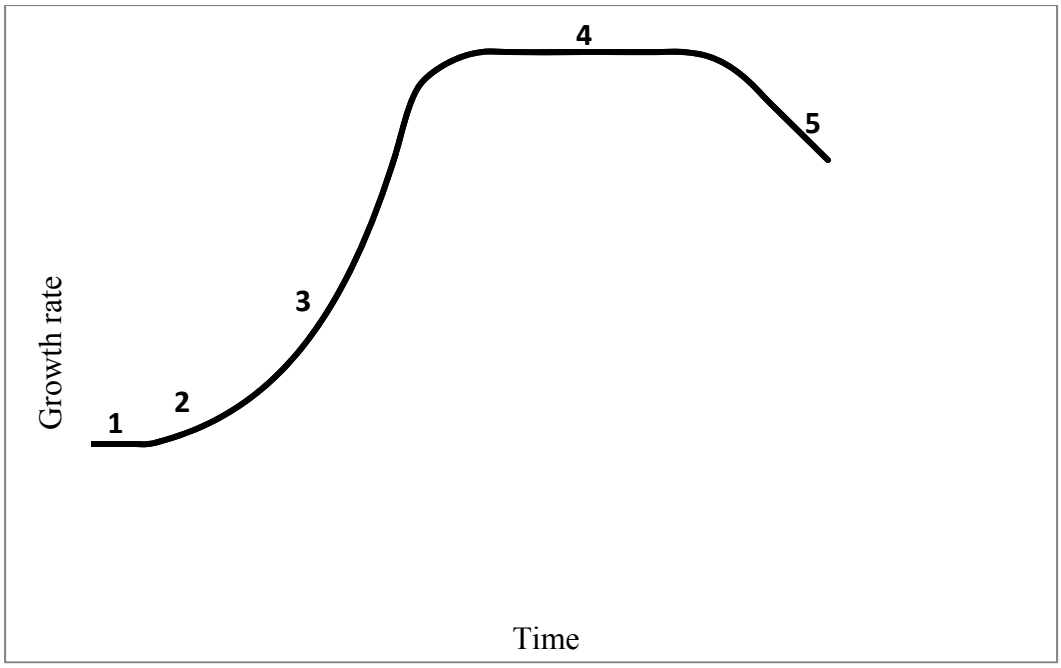

Figure 1-Schematic growth in a batch culture. Different growth phases are shown, i.e. 1=Lag phase, 2=Exponential phase, 3=Phase of linear growth, 4=Stationary growth phase, 5= Decline or death phase (Richmon, 2004)

The requirements for developing nutrient recipes for algal cultivation were summarized by Richmond (2004) in Handbook of Microalgal Culture:

1) The total salt content, which is determined by the habitat where the algae originates
2) Cell composition in terms of the major ionic components such as K^{+}, Mg^{2+}, Na^{+}, Ca^{2+}, SO_4^{-2} and Cl^{-}
3) The nitrogen sources, especially ammonia, nitrate and urea
4) Carbon source either CO_2 or HCO_3^{-}
5) pH
6) Trace elements and some chelating agent such as ethylene diamine tetra acetic acid (EDTA)
7) Vitamins

The three most vital nutrients for autotrophic algae growth are carbon, nitrogen and phosphorus.

CO_2 and HCO_3^- are the most important resources of carbon supply for the autotrophic growth of algae. The bicarbonate-carbonate buffer system (CO_2-H_2CO_3-HCO_3^--CO_3^{-2}) present in freshwater provides enough CO_2 through chemical reactions and maintains a specific pH that is optimal for cultivated species (Richmond, 2004). The injected air, which contains a specific amount of CO_2, provides the main resource of inorganic carbon for the cultivation of algae in photobioreactors.

In addition to carbon, nitrogen is the second most important nutrient for biomass production. The nitrogen content of the biomass can range from 1% to more than 10% (Richmond, 2004). Nitrogen can be supplied in the forms of nitrate, ammonia or urea for the utilization of algae. Ammonia nitrogen is the preferred nitrogen source for algae. When ammonia is used as a nitrogen source, the pH will decrease significantly due to the release of H^+. However, the pH increases when nitrate is used as a sole source of nitrogen because of increased alkalinity in the form of HCO_3^-. Ammonia could be lost from the growth media due to volatilization, particularly when pH increases. That will be an important factor to decide whether to supply nitrate or ammonia as nitrogen source (Richmond 2004).

Although algae contain less than 1% phosphorus, it is an important nutrient in many ecosystems (such as lakes, rivers, and estuaries). Algae also store excess phosphorus during the luxury uptake (Richmond, 2004). They used the stored phosphorus when the external supply of this nutrient is limited.

In addition to essential nutrients, light intensity is another factor that affects the growth rate of algae. Through the photosynthesis process, light energy and inorganic compounds are converted to organic matter by photoautotrophs. That is why light intensity affects the autotrophic growth rate of algae. In general, light is spatially distributed along the light path inside of the photobioreactors as it is absorbed and scattered by the microalgae instead of penetrating deeply into algal cells (Yun and Park, 2007).

Although ammonia is a good source of nitrogen for algal growth, free ammonia is toxic to most strains of microalgae (Yuan et al., 2011). High concentrations of ammonia in the culture could inhibit the growth of algae. Light intensity can also inhibit the growth at high irradiances (Dauta et al., 1990). High concentration of dissolved oxygen is also another factor that can inhibit or delay the growth of algae (Dalton and Postgate, 1968).

2.2 Literature Review: Algae Growth Kinetic Models

Algae growth kinetic models relate the growth rate of algae to the substrate concentration in a culture media. Kinetic models provide an understanding of biomass production and nutrient consumption rate, which are essential for designing efficient photobioreactors for the purpose of nutrient removal as well as predicting process performance, and optimizing operating conditions.

The most famous kinetic models are the Monod and Droop models. Many studies have been conducted for finding those two model's parameters for different species of algae (Novak and Brune, 1984; Aslan and Kapdan, 2006, Sasi et al., 2010; Chae et al., 2006; Goldman et al., 1974; Hsueh et al., 2004; Morais and Costa, 2007; Tang et al.,

2011; Smith 2002; Xin et al., 2010; Baldia et al., 1991; Huang and Chen, 1986; Chojnacka and Zielińska, 2011). In addition, some modifications to the Monod and Droop models have been proposed. The modified models relate the specific growth rate of algae to one of the following: nitrogen concentration (Sunda et al., 2009), phosphorus concentration (Flynn 2002; Yao et al., 2011), or light intensity (Martinez at al., 1997; Ogbonna et al., 1995). An integrated Monod model for two or three affecting factors, was also proposed for multi-limited cultures (Yang, 2011; Zhang et al., 1999). Several new models were suggested based on the Monod model and took into account the inhibition factor (Andrews model). Mayo (1997) showed that the specific algae growth rate is related to the pH in culture by Andrew's model. Sterner and Grover (1998) proposed a temperature dependent model for algae growth based on the Monod model.

This section is devoted to a description of the common kinetic models for algae growth. Existing kinetic models are divided into six groups:

1) Kinetic models related to inorganic carbon concentration
2) Kinetic models related to nitrogen concentration
3) Kinetic models related to phosphorus concentration
4) Kinetic models related to light intensity
5) Kinetic models with consideration of multiple factors
6) Kinetic models considering inhibition
7) Kinetic models related to temperature

Each group is described in a different sub-section. At the end of each sub-section, there is a table in which the models belonging to that group are indicated (Table 1-6).

The Monod model is a general kinetic model for describing the relationship between the microorganism growth and concentration of the limiting nutrient and is shown as:

$$\mu = \mu_{max} \frac{S}{(K_s + S)} \quad (1)$$

where μ_{max} is the maximum specific growth rate achieved at high, non-limiting nutrient concentrations and K_s is the half-saturation constant (the nutrient concentration at which the specific growth rate is half of the maximum).

Researchers would prefer to use the Monod model because the external substrate concentration is easily measured. However, the applicability of the Monod model is doubtful, because luxury uptake of nutrients and storage for later growth may lead to a temporal uncoupling between reproductive rates and dissolved nutrient concentrations (Sommer, 1991). Under unsteady state conditions and when intracellular storage happens, the cell quota of the limiting nutrient, (expressed as the total amount of nutrient per cell) is considered to be a better indicator of the nutritional status than ambient concentrations (Sommer, 1991). However, the cell quota of individual species cannot be measured easily under natural conditions. The growth rate of algae is more dependent on the internal cellular concentrations than on the external quantities (Richmond, 2004).

The contribution of the Droop model was to relate growth rate to the internal nutrient content of a cell rather than the nutrient concentration around the medium. The Droop model can be written as:

$$\mu = \mu_{max} \left(1 - \frac{K_q}{q}\right) \quad (2)$$

where K_q is the limiting cell quota for the limiting nutrient and q is the cell quota for the limiting substrate.

Attempts to fit the Monod model to the nitrogen-limited cases for net-plankton size spectrum algae (>30 μm) were shown to be correspondingly poor, although not extremely bad (Sommer 1991). Under these conditions the Droop model proved to be more applicable. However, in earlier studies (Sommer, 1989), better fits of N- and P-limited Monod-kinetics had been found for small, nanoplanktic algae (<30 μm). Because phosphorus may accumulate within cells, high growth rates can be maintained for several generations with no or little uptake. In such circumstances, internal cellular quotas become highly relevant (Chapele et al., 2010).

2.2.1 Kinetic Models Related to Inorganic Carbon Concentration

Existing kinetic models related to the inorganic carbon concentration are shown in Table 1. Previous work by Hsueh et al. (2009), Morais and Costa (2007), Goldman et al. (1974), Novak and Brune (1985) and Tang et al. (2011), were aimed at calculating Monod's parameters and optimal carbon concentration for algae growth in carbon limiting cultures.

Table 1- Existing kinetic models related to inorganic carbon concentration

Monod model		
Model	Nomenclature	Reference
$\mu = \mu_{max}\frac{S_c}{(K_{s,c} + S_c)}$	S_c: Carbon concentration	Hsueh et al., 2009; Morais and Costa, 2007; Goldman et al., 1974; Tang et al., 2011; Novak and Brune, 1985

2.2.2 Kinetic Models Related to Nitrogen Concentration

Existing kinetic models related to the nitrogen concentration are indicated in Table 2. Several studies have used the general form of the Monod model for a nitrogen limiting culture; most of them aimed at estimating Monod's parameters for different species of algae (Aslan and Kapdan, 2006; Baldia et al., 1991; Tam and Wong, 1996).

Sunda et al. (2009) made some modifications to the Monod model in order to describe the specific growth rate of *Thalassiosira pseudonana* and *Thalassiosira*. *weissflogii* cultured in seawater medium. The experimental data for algae specific growth rate versus the nitrogen concentration of ammonium in a nitrogen-limited medium were observed to fit better in the modified model as it is shown in Table 2.

Table 2-Existing kinetic models related to nitrogen concentration

Monod model		
Model	Nomenclature	Reference
$\boldsymbol{\mu = \mu_{max}\frac{S_N}{(K_{s,N} + S_N)}}$	μ_{max}: Maximum specific growth rate $K_{s,N}$: Half-saturation constant S_N: Nitrogen concentration	Aslan and Kapdan, 2006; Baldia et al., 1991; Tam and Wong, 1996
$\boldsymbol{R = R_{max}\frac{S_N}{(K_{s,N} + S_N)}}$	R_{max}: Maximum nitrogen uptake rate	Smith 2002;
Modified Monod model		
Model	Nomenclature	Reference
$\boldsymbol{\mu = \begin{cases} \mu_{max}(S - S_\mu)/(K + S - S_\mu) \; if \; S > S_\mu \\ 0 \qquad\qquad\qquad\qquad\quad Otherwise \end{cases}}$	S_μ: Finite ammonium concentration K : Half saturation concentration	Sunda et al., 2009

2.2.3 Kinetic Models Related to Phosphorus Concentration

Existing kinetic models related to the concentration of phosphorus are indicated in Table 3. There have been many modifications to Droop model for describing the relationship between specific growth rate and phosphorus quota. Flynn (2002) proposed a derived Droop function that links the growth rate of algae to the phosphorus quota. Yao et al. (2011) developed a two stage model for phosphorus uptake by *S. quadricauda* which considers surface adsorbed and intracellular phorphorus pool. Their model was based on the Michaelis-Menten equation, which has the form of the Monod model, and feedback control of cell quota. Feed back function of cell quota was also derived from previous studies by Flynn in 1997 (Yao et al., 2011).

Table 3-Existing kinetic models related to phosphorus concentration

Monod model		
Model	Nomenclature	Reference
$\boldsymbol{\mu = \mu_{max}\frac{S_p}{(K_{s,p} + S_p)}}$	S_p: Phosphorus concentration	Aslan and Kapdan, 2006
Droop model		
Model	Nomenclature	Reference
$\boldsymbol{\mu = \mu_{max}(1 - \frac{K_q}{q})}$	K_q : Limiting cell quota for the limiting nutrient q : Cell quota for the limiting substrate	Grover, 1991; Sommer, 2011; Lemesleand Maillere,2008;

Table 3 (Continued)

Modified Droop model		
Model	Nomenclature	Reference
$\boldsymbol{\mu} = \boldsymbol{\mu_{max}}\left(\frac{(\mathbf{1}+\boldsymbol{KQ}).(\boldsymbol{Q_p}-\boldsymbol{Q_{pmin}})}{(\boldsymbol{Q_p}-\boldsymbol{Q_{pmin}})+\boldsymbol{K_q}}\right).(\boldsymbol{Q_{pmax}} - \boldsymbol{Q_{pmin}})$	Q_{Pmin}, Q_{Pmax},Q_P :Minimum, maximum phosphorus quota, respectively. K_f : Dimensionless parameter to set the curve form.	Flynn, 2002
$\boldsymbol{T} = \boldsymbol{K_p} \times \boldsymbol{Q_{max}} \times \boldsymbol{\mu_{max}} \times \frac{\boldsymbol{WP}}{\boldsymbol{WP}+\boldsymbol{K_m}} \times \frac{(\mathbf{1}-{}^{\mathbf{Q_t}}/_{\mathbf{Q_{min}}})^{\mathbf{4}}}{(\mathbf{1}-{}^{\mathbf{Q_t}}/_{\mathbf{Q_{min}}})^{\mathbf{4}}+\mathbf{K_q}}$	T : Transport rate of surface-adsorbed P into algal cell (10^{-8}μmol/(cell·min)) K_m:Half-saturation constant for the substrate concentration (μmol/mL) Q_t: total cell quota (10^{-8}μmol/cell) Q_{max}: Maximum cell quota for algal existence(10^{-8}μmol/cell) K_p:Dimensionless coefficient K_f : Dimensionless constant used to control the shape of the feedback function curve WP :phosphate concentration in the substrate(μmol/mL)	Yao et al., 2011

2.2.4 Kinetic Models Related to Light Intensity

Light related kinetic models are shown in Table 4. Monod's parameters' estimation in a light limited culture, using the general form of the Monod model was reported in many studies (Chae and Shin, 2006; Huang and Chen, 1986; Sasi et al.,2011; Chojnacka and Zielińska, 2011).

Martinez et al. (1997) showed that the relationship between the specific growth rate of *C. pyrenoidosa* and light intensity can be described by either the Monod (Tamiya model) or the Exponential model. The estimated values for μ_m and I_s by both Tamiya and

exponential model were similar to those estimated by Camacho et al. (Martinez et al., 1997). However, Tamiya model gave a closer estimation.

Ogbonna et al. (1995) simulated effects of light intensity on the specific growth rate of *C. pyrenoidosa* C-212 and *S. platensis* using a more complicated form as shown in Table 4.

Table 4- Existing kinetic models related to light intensity

Monod model		
Model	Nomenclature	Reference
$\mu = \mu_{max} \frac{I}{(K_{s,I} + I)}$	I: Light intensity $Ks_{,I}$: Saturation light intensity	Chae and Shin, 2006; Martinez et al., 1997; Huang and Chen, 1986;Sasi et al.,2011; Chojnacka and Zielińska, 2011
Exponential model		
Model	Nomenclature	Reference
$\mu = \mu_m(1 - e^{-I/K_{s,I}})$	I: Light intensity $Ks_{,I}$: Saturation light intensity	Martinez et al., 1997
Ogbonna et al., 1995		
Model	Nomenclature	Reference
$\mu = K^{"}\left\{\frac{\varepsilon.a_l.X.I_0}{X.V} - I_m(1 - V_F)\right\}$	K":A proportionality constant (kg/mol), ε: A constant a_l:Effective light absorption surface area of each cell (m^2), X:Cell concentration (kg/m^3), V: Liquid volume in the reactor (m^3), I_0 :Incident light intensity (mol/m^2. d) I_m:Maintenance rate (mol/kg .d) and V_F:Illuminated volume fraction of the reactor	Ogbonna et al., 1995

2.2.5 Kinetic Models with Consideration of Multiple Factors

Existing kinetic models considering the effect of multiple factor on the specific growth rate of algae, are listed in Table 5. Yang (2011) offered an integrated Monod model for predicating the specific growth rate of algae in algal ponds. His model considers the effect of dissolved CO_2 (S_{CO2}) as well as total nitrogen concentration (S_N) and light intensity on the growth rate of algae:

Weiss and Ollis (1980) proposed a model depending on biomass concentration only by means of a logistical equation:

$$\mu = \mu_m(1 - \frac{C_x}{C_{xm}}) \quad (3)$$

where C_{Xm} and C_x are the achievable maximum cell concentration (g L^{-1}) and cell concentration (g L^{-1}), respectively.

Zhang et al., 1999 extended Andrews model using Tamiya and the model proposed by Weiss and Ollis to describe cell growth and sodium acetate concentration in a batch culture of H. pluvialis.

Table 5-Existing kinetic models with consideration of multiple factors

Model	Nomenclature	Reference
$\boldsymbol{\mu = \mu_m \frac{S_N}{S_N+K_{NA}} (\frac{S_{CO2}}{S_{CO2}+K_{CO2}}) f_I}$ $\boldsymbol{f_I = \frac{I_a}{I_s} \exp\,(1 - \frac{I_a}{K_{s,I}})}$	K_{NA}: A constant f_I: The light intensity factor I_a :Average light intensity	Yang, 2011

Table 5 (Continued)

Model	Nomenclature	Reference
$\mu = \mu_m \frac{S}{S+K_s+S/K_I}\left(\frac{I}{I_s+I}\right)\left(1-\frac{C_x}{C_{xm}}\right)(1-\frac{C_p}{C_{pm}})$	C_{pm}: Maximum product concentration (mg L^{-1}), C_P : Product concentration (mg L^{-1}) C_{Xm}:Achievable maximum cell concentration (g L^{-1}) C_x: cell concentration (g L^{-1})	Zhang et al., 1999
$R_{max} = R_{max}' \frac{S_N}{(K_{s,N}+S_N)} \frac{S_P}{(K_{s,P}+S_P)}$ $R_{max} = \frac{\mu K}{4}$	R_{max}: Maximum population growth rate (cells.(mL d)$^{-1}$), K: carrying capacity (cells mL^{-1}) R_{max}': Maximum value of R_{max} at the saturated N (P) conc. (cells.(mL d)-^{1})	Xin et al., 2010

2.2.6 Kinetic Models Considering Inhibition

It is possible for algal growth to be less than the maximum due to the presence of toxic agents, or a substance used for growth at high enough concentrations (Vaccari, 2006:338). The most common model to describe this substrate inhibition is a modification of the Monod expression, referred to as Andrews model (Vaccari, 2006:338). Magbanua et al. (1998) presented a method for calculating parameters of Andrews model. Mayo (1997) related the specific growth rate to the PH of the culture using the Andrews model. Existing kinetic models with consideration of inhibition are listed in Table 6.

Table 6- Existing kinetic models considering inhibition

Andrews model		
Model	Nomenclature	Reference
$\mu = \mu_{max} \frac{S}{S + K_s + S/K_I}$	K_I: Inhibition coefficient	Magbanua et al., 1998
$\mu = \frac{A' e^{(-E/RT)}[H^+]}{[H^+] + K_{OH} + [H^+]^2/K_H}$	$[H^+]$:Concentration of H^+ (mol L^{-1}) A': Constant (day^{-1}) E: Activated energy of the growth limiting reaction (J $mole^{-1}$), R: Universal gas constant (J $K^{-1}mol^{-1}$), T: Absolute temperature (°K), K_{OH} and K_H : Rate constants	Mayo, 1997

2.2.7 Kinetic Models Related to Temperature

Sterner and Grover (1998) developed a temperature dependent model based on the Monod model. This model represents the best estimate of N-limited algal growth in reservoirs and has the form of:

$$\mu = T\mu_T \frac{S}{(Ks + S)} \quad (4)$$

where μ_T is the coefficient for temperature-dependence for growth and T is temperature. However, this model tended to overestimate growth rate at low growth.

As it was shown in this chapter, all attempts for relating the specific growth rate of algae to the factors that affect it, have been towards modifying the Monod or Droop model as a function of one or two limiting factors. The most recent study by Yang (2011), considers the specific growth rate as a function of three factors (nitrogen, dissolved CO_2 and light intensity). No research has been done to date in order to prove the validity of an integrated Monod model for four main factors including carbon, nitrogen, phosphorus and light intensity. The goal of this study is to develop an integrated process model that is able to describe the growth rate of algae when all of those factors are limited at the same

time. Effect of all factors are considered in a new expresion for the specific growth rate of algae. The model was validated with experimental data and sensitivity analysis was done in order to identify sensitive parameters.

CHAPTER 3-MODEL DEVELOPMENT

This chapter is aimed at describing the model that was developed for predicting algae growth in the continuous culture of a photobioreactor. A schematic of a completely mixed photobioreactor is shown in Figure 2. Input and output variables are indicated in the figure. Model simulations are also shown at the end of this chapter, following with a detailed discussion of each.

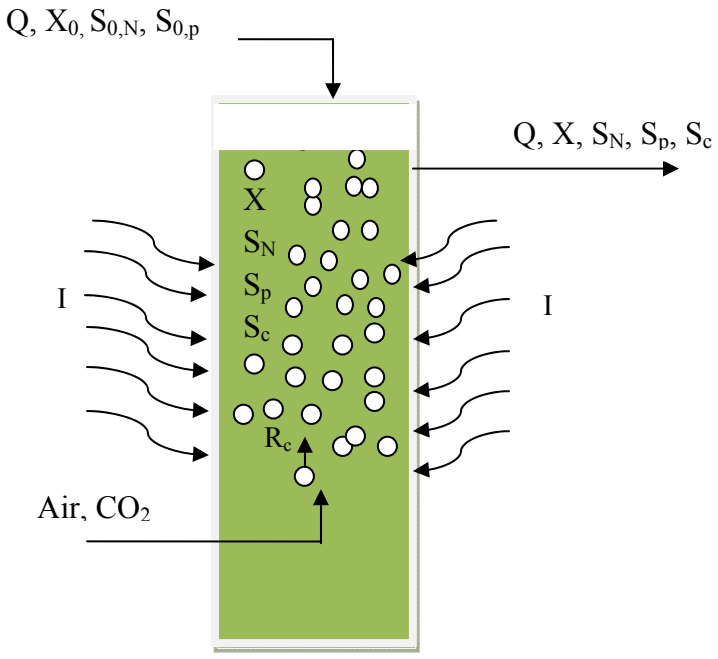

Figure 2-Schematic of a completely mixed photobioreactor.
Q_t: Wastewater flow rate (m^3 d^{-1}) as a function of time; $S_{0,N}$ and $S_{0,P}$: Influent concentrations of nitrogen and phosphorus, respectively (kg m^{-3}); S_N,S_P and S_c: Effluent concentrations of nitrogen, phosphorus and carbon, respectively; I: Light intensity (J d^{-1} m^{-2}); R_c: Input rate of CO_2 from the air in bubbles into the culture (kg d^{-1}); X_0 and X: biomass concentration in influent and effluent, respectively (kg m^{-3})

3.1 Model Assumptions and Limitations

Assumptions of the model were as follows:

1) The photobioreactor is completely mixed;
2) The specific growth rate of algae is related to the nitrogen, phosphorus and carbon concentration as well as light intensity;
3) There is no algae in the influent into the culture;
4) The influent concentration of nitrogen and phosphorus to the photobioreactor remains constant;
5) A light limited continuous flow culture was assumed for writing the energy balance, where all incident photosynthetically available radiance is absorbed;
6) The ideal gas law is applicable to the air in bubbles;
7) Although the size of gas bubbles are not constant inside the bioreactor and the gas-liquid mass transfer rate changes continuously (Becerril and Yescas 2010), it is assumed that the bubbles size remains almost constant due to the short length of the reactor (2.3 m);
8) Temperature and pH are constant in the culture;
9) Yield coefficients are constants and the same as their theoretical values.

Limitations to the model are listed as follows:

1) Kinetic parameters were obtained from previous studies that were not conducted under the exact same conditions as the experiments at the University of South Florida (USF);

2) Nutrient inhibition is not considered in the proposed expression for the specific growth rate;

3) The half saturation constant for carbon was based on the $NaHCO_3$-carbon from the literature (Chen et al., 2010). However, CO_2 has been the carbon source in the experiment;

4) As previously mentioned in Chapter 2, there are some limitations to the Monod model. Since the proposed model was derived on the basis of the Monod model, it will also have the same limitations of the Monod model.

3.2 Model Description

3.2.1 Mass and Energy Balances on Photobioreactor

The first step of the model development is to derive mass and energy balances on the photobioreactor. Mass balances were considered for all input and output materials to the reactor (biomass, nitrogen, phosphorus and inorganic carbon). An energy balance was written for assessing the change in energy in the culture. Mass balance equations below were derived for biomass, nitrogen and phosphorus in the reactor based on the assumptions described in Section 3.1:

$$Q_t X_0 - Q_t X + \mu X V = V \frac{dX}{dt} \tag{5}$$

$$Q_t S_{0,N} - Q_t S_N - \frac{\mu}{Y_N} X V = V \frac{dS_N}{dt} \tag{6}$$

$$Q_t S_{0,P} - Q_t S_P - \frac{\mu}{Y_P} X V = V \frac{dS_P}{dt} \tag{7}$$

where Q_t is the wastewater flow rate ($m^3\ d^{-1}$) as a function of time; X_0 is the influent concentration of biomass which is zero based on the assumption described in section 3.1;

$S_{0,N}$ and $S_{0,P}$ are the influent concentrations of nitrogen and phosphorus, respectively (kg m^{-3}); S_N and S_P are the effluent concentrations of nitrogen and phosphorus, respectively (kg m^{-3}); V is the reactor volume (m^3); Y_N and Y_P are yield coefficients for nitrogen and phosphorus, respectively; μ is algae specific growth rate (d^{-1}) and X is the algae biomass concentration (kg m^{-3}).

Carbon is provided by air injection into the photobioreactor, where the dissolved CO_2 in the air is transferred to the culture. Therefore the input rate of CO_2 into the culture will be:

$$R_c = K_L a(C_s - S_C)V \tag{8}$$

And the mass balance will have the form of:

$$K_L a(C_s - S_C)V - Q_t S_C - \frac{\mu}{Y_C} XV = V\frac{dS_C}{dt} \tag{9}$$

where R_c is the input rate of CO_2 from the air in bubbles into the culture (kg d^{-1}), K_L is the overall mass transfer coefficient (m d^{-1}), a is the surface area available for mass transfer per volume of the system (m^{-1}), C_s is the liquid-phase concentration of CO_2 in equilibrium with air in bubble (kg m^{-3}), S_C is the effluent concentration of inorganic carbon (kg m^{-3}), Y_C is the yield coefficient for carbon.

According to Richmond 2004, the energy balance for a continuous culture is:

$$IA - \frac{Q_t X}{Y} = V\frac{dE}{dt} \tag{10}$$

where A is the illuminated surface area (m^2), I is the light intensity entering the photobioreactor (J d^{-1} m^{-2}) and dE is the increase in energy content of the culture per volume of the culture (J m^{-3}).

Y, which is the overall growth yield of algae (kg J^{-1}), is defined as (Richmond 2004):

$$\frac{1}{Y} = \frac{1}{Y_G} + \frac{m}{\mu} \quad (11)$$

where Y_G is the maximum growth yield (kg J^{-1}) and m is the maintenance coefficient (J kg^{-1} d^{-1}).

The energy content of the culture per volume of the culture, E, can be expressed as (Hulatt and Thomas, 2011):

$$E = HHV \times X \quad (12)$$

where HHV is the higher heating value of algae biomass which can be estimated using the following equation proposed by Hulatt and Thomas (2011):

$$HHV = -0.049 + 0.069N + 0.533C + 0.226H \quad (13)$$

where the elements carbon, hydrogen and nitrogen (C, H, N) are measured as % mass, and HHV is in kJ g^{-1}.

Substituting equations 11-12 into equation 10 yields:

$$IA - Q_t X \left(\frac{1}{Y_G} + \frac{m}{\mu}\right) = V.HHV.\frac{dX}{dt} \quad (14)$$

Both equations 5 and 14 contain *dX/dt*. The change of biomass concentration with respect to time is either controlled by the mass balance (Eq. 5) or the energy balance (Eq. 14). It can be expressed in the following form,

$$\frac{dX}{dt} = min(\frac{dX}{dt}\ from\ biomass\ balance, \frac{dX}{dt}\ from\ energy\ balance) \quad (15)$$

3.2.2 Specific Growth Rate Expression

Two expressions were proposed for the specific growth rate of algae. Each expression is a different combination of the Monod model for nitrogen, phosphorus, carbon, and light intensity. Integrated forms were developed to describe the algae growth rate when more than one factor is limiting. According to a study by Okpokwasili and Nweke (2005), two ways were suggested for integrating the Monod model in order to describe the growth rate when the growth is affected by more than one substrate:

1) Double Monod model, which has the form of:

$$\mu = \mu_{max} \frac{S_1}{(K_1 + S_1)} \times \frac{S_2}{(K_2 + S_2)} \quad (16)$$

where 1 and 2 represent the substrates. The value of the maximum specific growth rate in a double-limiting culture is derived from experiment. According to Bader (1978), the Double Monod model has a narrow range of utility. He listed the limitations of the expressions as follows:

- There is a maximum level in the cell population, above which the model is not applicable due to crowding and stalling effects;
- There is a minimum level in the cell population, below which the population is both insignificant and difficult to measure with accuracy;
- For continuous systems there is an upper limit to the dimensionless growth rate, $(\mu/\mu_{max})_{max}$, above which the system approaches the critical dilution rate and becomes unstable to work with. For batch systems, above some value of $(\mu/\mu_{max})_{max}$, the organisms are basically not seriously limited by either substrate;
- Below some minimum value, $(\mu/\mu_{max})_{min}$, the yield coefficients are no longer

constant, and the model is not applicable.

2) Weighted model defining the specific growth rate in terms of weighted average of rates under individual substrate limitations:

$$\frac{\mu}{\mu_{max}} = (W_1)\frac{S_1}{(K_1 + S_1)} + (W_2)\frac{S_2}{(K_2 + S_2)} \quad (17)$$

where Wi is the weight assigned to substrate i. W_1 and W_2 are defined as:

$$W_1 = \frac{{}^{K_1}/_{S_1}}{{}^{K_1}/_{S_1} + {}^{K_2}/_{S_2}};\ W_2 = \frac{{}^{K_2}/_{S_2}}{{}^{K_1}/_{S_1} + {}^{K_2}/_{S_2}} \quad (18)$$

Based on the two ways of integrating the Monod model, two expressions are proposed in this study (Expression 1 and Expression 2). Model simulations of biomass, nitrogen, carbon and phosphorus concentrations from using each of those expressions, are compared in Chapter 4.

3.2.2.1 Expression 1

Expression 1 is based on the Double Monod model. Considering nitrogen, phosphorus, carbon and light intensity, as the growth affecting factors, the Double Monod model will have the form of:

$$\mu = \mu_{max}\frac{S_N}{(K_{s,N} + S_N)} \times \frac{S_P}{(K_{s,P} + S_P)} \times \frac{S_C}{(K_{s,C} + S_C)} \times \frac{I}{(K_{s,I} + I)} \quad (19)$$

where $K_{s,N}$, $K_{s,p}$, $K_{s,c}$ and $K_{s,I}$ are half saturation constants in a nitrogen, phosphorus, carbon and light-limited culture, respectively (kg m^{-3}). μ_{max} in this expression is the same as the μ_{max} for the limiting factor in the culture. The limiting factor is the factor that has the lowest value of S/K_s in the photobioreactor during the algae cultivation.

3.2.2.2 Expression 2

Expression 2 is based on the weighted average of the Monod model under individual substrate limitations. The maximum specific growth rates under individual substrate limitations are also weighed in the proposed expression.

$$\mu = \mu_{max}\left(\alpha \times \frac{S_N}{(K_{s,N}+ S_N)} + \beta \times \frac{S_P}{(K_{s,P} + S_P)} + \delta \times \frac{S_C}{(K_{s,C} + S_C)} + \lambda \times \frac{I}{(K_{s,I} + I)}\right) \quad (20)$$

where μ_{max} is the overall maximum specific growth rate (d^{-1}); $\mu_{max,N}$, $\mu_{max,p}$, $\mu_{max,c}$ and $\mu_{max,I}$ are maximum specific growth rates in a nitrogen, phosphorus, carbon and light-limited culture, respectively (d^{-1}).

Weighting factors α, β, δ and λ are described as:

$$\alpha = \frac{\mu_{max,N}}{\mu_{max}} \times \frac{{K_{s,N}}/{S_N}}{{K_{s,N}}/{S_N} + {K_{s,p}}/{S_p} + {K_{s,c}}/{S_c} + {K_{s,I}}/{I}} \quad (21)$$

$$\beta = \frac{\mu_{max,p}}{\mu_{max}} \times \frac{{K_{s,p}}/{S_p}}{{K_{s,N}}/{S_N} + {K_{s,p}}/{S_p} + {K_{s,c}}/{S_c} + {K_{s,I}}/{I}} \quad (22)$$

$$\delta = \frac{\mu_{max,c}}{\mu_{max}} \times \frac{{K_{s,c}}/{S_c}}{{K_{s,N}}/{S_N} + {K_{s,p}}/{S_p} + {K_{s,c}}/{S_c} + {K_{s,I}}/{I}} \quad (23)$$

$$\lambda = \frac{\mu_{max,I}}{\mu_{max}} \times \frac{{K_{s,I}}/{I}}{{K_{s,N}}/{S_N} + {K_{s,p}}/{S_p} + {K_{s,c}}/{S_c} + {K_{s,I}}/{I}} \quad (24)$$

In a single limited culture, where the limited component controls the growth rate, the proposed rate expression will have the same form of the Monod model for the single

limited culture. For example, in a carbon-limited culture, the ratio of K_s/S for abundant components (nitrogen, phosphorus and light) approaches to zero ($S>>K_s$). Therefore, α, β and λ will be close to zero; while, the value of δ approaches one. As a result, the final specific growth rate will have the form of: $\mu_{max,C}\frac{S_C}{(K_{s,C}+S_C)}$.

3.3 Parameter Estimation

In order to solve the mass and energy balance equations, the parameters in those equations have to be obtained. Some parameters are known from the experimental set-up by the algae group. The rest of the parameters, were either calculated or obtained from existing literature.

3.3.1 Parameters Related to Experimental Set-Up

Parameters from the experimental set-up are shown in Table 7. This experiment was conducted by the algae group at USF from August-November 2011 (Dalrymple et al., 2012). Energy received by the culture was the natural light during the experiment. Light intensity was measured every 15 minutes by an Onset HOBO U12 data logger during the experiment. Light intensity measurements in November 2011 are provided in Appendix A.

Table 7- Parameters related to experimental set-up

Parameter	Value	Parameter	Value	Parameter	Value
wastewater flow rate ($m^3\ d^{-1}$)	0.096	Influent TP concentration ($kg\ m^{-3}$)	Variable between 0.15-0.0017	Bubble size	Fine bubble (2mm dia.)
Volume of reactor (m^3)	0.007	Air flow rate ($m^3\ d^{-1}$)	0.72	Diffuser dimensions (mm)	22 dia. x 25 H
illuminated surface area of reactor (m^2)	0.9	CO_2 content of air (%volume)	2	Diameter of the reactor (m)	0.12
Initial biomass density($kg\ m^{-3}$)	1.67	Air pressure (atm)	8.5	Height of the reactor (m)	2.37
Influent TN concentration ($kg\ m^{-3}$)	0.25	Diffuser shape	cylinder	Temperature (◦C)	30

3.3.2 Parameters Estimated

Around five correlations have been proposed for calculating K_La in bubble reactors, where each correlation is applicable under specific conditions (e.g., gas superficial velocity and reactor dimensions) (Shah 1982). The correlation proposed by Fair in 1967 fits the conditions of this study best (Shah 1982):

$$K_L.a = 3.31 \frac{D_l \epsilon_G}{{d_b}^2} \left(\frac{\mu_L}{\rho_L D_l}\right)^{1/3} \left(\frac{d_b \rho_L u_G}{\mu_L \epsilon_G}\right)^{1/2} \quad (25)$$

where D_l is the molecular diffusivity of CO_2 in water ($m^2\ s^{-1}$), ϵ_G is the gas hold up, u_G is the air superficial velocity ($m\ s^{-1}$), ρ_l is the water density ($kg\ m^{-3}$), μ_l is the dynamic viscosity of water (Pa s) and d_b is individual bubble diameter (m). In Equation 25, ϵ_G was estimated using Mersmann equation (Shah 1982):

$$\frac{\epsilon_G}{(1-\epsilon_G)^4} = 0.14 u_G \left(\frac{{\rho_L}^2}{\sigma(\rho_L-\rho_G)g}\right)^{1/4} \left(\frac{{\rho_L}^2\sigma^3}{{\mu_L}^4(\rho_L-\rho_G)g}\right)^{1/24} \left(\frac{{\rho_L}^2}{\rho_L-\rho_G}\right)^{1/3} \left(\frac{\rho_L}{\rho_G}\right)^{5/72} \quad (26)$$

where ρ_G is the air density ($kg\ m^{-3}$) and σ is the interfacial tension ($N\ m^{-1}$).

Values of ϵ_G and K_La were calculated to be 0.01 and 0.22 min^{-1} (see appendix B). The range of K_La value for CO_2 mass transfer into the water was reported to be 7.59×10^{-2} - 21.7×10^{-2} min^{-1} (Talbot et al., 1991) and 0.09 - 0.94 min^{-1} (Molina-Grima et al., 1993) in bubble column algae photobioreactors.

Gillie (2011) conducted gas transfer experiment from May to July 2011 in the same photobioreactors used by the algae group at USF and estimated K_La for CO_2 mass transfer to be approximately 2×10^{-3} min^{-1}. This value was lower than the reported values of K_La in previous studies by Talbot et al. (1991) and Molina-Grima et al. (1993). In August, the air diffusers in those photobioreactors were changed and gas transfer was improved. Therefore, as a conservative choice, the lowest value in the reported ranges of K_La, 7.59×10^{-2} min^{-1} (Talbot et al., 1991) was used as a model input.

The theoretical yield coefficient for each substrate is obtained based on the biomass biosynthesis chemical reaction (see appendix B) and the estimated values are as below.

$$Y_C = 16\ \frac{g\ algae}{g\ substrate};\ Y_P = 115\ \frac{g\ algae}{g\ substrate};\ Y_C = 2.8\ \frac{g\ algae}{g\ substrate}$$

C_s was estimated to be 0.22 kgm^{-3} based on carbon concentration in bubble and Henry's law constant (see appendix B).

3.3.3 Parameters Obtained from Literature

Half saturation concentrations and maximum specific growth rates were obtained from existing literatures. The parameters were chosen from studies with similar experimental conditions as the algae experiment here at USF. All the parameters that were obtained from previous studies are shown in Table 8.

Table 8- Parameters for *Chlorella vulgaris* from existing literature

Reference	Conditions	Parameters
Sasi et al. 2011	Light-limited; T= 25°C; % CO_2 in air=10 pH=6.8	$\mu_{max,I}$=0.96 d^{-1} $I_s \times A$=0.0126 w
Chen et al., 2010	Carbon-limited; T= 28°C; pH=6, Carbon source: $NaHCO_3$	$\mu_{max,c}$=0.6 d^{-1} $K_{s,c}$=0.12 Kg m^{-3}
Aslan and Kapdan, 2006	N-limited ; T=20°C pH=7	$K_{s,N}$= 0.0315 (kg m^{-3}) $R_{max,N}$=0.23 d^{-1}
	P-limited ; T=20°C pH=7	$K_{s,p}$= 0.01 (kg m^{-3}) $\mu_{max,p}$=0.07 d^{-1}
Pirt et al., 2007	-	Y_G=1.53×10^{-8} kg J^{-1}
Richmond, 2004	-	m=4.8×10^5 J kg^{-1} d^{-1}
Hulatt and Thomas, 2011		HHV= 1.630×10^7 J kg^{-1}

3.4 Solving Mass Balance Equations

Equations 5-7, 9, 14, make a series of first-order differential equations. Using the Euler method X, S_N, S_P and S_c were calculated for time intervals (0.01 day).

For a first-order differential equation of the form

$$\frac{dy}{dt} = f(t, y) \tag{27}$$

With the initial condition y(0)=A, Euler's method begins by approximating the first derivative as:

$$\frac{dy}{dt} \approx \frac{y(t+\Delta t)-y(t)}{\Delta t} \tag{28}$$

Setting Equation 24 equal to f(t,y) and solving for y(t+Δt) yields the following algorithm for advancing the numerical solution of an ordinary differential equation:

$$y(t + \Delta t) = y(t) + \Delta t \times f(t, y(t)) \tag{29}$$

Initial conditions for this study were defined as:

X_0=1.03 kg m^{-3}; $S_{C,0}$=0.0045 kg m^{-3} (Gillie, 2011); $S_{N,0}$=0.092 kg m^{-3}; $S_{P,0}$=0.054 kg m^{-3}; I_0=3450 J m^{-2} d^{-1}

CHAPTER 4-RESULTS AND DISCUSSION

The model was run for a semi-continuous culture of the photobioreactor using both growth rate expressions discussed in section 3.2.2 and for a continuous culture of the same reactor using expression 2.

Model simulations for a semi-continuous culture are discussed in Sections 4.1 (Figure 3-6) and Section 4.2 (Figure 7-10). Model simulations for a continuous culture are discussed in Section 4.3 (Figure 11-14).

4.1 Model Results from Using Expression 1 for a Semi-Continuous Culture

Mass and energy balances were solved using the expression 1 (section 3.2.2.1) for the specific growth rate of algae. Concentration profiles for X, S_N, S_P and S_c are plotted in Figures 3-6. As it was discussed in sub-section 3.2.2.1, μ_{max} in expression 1 equals to μ_{max} of the limiting factor, which has the lowest value of S/K_s during the algae cultivation in the culture. The ratio of S/K_s for nitrogen, carbon, phosphorus and light intensity in the reactor during the algae group experiment, are indicated in Table C in Appendix C.

According to Table C, carbon had the lowest value of S/K_s during the first 20 days of algae cultivation; Thus, carbon has been the most limited factor ($\mu_{max}= \mu_{max,c}$). After 20 days, Phosphorus became the most limited substrate due to a very low concentration in the culture ($\mu_{max}= \mu_{max,p}$). During the experiment, light became limited when there was output from the reactor and also during the nights ($\mu_{max}= \mu_{max,I}$). Nitrogen had also the

least value of S/K_s in a few specific time intervals during the 10^{th} and 12^{th} day of cultivation ($\mu_{max}= \mu_{max,N}$).

4.1.1 Model Prediction of Biomass Concentration

The change in biomass concentration versus time is shown in Figure 3. Abrupt decreases in biomass density in each day are due to the biomass output from the reactor (once in a day) and controlled by the energy balance. After taking out one liter of the biomass, algae starts to grow as a result of the addition of nitrogen and phosphorus to the culture. Small fluctuations in the graph are due to light variations during each 24 hours period. During the night, light intensity is near zero. That means, growth is light limited during the nights and growth is constrained by energy. However, during the day, light intensity raises up to 10^6 j d^{-1} m^{-2}, which is pretty abundant for the growth of algae. Therefore, the algae growth is controlled by carbon, nitrogen and phosphorus. The algae biomass density begins to decline after 12^{th} day because phosphorus concentration in the influent became very low. After 24 days, a relatively sharper biomass decline occurs, when there is biomass output from the reactor. The sharper decline is due to the low light intensity.

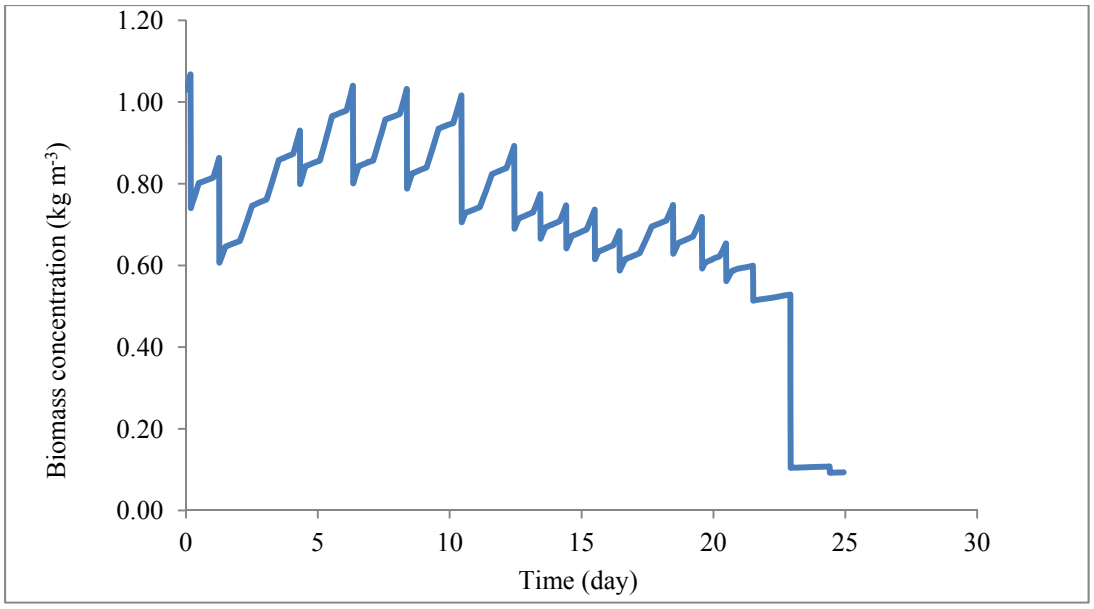

Figure 3-Modeled results for algae biomass concentration as a function of time (Expression 1; Semi-continuous)

4.1.2 Model Prediction of Nitrogen Concentration

Figure 4 shows a model prediction for nitrogen concentration in the photobioreactor as a function of time. Sharp increases are due to nitrogen input to the culture once in a day. Nitrogen is then consumed due to the algae uptake. After 12 days, nitrogen concentration starts to increase. This is because the biomass concentration starts to decline after 12 days and nitrogen uptake by algae decreases.

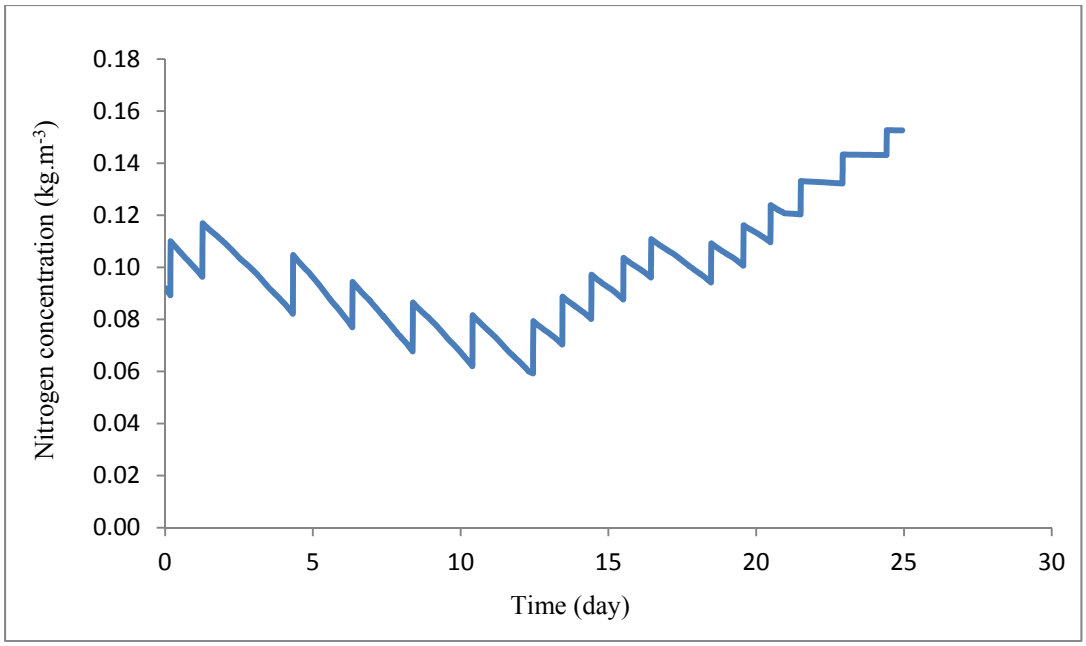

Figure 4-Modeled results for nitrogen concentration as a function of time (Expression 1; Semi-continuous)

4.1.3 Model Prediction of Inorganic Carbon Concentration

Figure 5 indicates that carbon reaches its highest value of concentration, immediately after the experiment starts. The sharp increase of carbon concentration is due to a high rate CO_2 mass transfer that happens between the air and liquid in the culture media. The culture initially contains a very low amount of inorganic carbon. After one day, the carbon concentration in the culture reaches the equilibrium concentration as calculated in Appendix B. This is because carbon is continuously injected into the reactor; however, carbon is consumed by algae at a very low rate due to the low specific growth rate.

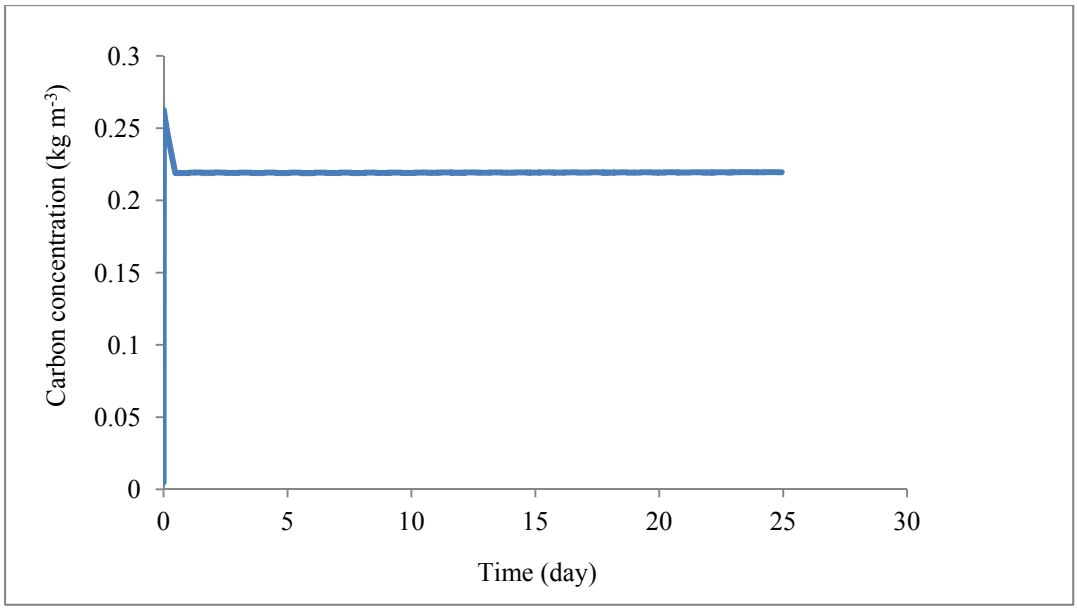

Figure 5-Modeled results for inorganic carbon concentration as a function of time (Expression 1; Semi-continuous)

4.1.4 Model Prediction of Phosphorus Concentration

The model results for phosphorus concentration are indicated in Figure 6. Sharp increases in the first 5 days are due to phosphorus input to the culture once in a day. Phosphorus is then consumed by the algae growth. After 5 days, phosphorus concentration in the influent decreases to a great extent and phosphorus concentration in the culture continuously decreases due to the uptake by algae and phosphorus output once in a day. After 20 days phosphorus becomes most limited in the culture.

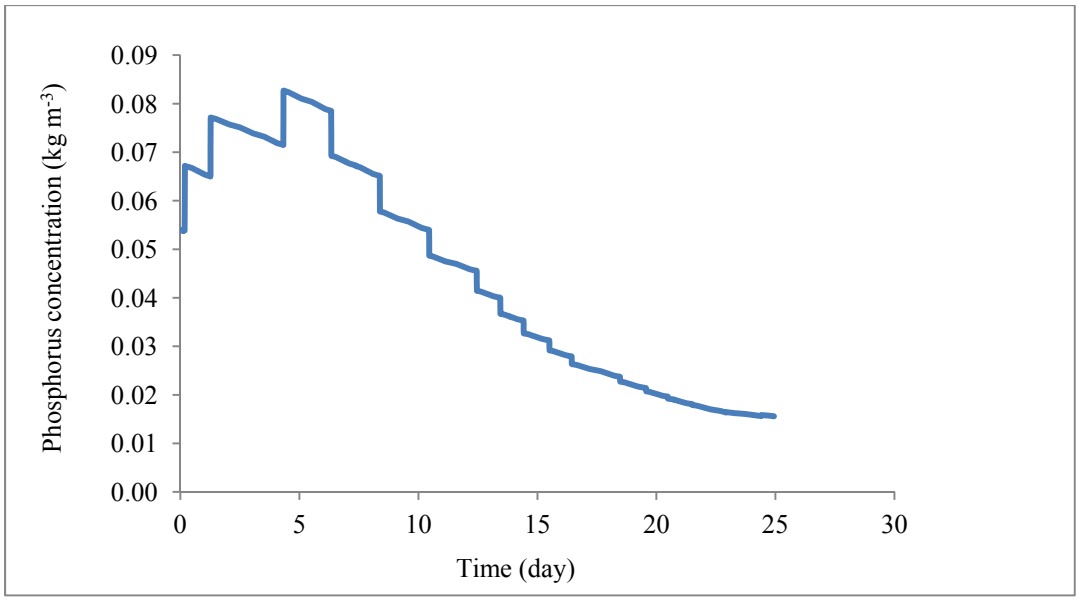

Figure 6-Modeled results for phosphorus concentration as a function of time (Expression 1; Semi-continuous)

4.2 Model Results from Using Expression 2 for a Semi-Continuous Culture

Mass and energy balances were solved using expression 2 for the specific growth rate of algae. Concentration profiles for X, S_N, S_P and S_c are plotted in Figures 7-10.

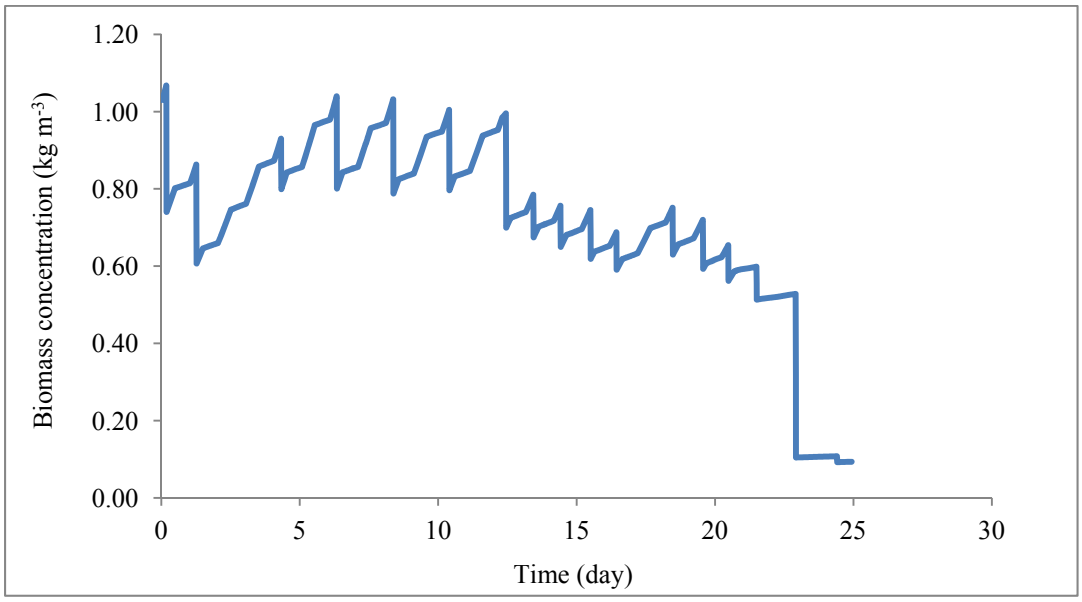

Figure 7-Modeled results for algae biomass concentration as a function of time (Expression 2; Semi-continuous)

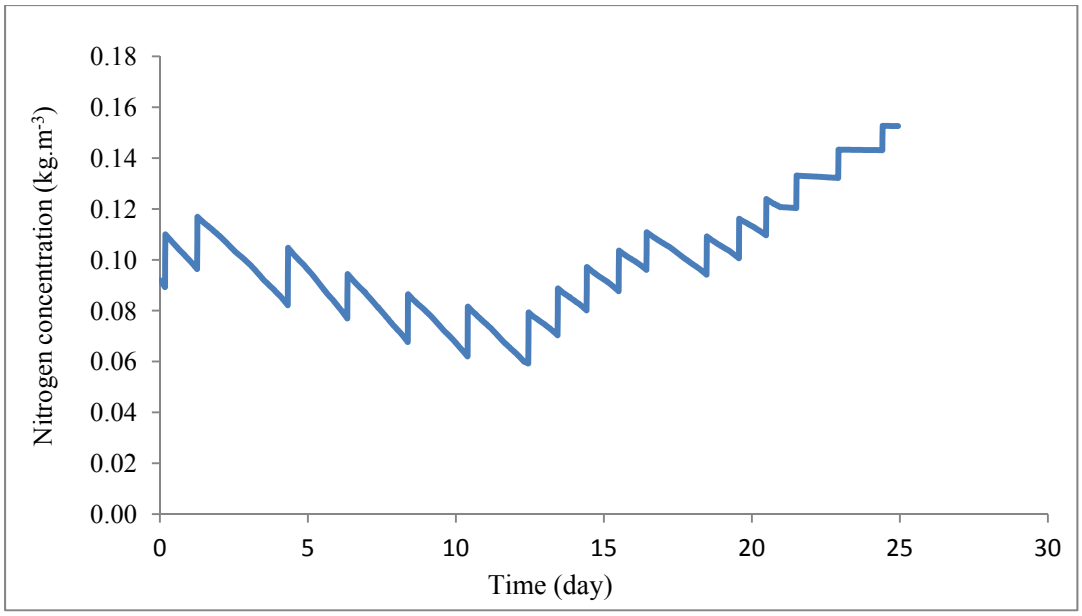

Figure 8-Modeled results for nitrogen concentration as a function of time (Expression 2; Semi-continuous)

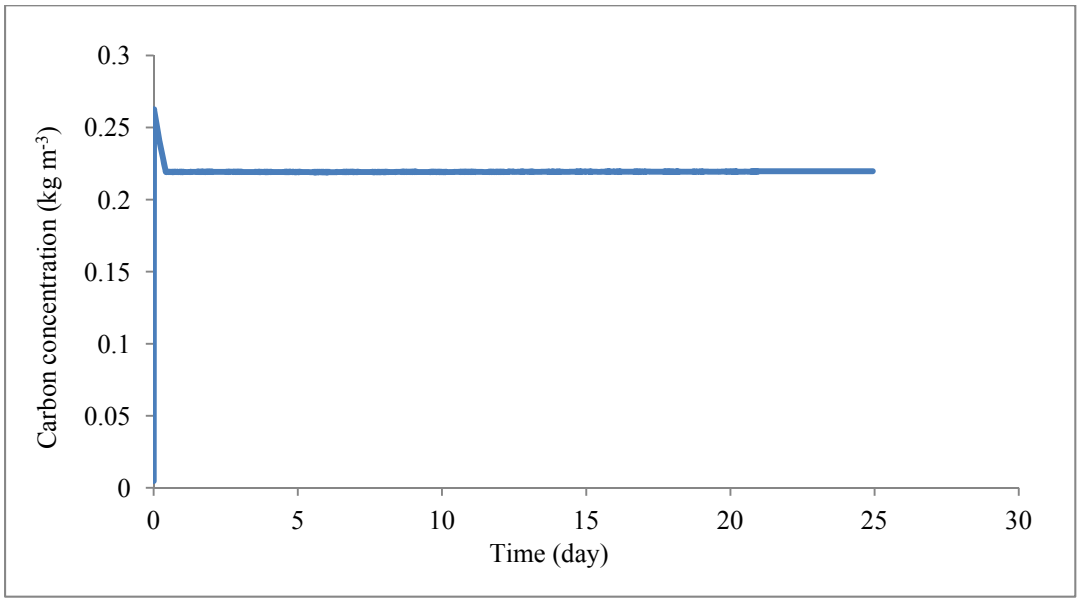

Figure 9-Modeled results for inorganic carbon concentration as a function of time (Expression 2; Semi-continuous)

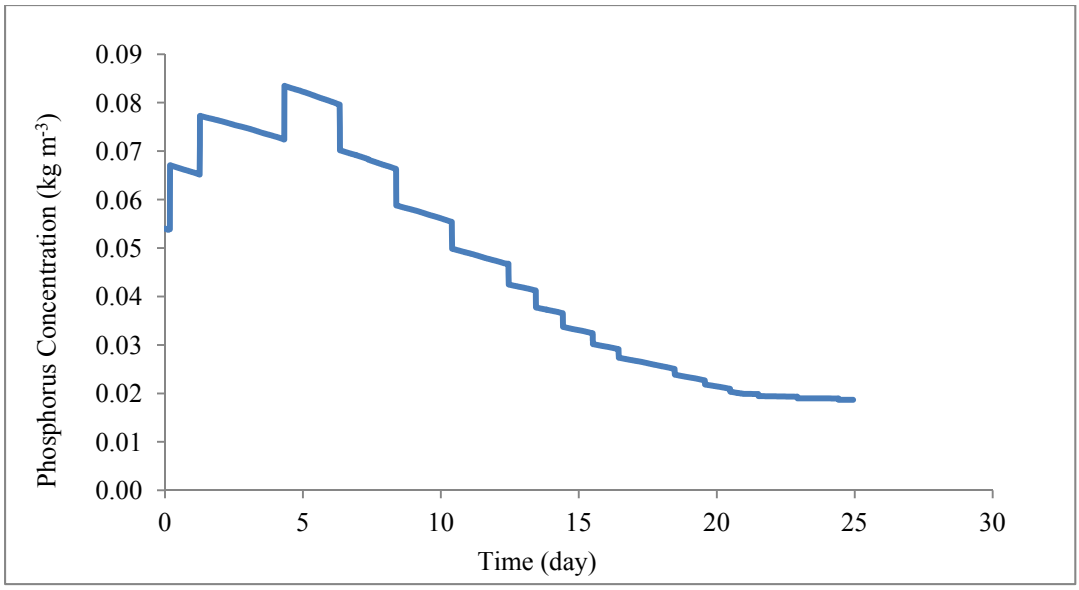

Figure 10-Modeled results for phosphorus concentration as a function of time (Expression 2; Semi-continuous)

Comparing the results in Section 4.1 and 4.2, no significance differences were observed between the model simulations using expression 1 and expression 2. Thus, both expressions are able to describe the algae growth kinetics in the photobioreactor.

4.3 Model Results for a Continuous Culture

The same parameters (real light intensity data, nitrogen and phosphorus influent concentrations vary daily) were used to run the model for a continuous culture. Expression 2 was used for the specific growth rate of algae. Continuous nitrogen and phosphorus input and biomass out from the reactor were assumed.

First, the model was run with a hydraulic retention time (HRT) of 7 days. The biomass concentration profile is shown in Figure 11.

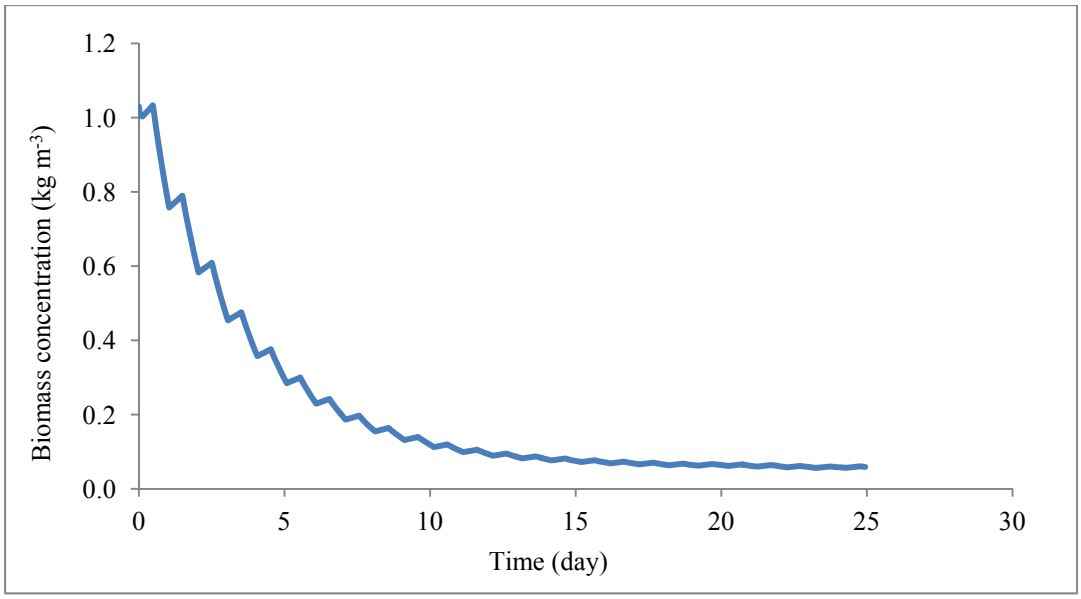

Figure 11-Modeled results for biomass concentration as a function of time (Continuous; HRT=7 d)

Figure 11 shows that under a continuous condition and with a HRT of 7 days, algae wash out of the reactor faster than they grow. Therefore, HRT has to be higher for the growth of algae. In order to find a minimum HRT, the model was run with two other values (20 and 30 days). Results are shown in Figures 12 and 13. It is concluded that HRT needs to be more than 30 days to avoid biomass flush out from the reactor under the same light condition, carbon and nutrient input as the semi-continuous experiments.

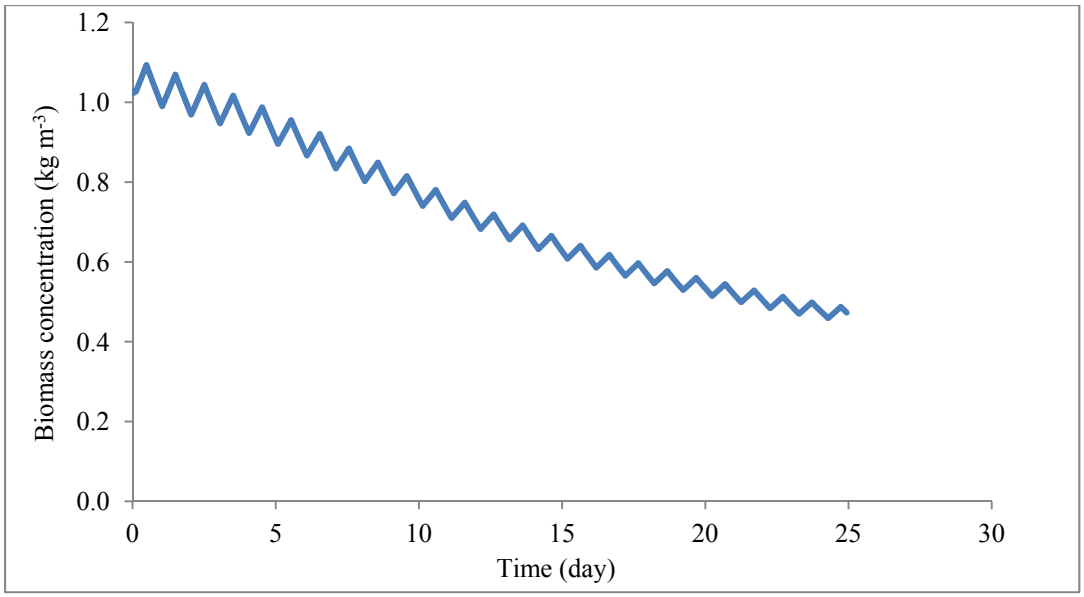

Figure 12-Modeled results for biomass concentration as a function of time (Continuous; HRT=20 d)

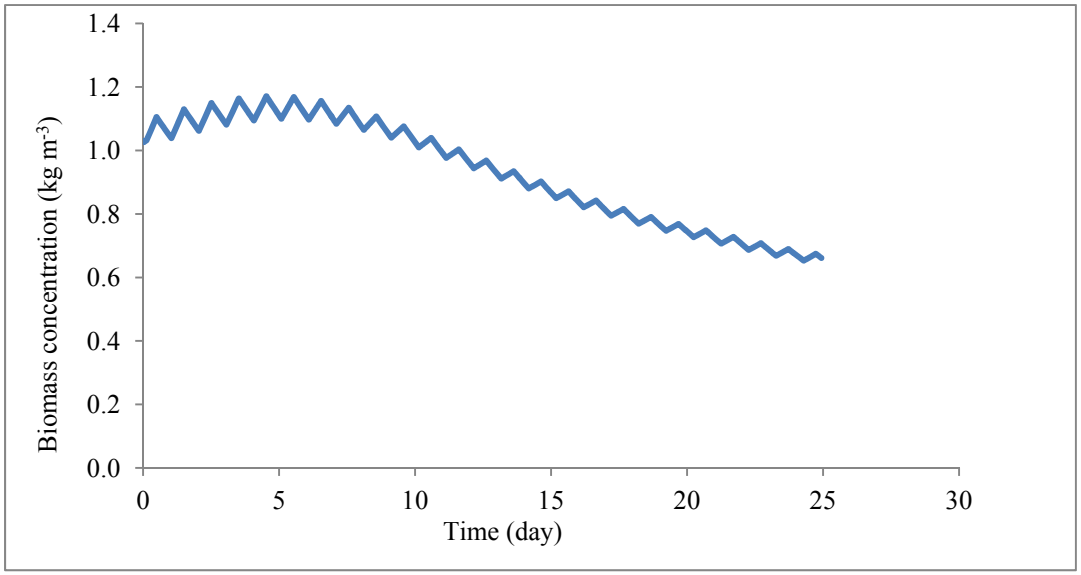

Figure 13-Modeled results for biomass concentration as a function of time (Continuous; HRT=30 d)

From a theoretical perspective, the minimum HRT can be determined based on the maximum specific growth rate as below:

$$-Q_t X + \mu XV = 0 \rightarrow \qquad HRT_{min} = \frac{V}{Q} = \frac{1}{\mu_{max}}$$

Thus, for a continuous culture system, HRT should be great than $\frac{1}{\mu_{max}}$ to ensure algae growth happens.

CHAPTER 5-COMPARISON OF EXPERIMENTAL RESULTS WITH THE MODEL SIMULATIONS

5.1 Experimental Set-Up

In this study, the model results were compared with a series of experimental data which was collected by the algae group at University of South Florida. Algae were cultivated in a set of photobiorectors using wastewater (Halfhide, 2011).

Dalrymple et al., 2012 explained the experimental-setup as follows:

> "The algal cultivation set-up consists of three tubular plastic bag photobioreactors (obtained from the Norwegian University of Life Sciences, Norway), which are housed in a greenhouse at the Botanical Gardens of the University of South Florida in Tampa, FL. The set-up of the bag reactors, which began operation in February 2011, is shown in Figure 14. The reactors are 237.13 cm high with a diameter of 12.32 cm. They were each operated at a volume of 7 L and were seeded with algae harvested from the secondary clarifiers of the Howard F. Current Advanced Wastewater Treatment Plant (HFC AWTP). Air containing CO_2 was bubbled through the reactor using coarse bubble diffusers to provide inorganic carbon for photoautotrophic growth, as well as mixing. The gas flow rate was maintained at 500 ml/min."

Model simulations were compared with the measured data from one of the photobioreactors, which receives a 2% CO_2 /air mixture and includes wild type algae. This reactor is indicated by a red circle in Figure 7.

Each day, 1 L of the reactor volume was replaced with wastewater centrate collected from the HFC AWTP. A pretreatment process was conducted on the centrate for adjusting the nitrogen content to 200-300 mg/L. Biomass concentration in the effluent

of the reactor was measured every day. Total nitrogen and phosphorus in the effluent were also measured weekly. “An Onset® HOBO U12 data logger (Pocasset, MA) automatically recorded the incident light intensity, ambient temperature, reactor temperature, and relative humidity every 15 minutes” (Dalrymple et al., 2012). The data from data logger shows that the temperature has been variable between 12-38 ˚C. The pH was also measured during the experiment. Measured data show that pH has been also variable between 3-6.

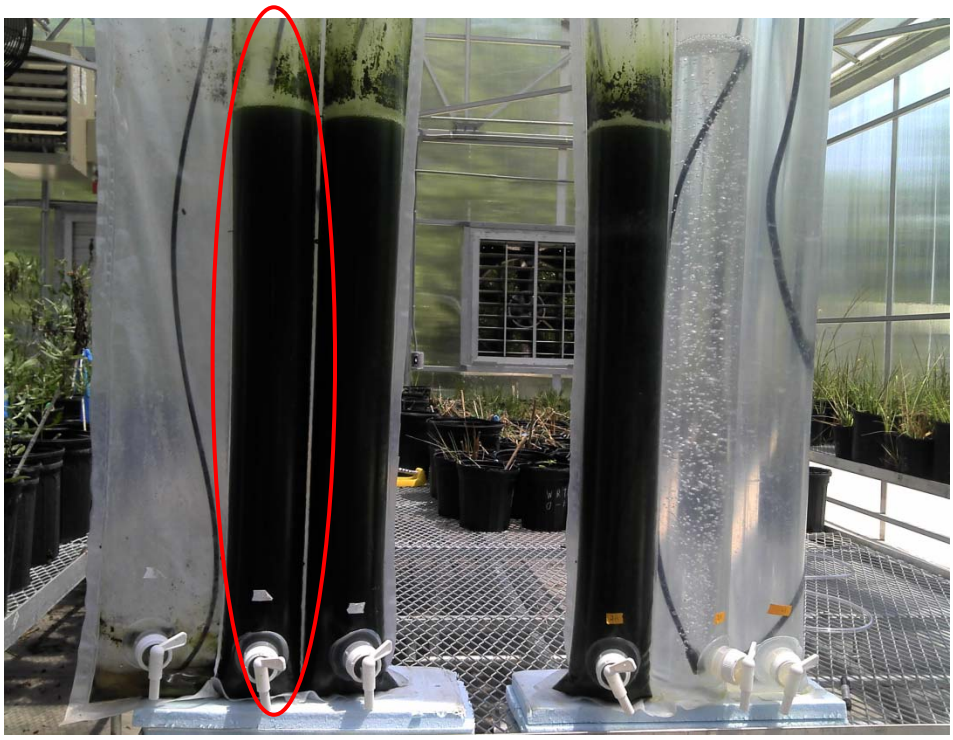

Figure 14-Tubular photobioreactors located in greenhouse (Halfhide, 2011)

5.2 Comparison of Modeled Biomass Concentration with Measured Data

This section compares algae biomass density predicted by the model with the measured data in November 2011 (as discussed in section 4.1). The experimental data in this time period was used for comparison, because a different air diffuser was used, and

the concentration of nitrogen in influent flow was better controlled during this time period. As there was no significant difference between the results from using two expressions, modeled result from expression 2 was used for comparison.

The modeled and experimental results are shown in Figure 9. The model simulations of biomass change follow the same pattern as the experimental results.

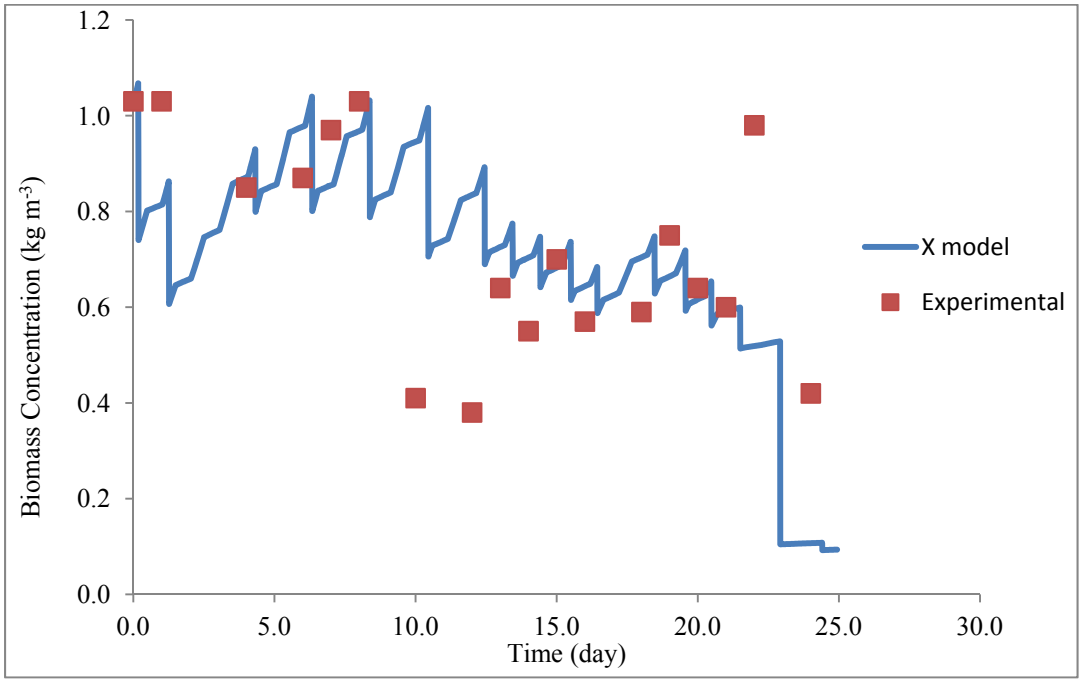

Figure 15-Comparison of experimental results with model simulations for biomass concentration

The discrepancy between model predictions and experimental data could be because of three main reasons. As previously mentioned in model limitations section, some of the model's parameters (e.g., K and μ_{max} values) were not determined by kinetic experiments directly. Instead, those parameters were obtained from other studies of algae growth described in literature. Even the experimental conditions of those studies were close to the conditions of the experiments conducted at the USF, they are not exactly the

same. Secondly, some parameters such as the yield coefficient for phosphorus were derived theoretically and were assumed to remain constant during the experiment. However, yield coefficients vary with the change of the light intensity (Chojnack and Zielinska, 2012). Lastly, the experiments were not conducted in a fully controlled environment and many other factors could impact the algae growth, which could be one reason for scattered experimental data. And some of those factors were not considered in the model developed, such as temperature and pH.

CHAPTER 6-SENSITIVITY ANALYSIS

Sensitivity analysis was conducted to determine how and to what extent the changes in certain parameters affected maximum biomass concentration. Sensitivity is represented by sensitivity degree and calculated using the following equation.

$$\mathbf{SD} = \frac{\mathbf{\Delta X}}{\mathbf{X}} \Big/ \frac{\mathbf{\Delta K}}{\mathbf{K}} \tag{30}$$

where SD is the sensitivity degree of the maximum biomass concentration X to parameter K; ΔX and ΔK are the changes of X and K. A higher SD refers to a higher sensitivity.

The sensitivity analysis performed by altering the model parameters by +/- 20%. The 20% value was picked according to the previous study by Quinn (2011) for analyzing the sensitivity of an algae growth model to the model's parameters. Test values and model responses are shown in Table 9. The last column is sensitivity degree which highlights the sensitivity of model to the related parameter.

Table 9- Results of sensitivity analysis for variations in model parameters on X_{max}

Parameter	Control Value	Test value	Model response for X_{max}	SD
K_N (kg m^{-3})	0.0315	0.0378	1.06	-0.018
		0.0252	1.07	
K_p (kg m^{-3})	0.0105	0.0126	1.066	-0.0053
		0.0084	1.068	
K_c (kg m^{-3})	0.115	0.138	1.06	-0.011
		0.092	1.07	
K_I (kg m^{-3})	1088	1306	1.067	-0.00012
		870	1.067	
$\mu_{max,N}$ (d^{-1})	0.23	0.276	1.067	0
		0.184	1.067	

Table 9 (Continued)

$\mu_{max,p}$ (d^{-1})	0.07	0.084	1.067	0
		0.056	1.067	
$\mu_{max,c}$ (d^{-1})	0.6	0.72	1.17	0.26
		0.48	1.067	
$\mu_{max,I}$ (d^{-1})	1	1.2	1.06	0
		0.8	1.067	
Y_G (kg J^{-1})	$1.53E^{-08}$	$1.84E^{-08}$	1.240	0.40
		$1.22E^{-08}$	1.067	
m (J kg^{-1} d^{-1})	$4.80E^{+05}$	5.76×10^{5}	1.067	0
		3.84×10^{5}	1.067	
HHV (J kg^{-1})	$1.63E^{+07}$	1.95×10^{7}	1.129	0.14
		1.30×10^{7}	1.068	
Y_N	16	19.2	1.067	0.00014
		12.8	1.067	
Y_P	114	136.8	1.067	2.34×10^{-5}
		91.2	1.067	
Y_c	3.2	3.84	1.067	4.68×10^{-5}
		2.56	1.067	
K_La (d^{-1})	115	138	1.067	-7.7×10^{-4}
		92	1.067	

Based on Table 9, the most sensitive parameter is the maximum growth yield (Y_G). The model is also largely affected by the maximum specific growth rate for carbon ($\mu_{max,c}$) and higher heating value of algae biomass (HHV).

CHAPTER 7-CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

A model was developed for predicting the algae growth in a continuous culture of a photobioreactor. Two expressions were proposed based on the Double Monod model and weighted average of the Monod model. Unlike the Monod model which relates specific growth rate of algae to concentration of the limiting compound in a single-limited culture, the proposed expressions account for the effect of four factors that control the growth rate in a multi-limited culture: inorganic carbon, nitrogen, phosphorus and light intensity. Biomass and substrate concentrations of culture media as a function of time were predicted by solving mass and energy balances around the photobioreactor. Modeled results were compared with experimental data obtained by the algae group at USF, which was done for a semi-continuous culture. The model was also run for a continuous culture.

The model predicted almost the same results from using both proposed expressions for the specific growth rate of algae. Biomass concentration predicted by the model followed the same pattern as the measured biomass concentration in the photobioreactor. Carbon has been limited in the culture during the experiment. Light intensity was also limited at different specific time periods, and after 20 days, phosphorus becomes the most limited factor. Overall, the proposed model has been able to simulate the pattern of biomass concentration change in a multi-limited culture.

However, there are discrepancies between model perditions and experimental data. This could be attributed to the fact that the environmental conditions varied during the experiment and some factors were not considered in the model developed. The parameters used in the model were not measured directly, but either obtained from literature or derived theoretically.

Model simulations for a continuous culture indicated that the HRT is very low for the growth of algae. In general, the HRT has to be greater than the inverse of the maximum specific growth rate to ensure algae growth. In order to operate the same photobioreactor as a continuous culture system under the same light condition and carbon and nutrient input, the HRT should be at least 30 days.

It was found through sensitivity analysis that the maximum biomass density predicted by the model is very sensitive to parameters of maximum growth yield (Y_G), the maximum specific growth rate for carbon ($\mu_{max,c}$) and higher heating value of algae biomass (HHV).

7.2 Recommendations for Future Research

Factors that were not considered in the proposed expression of specific growth rate include: temperature, pH, inhibition factors and decay rate. Future work towards integrating those factors in the kinetic expression, will lead to a better prediction of algae growth.

The model parameters should be determined directly by batch experiments, especially for highly sensitive parameters (Y_G, $\mu_{max,c}$ and HHV) identified by sensitivity analysis.

For a better model validation, it is recommended that an experiment is set up in a laboratory under more controlled environment. If the model's results fit well to the results of the controlled experiment, further validations will be possible with the results of an experiment under natural environment. Overall, the proposed model should have more proven validity through future experiments.

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APPENDICES

Appendix A-List of Nomenclature

Symbol	Unit	Definition
A	m^2	Illuminated surface area
a	m^{-1}	Surface area available for mass transfer per volume of the system
a_l	m^2	Effective light absorption surface area of each cell
b	-	Decay coefficient
C_{pm}	mg L^{-1}	Maximum product concentration
C_P	mg L^{-1}	Product concentration
C_{Xm}	g L^{-1}	Achievable maximum cell concentration
C_x	g L^{-1}	cell concentration
C_s	kg m^{-3}	Liquid-phase concentration of CO_2 at air-water interface
d_b	m	Individual bubble diameter
dE	J L^{-1}	Change in energy content of the culture per volume of the culture
D_l	m^2 s^{-1}	Molecular diffusivity of CO_2 in water
H	-	Henry's law constant
HHV	kJ g^{-1}	higher heating value
I	J d^{-1} m^{-2}	Average light intensity in the culture
I_0	mol m^{-2} d^{-1}	Incident light intensity
I_a		Average light intensity in the pond at a particular point in time
I_m	mol kg^{-1} d^{-1}	Maintenance rate
K"	kg mol^{-1}	A proportionality constant which is akin in meaning to growth yield
K_c	-	Constant used for cell quota control of growth
K_I	-	Inhibition coefficient
K_L	m d^{-1}	Overall mass transfer coefficient
K_m	mmol ml^{-1}	Half-saturation constant for the substrate concentration at that P transport rate attains half of its maximum

Appendix A (Continued)

Symbol	Unit	Definition
K_p	-	Dimensionless coefficient describing Pstress
KQ	-	Dimensionless parameter to set the curve form
K_q	-	Limiting cell quota
K_q	-	Dimensionless constant used to control the shape of the feedback function curve
$K_{s,C}$	kg m^{-3}	Half saturation constant in a carbon-limited culture
$K_{s,N}$	kg m^{-3}	Half saturation constant in a nitrogen-limited culture
$K_{s,P}$	kg m^{-3}	Half saturation constant in a phosphorus -limited culture
$K_{s,I}$	J d^{-1} m^{-2}	Saturation light intensity
m	J kg^{-1} d^{-1}	Maintenance coefficient
q	fmol $cell^{-1}$	Cell quota(total amount of nutrient per cell)
Q_t	m^3 d^{-1}	Wastewater flow rate as a function of time
q_E	J kg^{-1} d^{-1}	Specific rate of energy uptake
Qmax	mmol $cell^{-1}$	Maximum cell quota for algal existence
Q_P	-	Phosphorus quota
Q_{Pmax}	-	Maximum phosphorus quota
Q_{Pmin}	-	Minimum phosphorus quota
Q_t	mmol $cell^{-1}$	Total cell quota including surface-adsorbed phosphate and internal phosphorus content.
R	L atm mol^{-1} K	Ideal gas constant
R_c	kg d^{-1}	CO_2 input rate
S	kg m^{-3}	Nutrient concentration
S_μ		Finite concentration
$S_{0,N}$	kg m^{-3}	Influent concentration of nitrogen
$S_{0,P}$	kg m^{-3}	Influent concentration of phosphor
S_N	kg m^{-3}	Effluent concentration of nitrogen
SD	-	Sensitivity degree
S_P	kg m^{-3}	Effluent concentration of phosphor

Appendix A (Continued)

Symbol	Unit	Definition
T	K	Temperature
T	μmol/(cell·min)	Transport rate of surface-adsorbed P into algal cell
u_G	m s^{-1}	air superficial velocity
V	m^3	Reactor volume
V	m^3	Liquid volume in the reactor
V_F	-	Illuminated volume fraction of the reactor
WP	mmol ml^{-1}	Phosphate concentration in the substrate.
X	kg m^{-3}	Biomass concentration
Y	kg J^{-1}	Overall growth yield
Y_C	-	Yield coefficient for carbon
Y_G	kg J^{-1}	Maximum growth yield
Y_N	-	Yield coefficient for nitrogen
Y_P	-	Yield coefficient for phosphor
y_s	kg m^{-3}	Gas-phase concentration of CO_2 at air-water interface
$\mu_{max,c}$	d^{-1}	Maximum specific growth rate in a carbon-limited culture
$\mu_{max,I}$	d^{-1}	Maximum specific growth rate in a light-limited culture
$\mu_{max,N}$	d^{-1}	Maximum specific growth rate in a nitrogen-limited culture
$\mu_{max,p}$	d^{-1}	Maximum specific growth rate in a phosphorus-limited culture

Appendix B-Light Intensity Data

Light intensity data, which was recorded every 15 minutes in greenhouse, is provided in the following table. The data was recorded by a data logger in the unit of W/m^2 from Nov. 4^{th} 2011to Nov. 30^{th} 2011.

Table A-Light intensity data for November 2011

Date/Time	W/m^2	$j/m^2.d$	Date/Time	W/m^2	$J/m^2.d$
11/4/2011 7:09	0.08	3448.58	11/4/2011 14:39	74.10	3.2E+06
11/4/2011 7:24	0.08	3448.58	11/4/2011 14:54	84.96	3.7E+06
11/4/2011 7:39	0.11	4831.51	11/4/2011 15:09	71.10	3.1E+06
11/4/2011 7:54	0.53	22774.62	11/4/2011 15:24	65.09	2.8E+06
11/4/2011 8:09	1.52	65557.99	11/4/2011 15:39	59.28	2.6E+06
11/4/2011 8:24	2.51	108341.36	11/4/2011 15:54	49.85	2.2E+06
11/4/2011 8:39	8.03	347098.47	11/4/2011 14:39	74.10	3.2E+06
11/4/2011 8:54	8.74	377452.95	11/4/2011 14:54	84.96	3.7E+06
11/4/2011 9:09	13.24	572043.76	11/4/2011 15:09	71.10	3.1E+06
11/4/2011 9:39	17.91	7.7E+05	11/4/2011 17:24	33.59	1.5E+06
11/4/2011 9:54	38.99	1.7E+06	11/4/2011 17:39	25.80	1.1E+06
11/4/2011 10:09	33.69	1.5E+06	11/4/2011 17:54	9.09	3.9E+05
11/4/2011 10:24	22.63	9.8E+05	11/4/2011 18:09	8.35	3.6E+05
11/4/2011 10:39	43.37	1.9E+06	11/4/2011 18:24	2.83	1.2E+05
11/4/2011 10:54	48.13	2.1E+06	11/4/2011 18:39	0.97	4.2E+04
11/4/2011 11:09	60.36	2.6E+06	11/4/2011 18:54	0.08	3.4E+03
11/4/2011 11:24	71.16	3.1E+06	11/4/2011 19:09	0.08	3.4E+03
11/4/2011 11:39	81.00	3.5E+06	11/4/2011 17:24	33.59	1.5E+06
11/4/2011 12:09	86.81	3.8E+06	11/4/2011 17:39	25.80	1.1E+06
11/4/2011 12:24	93.87	4.1E+06	11/4/2011 20:09	0.08	3.4E+03
11/4/2011 12:39	105.82	4.6E+06	11/4/2011 20:24	0.08	3.4E+03
11/4/2011 12:54	41.42	1.8E+06	11/4/2011 20:39	0.05	2.1E+03
11/4/2011 13:09	98.35	4.2E+06	11/4/2011 20:54	0.05	2.1E+03
11/4/2011 13:24	52.98	2.3E+06	11/4/2011 21:09	0.05	2.1E+03
11/4/2011 13:39	110.10	4.8E+06	11/4/2011 21:24	0.05	2.1E+03
11/4/2011 13:54	100.58	4.3E+06	11/4/2011 21:39	0.08	3.4E+03
11/4/2011 14:09	110.93	4.8E+06	11/4/2011 21:54	0.05	2.1E+03

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	j/m^2.d	Date/Time	W/m^2	J/m^2.d
11/4/2011 19:24	0.05	2.1E+03	11/5/2011 4:54	0.05	2.1E+03
11/4/2011 19:39	0.05	2.1E+03	11/5/2011 5:09	0.05	2.1E+03
11/4/2011 19:54	0.05	2.1E+03	11/5/2011 5:24	0.08	3.4E+03
11/5/2011 1:24	0.05	2.1E+03	11/5/2011 5:39	0.08	3.4E+03
11/5/2011 1:39	0.05	2.1E+03	11/5/2011 5:54	0.08	3.4E+03
11/4/2011 22:09	0.08	3.4E+03	11/5/2011 6:09	0.05	2.1E+03
11/4/2011 22:24	0.05	2.1E+03	11/5/2011 6:24	0.05	2.1E+03
11/4/2011 22:39	0.05	2.1E+03	11/5/2011 6:39	0.08	3.4E+03
11/5/2011 4:09	0.08	3.4E+03	11/5/2011 4:09	0.08	3.4E+03
11/5/2011 4:24	0.08	3.4E+03	11/5/2011 1:09	0.08	3.4E+03
11/4/2011 23:24	0.05	2.1E+03	11/5/2011 6:54	0.05	2.1E+03
11/4/2011 22:54	0.08	3.4E+03	11/5/2011 7:09	0.05	2.1E+03
11/4/2011 23:09	0.05	2.1E+03	11/5/2011 7:24	0.08	3.4E+03
11/4/2011 23:24	0.05	2.1E+03	11/5/2011 7:39	0.30	1.3E+04
11/4/2011 23:39	0.08	3.4E+03	11/5/2011 7:54	1.61	7.0E+04
11/4/2011 23:54	0.08	3.4E+03	11/5/2011 8:09	3.21	1.4E+05
11/5/2011 0:00	0.00	3.4E+03	11/5/2011 8:24	5.35	2.3E+05
11/5/2011 0:09	0.08	3.4E+03	11/5/2011 8:39	7.68	3.3E+05
11/5/2011 0:24	0.05	2.1E+03	11/5/2011 1:09	0.08	3.4E+03
11/5/2011 0:39	0.08	3.4E+03	11/5/2011 6:54	0.05	2.1E+03
11/5/2011 0:54	0.08	3.4E+03	11/5/2011 7:09	0.05	2.1E+03
11/5/2011 1:54	0.05	2.1E+03	11/5/2011 7:24	0.08	3.4E+03
11/5/2011 1:24	0.05	2.1E+03	11/5/2011 7:39	0.30	1.3E+04
11/5/2011 1:39	0.05	2.1E+03	11/5/2011 7:54	1.61	7.0E+04
11/5/2011 1:54	0.05	2.1E+03	11/5/2011 8:09	3.21	1.4E+05
11/5/2011 2:09	0.08	3.4E+03	11/5/2011 8:24	5.35	2.3E+05
11/5/2011 2:24	0.08	3.4E+03	11/5/2011 8:39	7.68	3.3E+05
11/5/2011 2:39	0.08	3.4E+03	11/5/2011 8:54	10.30	4.5E+05
11/5/2011 2:54	0.05	2.1E+03	11/5/2011 9:09	14.04	6.1E+05
11/5/2011 3:09	0.05	2.1E+03	11/5/2011 1:39	0.05	2.1E+03
11/5/2011 3:24	0.05	2.1E+03	11/5/2011 9:39	22.19	9.6E+05
11/5/2011 3:39	0.05	2.1E+03	11/5/2011 9:54	26.60	1.1E+06
11/5/2011 4:39	0.08	3.4E+03	11/5/2011 10:09	29.63	1.3E+06
11/5/2011 4:09	0.08	3.4E+03	11/5/2011 10:24	36.47	1.6E+06
11/5/2011 4:24	0.08	3.4E+03	11/5/2011 10:39	41.32	1.8E+06
11/5/2011 4:39	0.08	3.4E+03	11/5/2011 10:54	47.07	2.0E+06

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	$j/m^2.d$	Date/Time	W/m^2	$J/m^2.d$
11/5/2011 4:24	0.08	3.4E+03	11/5/2011 9:39	22.19	9.6E+05
11/5/2011 12:39	96.18	4.2E+06	11/5/2011 9:54	26.60	1.1E+06
11/5/2011 12:54	86.85	3.8E+06	11/5/2011 10:09	29.63	1.3E+06
11/5/2011 13:09	64.00	2.8E+06	11/5/2011 18:09	9.57	4.1E+05
11/5/2011 13:24	46.53	2.0E+06	11/5/2011 18:24	2.86	1.2E+05
11/5/2011 13:39	100.81	4.4E+06	11/5/2011 18:39	0.88	3.8E+04
11/5/2011 13:54	92.50	4.0E+06	11/5/2011 18:54	0.08	3.4E+03
11/5/2011 14:09	105.85	4.6E+06	11/5/2011 19:09	0.05	2.1E+03
11/5/2011 14:24	116.37	5.0E+06	11/5/2011 19:24	0.08	3.4E+03
11/5/2011 14:39	57.74	2.5E+06	11/5/2011 19:39	0.08	3.4E+03
11/5/2011 14:54	80.36	3.5E+06	11/5/2011 19:54	0.08	3.4E+03
11/5/2011 15:09	31.36	1.4E+06	11/5/2011 20:09	0.05	2.1E+03
11/5/2011 7:09	0.05	2.1E+03	11/5/2011 20:24	0.08	3.4E+03
11/5/2011 7:24	0.08	3.4E+03	11/5/2011 9:39	22.19	9.6E+05
11/5/2011 7:39	0.30	1.3E+04	11/5/2011 9:54	26.60	1.1E+06
11/5/2011 15:24	22.19	9.6E+05	11/5/2011 10:09	29.63	1.3E+06
11/5/2011 15:39	24.26	1.0E+06	11/5/2011 18:09	9.57	4.1E+05
11/5/2011 15:54	32.38	1.4E+06	11/5/2011 18:24	2.86	1.2E+05
11/5/2011 16:09	38.13	1.6E+06	11/5/2011 18:39	0.88	3.8E+04
11/5/2011 16:24	41.83	1.8E+06	11/5/2011 18:54	0.08	3.4E+03
11/5/2011 16:39	23.62	1.0E+06	11/5/2011 19:09	0.05	2.1E+03
11/5/2011 16:54	45.38	2.0E+06	11/5/2011 19:24	0.08	3.4E+03
11/5/2011 17:09	40.81	1.8E+06	11/5/2011 19:39	0.08	3.4E+03
11/5/2011 17:24	29.92	1.3E+06	11/5/2011 19:54	0.08	3.4E+03
11/5/2011 17:39	23.34	1.0E+06	11/5/2011 20:09	0.05	2.1E+03
11/5/2011 7:09	0.05	2.1E+03	11/5/2011 20:24	0.08	3.4E+03
11/5/2011 7:24	0.08	3.4E+03	11/5/2011 9:39	22.19	9.6E+05
11/5/2011 7:39	0.30	1.3E+04	11/5/2011 9:39	22.19	9.6E+05
11/5/2011 15:24	22.19	9.6E+05	11/5/2011 9:54	26.60	1.1E+06
11/5/2011 15:39	24.26	1.0E+06	11/5/2011 10:09	29.63	1.3E+06
11/5/2011 15:54	32.38	1.4E+06	11/5/2011 18:09	9.57	4.1E+05
11/5/2011 16:09	38.13	1.6E+06	11/5/2011 18:24	2.86	1.2E+05
11/5/2011 16:24	41.83	1.8E+06	11/5/2011 18:39	0.88	3.8E+04
11/5/2011 16:39	23.62	1.0E+06	11/5/2011 18:54	0.08	3.4E+03
11/5/2011 16:54	45.38	2.0E+06	11/5/2011 19:09	0.05	2.1E+03
11/5/2011 17:09	40.81	1.8E+06	11/5/2011 19:24	0.08	3.4E+03
11/5/2011 17:24	29.92	1.3E+06	11/5/2011 19:39	0.08	3.4E+03

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	$j/m^2.d$	Date/Time	W/m^2	$J/m^2.d$
11/5/2011 12:54	86.85	3.8E+06	11/6/2011 4:09	0.05	2.1E+03
11/5/2011 13:09	64.00	2.8E+06	11/6/2011 4:24	0.08	3.4E+03
11/5/2011 13:24	46.53	2.0E+06	11/6/2011 4:39	0.05	2.1E+03
11/5/2011 20:54	0.08	3.4E+03	11/6/2011 2:09	0.08	3.4E+03
11/5/2011 21:09	0.08	3.4E+03	11/6/2011 2:24	0.05	2.1E+03
11/5/2011 21:24	0.08	3.4E+03	11/6/2011 2:39	0.08	3.4E+03
11/5/2011 21:39	0.05	2.1E+03	11/6/2011 10:24	39.18	1.7E+06
11/5/2011 21:54	0.05	2.1E+03	11/6/2011 4:09	0.05	2.1E+03
11/5/2011 22:09	0.08	3.4E+03	11/6/2011 4:24	0.08	3.4E+03
11/5/2011 22:24	0.08	3.4E+03	11/6/2011 4:39	0.05	2.1E+03
11/5/2011 22:39	0.08	3.4E+03	11/6/2011 5:24	0.08	3.4E+03
11/5/2011 22:54	0.05	2.1E+03	11/6/2011 5:39	0.05	2.1E+03
11/5/2011 23:09	0.08	3.4E+03	11/6/2011 5:54	0.08	3.4E+03
11/5/2011 12:54	86.85	3.8E+06	11/6/2011 6:09	0.08	3.4E+03
11/6/2011 0:00	0.00	3.4E+03	11/6/2011 6:24	0.05	2.1E+03
11/6/2011 0:09	0.08	3.4E+03	11/6/2011 6:39	0.08	3.4E+03
11/6/2011 0:24	0.08	3.4E+03	11/6/2011 6:54	0.08	3.4E+03
11/6/2011 0:39	0.08	3.4E+03	11/6/2011 8:09	3.24	1.4E+05
11/6/2011 0:54	0.05	2.1E+03	11/6/2011 8:24	6.02	2.6E+05
11/6/2011 1:09	0.05	2.1E+03	11/6/2011 8:39	7.97	3.4E+05
11/6/2011 1:24	0.05	2.1E+03	11/6/2011 8:54	12.48	5.4E+05
11/6/2011 1:39	0.05	2.1E+03	11/6/2011 9:09	14.90	6.4E+05
11/6/2011 1:54	0.05	2.1E+03	11/6/2011 9:24	18.99	8.2E+05
11/5/2011 23:39	0.08	3.4E+03	11/6/2011 9:39	14.62	6.3E+05
11/5/2011 23:54	0.08	3.4E+03	11/6/2011 9:54	19.73	8.5E+05
11/6/2011 0:00	0.00	3.4E+03	11/6/2011 10:09	15.80	6.8E+05
11/6/2011 7:39	0.27	1.2E+04	11/6/2011 7:39	0.27	1.2E+04
11/6/2011 0:00	0.00	3.4E+03	11/6/2011 7:54	1.61	7.0E+04
11/6/2011 0:09	0.08	3.4E+03	11/6/2011 8:09	3.24	1.4E+05
11/6/2011 0:24	0.08	3.4E+03	11/6/2011 8:09	3.24	1.4E+05
11/6/2011 0:39	0.08	3.4E+03	11/6/2011 8:24	6.02	2.6E+05
11/6/2011 0:54	0.05	2.1E+03	11/6/2011 8:39	7.97	3.4E+05
11/6/2011 2:39	0.08	3.4E+03	11/6/2011 8:54	12.48	5.4E+05
11/6/2011 2:54	0.08	3.4E+03	11/6/2011 9:09	14.90	6.4E+05
11/6/2011 3:09	0.08	3.4E+03	11/6/2011 9:24	18.99	8.2E+05
11/6/2011 3:24	0.05	2.1E+03	11/6/2011 9:39	14.62	6.3E+05
11/6/2011 3:39	0.08	3.4E+03	11/6/2011 9:54	19.73	8.5E+05

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	j/m^2.d	Date/Time	W/m^2	J/m^2.d
11/6/2011 10:54	47.11	2.0E+06	11/18/2011 13:39	103.36	4.5E+06
11/6/2011 11:09	57.14	2.5E+06	11/18/2011 13:54	88.12	3.8E+06
11/6/2011 11:24	68.70	3.0E+06	11/18/2011 14:09	81.77	3.5E+06
11/6/2011 11:39	75.03	3.2E+06	11/18/2011 14:24	77.84	3.4E+06
11/6/2011 11:54	76.05	3.3E+06	11/18/2011 14:39	67.23	2.9E+06
11/6/2011 12:09	85.54	3.7E+06	11/18/2011 14:54	34.81	1.5E+06
11/6/2011 12:24	93.20	4.0E+06	11/18/2011 15:09	71.06	3.1E+06
11/6/2011 12:39	93.59	4.0E+06	11/18/2011 15:24	58.16	2.5E+06
11/6/2011 12:54	92.53	4.0E+06	11/18/2011 15:39	23.53	1.0E+06
11/6/2011 10:24	39.18	1.7E+06	11/18/2011 17:24	30.91	1.3E+06
11/6/2011 10:39	42.79	1.8E+06	11/18/2011 17:39	19.34	8.4E+05
11/6/2011 10:54	47.11	2.0E+06	11/18/2011 17:54	10.14	4.4E+05
11/6/2011 11:09	57.14	2.5E+06	11/18/2011 18:09	4.94	2.1E+05
11/6/2011 13:39	90.78	3.9E+06	11/18/2011 18:24	1.74	7.5E+04
11/6/2011 13:54	94.13	4.1E+06	11/18/2011 18:39	0.30	1.3E+04
11/15/2011 1:24	0.08	3.4E+03	11/18/2011 18:54	0.08	3.4E+03
11/15/2011 1:39	0.08	3.4E+03	11/19/2011 0:39	0.08	3.4E+03
11/15/2011 1:54	0.08	3.4E+03	11/19/2011 0:54	0.08	3.4E+03
11/15/2011 2:09	0.08	3.4E+03	11/19/2011 1:09	0.08	3.4E+03
11/15/2011 2:24	0.05	2.1E+03	11/19/2011 1:24	0.08	3.4E+03
11/15/2011 2:39	0.05	2.1E+03	11/19/2011 1:39	0.08	3.4E+03
11/15/2011 2:54	0.08	3.4E+03	11/19/2011 1:54	0.08	3.4E+03
11/15/2011 3:09	0.08	3.4E+03	11/18/2011 17:24	30.91	1.3E+06
11/15/2011 3:24	0.08	3.4E+03	11/18/2011 20:09	0.08	3.4E+03
11/15/2011 3:39	0.08	3.4E+03	11/18/2011 20:24	0.08	3.4E+03
11/18/2011 16:24	25.64	1.1E+06	11/18/2011 20:39	0.08	3.4E+03
11/18/2011 16:39	34.07	1.5E+06	11/18/2011 20:54	0.05	2.1E+03
11/18/2011 16:54	40.88	1.8E+06	11/18/2011 21:09	0.05	2.1E+03
11/15/2011 1:24	0.08	3.4E+03	11/18/2011 21:24	0.05	2.1E+03
11/15/2011 1:39	0.08	3.4E+03	11/18/2011 21:39	0.08	3.4E+03
11/15/2011 1:54	0.08	3.4E+03	11/19/2011 3:39	0.08	3.4E+03
11/15/2011 2:09	0.08	3.4E+03	11/19/2011 3:54	0.08	3.4E+03
11/15/2011 2:24	0.05	2.1E+03	11/19/2011 4:09	0.08	3.4E+03
11/15/2011 4:24	0.08	3.4E+03	11/19/2011 4:24	0.08	3.4E+03
11/15/2011 4:39	0.05	2.1E+03	11/19/2011 4:39	0.08	3.4E+03
11/15/2011 4:54	0.08	3.4E+03	11/19/2011 4:54	0.08	3.4E+03
11/15/2011 5:09	0.08	3.4E+03	11/18/2011 20:09	0.08	3.4E+03

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	j/m^2.d	Date/Time	W/m^2	J/m^2.d
11/18/2011 23:09	0.05	2.1E+03	11/19/2011 8:24	3.95	1.7E+05
11/18/2011 23:24	0.08	3.4E+03	11/19/2011 8:39	7.71	3.3E+05
11/18/2011 23:39	0.08	3.4E+03	11/19/2011 8:54	8.80	3.8E+05
11/18/2011 23:54	0.08	3.4E+03	11/19/2011 9:09	12.06	5.2E+05
11/19/2011 0:00	0.00	3.4E+03	11/20/2011 7:39	0.08	3.4E+03
11/19/2011 0:09	0.08	3.4E+03	11/20/2011 7:54	0.56	2.4E+04
11/19/2011 0:24	0.08	3.4E+03	11/20/2011 8:09	1.96	8.5E+04
11/19/2011 6:39	0.05	2.1E+03	11/20/2011 8:24	3.56	1.5E+05
11/19/2011 6:54	0.08	3.4E+03	11/20/2011 8:39	5.64	2.4E+05
11/19/2011 7:09	0.05	2.1E+03	11/20/2011 4:39	0.08	3.4E+03
11/19/2011 2:24	0.08	3.4E+03	11/20/2011 7:39	0.08	3.4E+03
11/19/2011 2:39	0.08	3.4E+03	11/20/2011 7:54	0.56	2.4E+04
11/19/2011 2:54	0.08	3.4E+03	11/20/2011 8:09	1.96	8.5E+04
11/19/2011 3:09	0.08	3.4E+03	11/20/2011 8:24	3.56	1.5E+05
11/20/2011 2:09	0.08	3.4E+03	11/20/2011 8:39	5.64	2.4E+05
11/20/2011 2:24	0.08	3.4E+03	11/20/2011 8:54	8.39	3.6E+05
11/20/2011 2:39	0.08	3.4E+03	11/20/2011 9:09	11.26	4.9E+05
11/20/2011 2:54	0.08	3.4E+03	11/20/2011 9:24	14.84	6.4E+05
11/20/2011 3:09	0.08	3.4E+03	11/20/2011 9:39	18.51	8.0E+05
11/20/2011 3:24	0.08	3.4E+03	11/20/2011 7:39	0.08	3.4E+03
11/20/2011 3:39	0.08	3.4E+03	11/20/2011 9:54	22.06	9.5E+05
11/20/2011 3:54	0.08	3.4E+03	11/20/2011 10:09	23.91	1.0E+06
11/20/2011 4:09	0.08	3.4E+03	11/20/2011 7:24	0.05	2.1E+03
11/19/2011 2:24	0.08	3.4E+03	11/20/2011 10:24	30.14	1.3E+06
11/19/2011 2:39	0.08	3.4E+03	11/20/2011 10:39	34.90	1.5E+06
11/19/2011 5:24	0.08	3.4E+03	11/20/2011 10:54	46.24	2.0E+06
11/19/2011 5:39	0.08	3.4E+03	11/20/2011 11:09	47.11	2.0E+06
11/19/2011 5:54	0.05	2.1E+03	11/20/2011 11:24	68.16	2.9E+06
11/19/2011 6:09	0.08	3.4E+03	11/20/2011 11:39	25.41	1.1E+06
11/20/2011 4:54	0.08	3.4E+03	11/20/2011 11:54	26.02	1.1E+06
11/20/2011 5:09	0.05	2.1E+03	11/20/2011 12:09	75.35	3.3E+06
11/20/2011 5:24	0.05	2.1E+03	11/20/2011 12:24	27.43	1.2E+06
11/20/2011 5:39	0.05	2.1E+03	11/20/2011 10:24	30.14	1.3E+06
11/20/2011 5:54	0.08	3.4E+03	11/20/2011 12:39	37.14	1.6E+06
11/20/2011 6:09	0.08	3.4E+03	11/20/2011 12:54	78.70	3.4E+06
11/20/2011 6:24	0.08	3.4E+03	11/20/2011 10:09	23.91	1.0E+06
11/20/2011 6:39	0.05	2.1E+03	11/23/2011 16:09	55.32	2.4E+06

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	$j/m^2.d$	Date/Time	W/m^2	$J/m^2.d$
11/23/2011 16:24	25.22	1.1E+06	11/25/2011 1:24	0.08	3.4E+03
11/23/2011 16:39	31.87	1.4E+06	11/25/2011 1:39	0.05	2.1E+03
11/23/2011 16:54	18.35	7.9E+05	11/25/2011 1:54	0.08	3.4E+03
11/23/2011 17:09	31.07	1.3E+06	11/25/2011 2:09	0.08	3.4E+03
11/23/2011 17:24	7.75	3.3E+05	11/25/2011 2:24	0.05	2.1E+03
11/23/2011 17:39	7.33	3.2E+05	11/25/2011 2:39	0.08	3.4E+03
11/23/2011 17:54	3.88	1.7E+05	11/25/2011 2:54	0.05	2.1E+03
11/23/2011 16:24	25.22	1.1E+06	11/25/2011 3:09	0.05	2.1E+03
11/23/2011 16:39	31.87	1.4E+06	11/25/2011 11:09	45.41	2.0E+06
11/23/2011 16:54	18.35	7.9E+05	11/25/2011 11:24	49.02	2.1E+06
11/23/2011 17:09	31.07	1.3E+06	11/25/2011 11:39	56.18	2.4E+06
11/23/2011 17:24	7.75	3.3E+05	11/25/2011 11:54	56.75	2.5E+06
11/23/2011 17:39	7.33	3.2E+05	11/25/2011 5:24	0.05	2.1E+03
11/23/2011 17:54	3.88	1.7E+05	11/25/2011 5:39	0.05	2.1E+03
11/23/2011 18:09	4.71	2.0E+05	11/25/2011 5:54	0.08	3.4E+03
11/23/2011 18:24	1.68	7.2E+04	11/25/2011 6:09	0.08	3.4E+03
11/23/2011 18:39	0.30	1.3E+04	11/25/2011 6:24	0.08	3.4E+03
11/24/2011 10:24	28.32	1.2E+06	11/25/2011 6:39	0.08	3.4E+03
11/24/2011 10:39	31.52	1.4E+06	11/25/2011 6:54	0.08	3.4E+03
11/24/2011 10:54	38.03	1.6E+06	11/25/2011 7:09	0.08	3.4E+03
11/24/2011 11:09	43.37	1.9E+06	11/25/2011 9:09	10.65	4.6E+05
11/24/2011 11:24	49.79	2.2E+06	11/25/2011 9:24	18.19	7.9E+05
11/24/2011 11:39	57.36	2.5E+06	11/25/2011 9:39	14.68	6.3E+05
11/24/2011 11:54	57.49	2.5E+06	11/25/2011 9:54	23.37	1.0E+06
11/24/2011 12:09	63.11	2.7E+06	11/25/2011 10:09	23.66	1.0E+06
11/24/2011 12:24	64.23	2.8E+06	11/25/2011 10:24	28.35	1.2E+06
11/24/2011 12:39	78.70	3.4E+06	11/25/2011 10:39	34.04	1.5E+06
11/24/2011 10:39	31.52	1.4E+06	11/25/2011 10:54	28.93	1.2E+06
11/25/2011 4:39	0.08	3.4E+03	11/25/2011 17:09	11.71	5.1E+05
11/25/2011 4:54	0.08	3.4E+03	11/25/2011 12:39	67.39	2.9E+06
11/24/2011 13:09	85.92	3.7E+06	11/25/2011 12:54	77.01	3.3E+06
11/24/2011 13:24	44.13	1.9E+06	11/25/2011 13:09	39.85	1.7E+06
11/24/2011 13:39	87.61	3.8E+06	11/25/2011 13:24	35.83	1.5E+06
11/24/2011 13:54	85.54	3.7E+06	11/25/2011 13:39	86.75	3.7E+06
11/24/2011 14:09	80.62	3.5E+06	11/25/2011 20:09	0.08	3.4E+03
11/24/2011 14:24	85.92	3.7E+06	11/25/2011 20:24	0.05	2.1E+03
11/24/2011 14:39	79.95	3.5E+06	11/25/2011 20:39	0.08	3.4E+03

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	j/m^2.d	Date/Time	W/m^2	J/m^2.d
11/25/2011 15:39	67.97	2.9E+06	11/26/2011 1:09	0.05	2.1E+03
11/25/2011 15:54	54.39	2.3E+06	11/26/2011 7:39	0.05	2.1E+03
11/25/2011 16:09	57.55	2.5E+06	11/26/2011 7:54	0.27	1.2E+04
11/25/2011 16:24	20.11	8.7E+05	11/26/2011 8:09	1.45	6.3E+04
11/25/2011 16:39	25.67	1.1E+06	11/26/2011 8:24	3.43	1.5E+05
11/25/2011 22:54	0.08	3.4E+03	11/26/2011 8:39	5.45	2.4E+05
11/25/2011 23:09	0.08	3.4E+03	11/26/2011 8:54	7.75	3.3E+05
11/25/2011 23:24	0.08	3.4E+03	11/26/2011 9:09	10.72	4.6E+05
11/25/2011 23:39	0.05	2.1E+03	11/26/2011 9:24	13.53	5.8E+05
11/25/2011 23:54	0.08	3.4E+03	11/26/2011 9:39	17.01	7.3E+05
11/26/2011 0:00	0.00	2.1E+03	11/26/2011 4:09	0.05	2.1E+03
11/26/2011 0:39	0.08	3.4E+03	11/26/2011 10:54	36.47	1.6E+06
11/25/2011 18:39	0.27	1.2E+04	11/26/2011 11:09	42.15	1.8E+06
11/25/2011 18:54	0.08	3.4E+03	11/26/2011 11:24	48.64	2.1E+06
11/25/2011 19:09	0.05	2.1E+03	11/26/2011 11:39	53.91	2.3E+06
11/25/2011 19:24	0.08	3.4E+03	11/26/2011 11:54	57.14	2.5E+06
11/25/2011 19:39	0.05	2.1E+03	11/26/2011 12:09	68.76	3.0E+06
11/26/2011 1:39	0.08	3.4E+03	11/26/2011 12:24	23.08	1.0E+06
11/26/2011 1:54	0.05	2.1E+03	11/26/2011 12:39	85.54	3.7E+06
11/26/2011 2:09	0.05	2.1E+03	11/26/2011 12:54	80.23	3.5E+06
11/26/2011 2:24	0.08	3.4E+03	11/26/2011 13:09	68.83	3.0E+06
11/26/2011 2:39	0.08	3.4E+03	11/26/2011 14:54	29.34	1.3E+06
11/26/2011 2:54	0.05	2.1E+03	11/26/2011 15:09	59.56	2.6E+06
11/26/2011 3:39	0.05	2.1E+03	11/26/2011 15:24	29.76	1.3E+06
11/25/2011 22:39	0.05	2.1E+03	11/26/2011 15:39	51.00	2.2E+06
11/26/2011 4:39	0.05	2.1E+03	11/26/2011 15:54	54.04	2.3E+06
11/26/2011 4:54	0.08	3.4E+03	11/26/2011 16:09	36.59	1.6E+06
11/26/2011 5:09	0.05	2.1E+03	11/26/2011 16:24	44.55	1.9E+06
11/26/2011 5:24	0.05	2.1E+03	11/26/2011 16:39	25.73	1.1E+06
11/26/2011 5:39	0.05	2.1E+03	11/26/2011 16:54	33.82	1.5E+06
11/26/2011 5:54	0.08	3.4E+03	11/27/2011 0:09	0.08	3.4E+03
11/26/2011 6:09	0.05	2.1E+03	11/27/2011 0:24	0.05	2.1E+03
11/26/2011 6:24	0.05	2.1E+03	11/27/2011 0:39	0.05	2.1E+03
11/26/2011 6:39	0.08	3.4E+03	11/27/2011 0:54	0.05	2.1E+03
11/26/2011 6:54	0.08	3.4E+03	11/26/2011 18:09	3.56	1.5E+05
11/26/2011 7:09	0.08	3.4E+03	11/26/2011 18:24	1.61	7.0E+04
11/26/2011 14:24	46.69	2.0E+06	11/26/2011 18:39	0.24	1.0E+04

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	$j/m^2.d$	Date/Time	W/m^2	$J/m^2.d$
11/26/2011 18:54	0.05	2.1E+03	11/27/2011 4:54	0.05	2.1E+03
11/26/2011 19:09	0.05	2.1E+03	11/27/2011 5:09	0.05	2.1E+03
11/26/2011 19:24	0.05	2.1E+03	11/27/2011 5:24	0.08	3.4E+03
11/26/2011 19:39	0.05	2.1E+03	11/27/2011 5:39	0.08	3.4E+03
11/26/2011 19:54	0.05	2.1E+03	11/27/2011 5:54	0.08	3.4E+03
11/26/2011 20:09	0.05	2.1E+03	11/27/2011 11:54	54.96	2.4E+06
11/27/2011 3:24	0.05	2.1E+03	11/27/2011 12:09	62.02	2.7E+06
11/27/2011 3:39	0.05	2.1E+03	11/27/2011 12:24	66.88	2.9E+06
11/27/2011 3:54	0.05	2.1E+03	11/27/2011 12:39	69.21	3.0E+06
11/27/2011 4:09	0.05	2.1E+03	11/27/2011 12:54	72.02	3.1E+06
11/26/2011 21:39	0.08	3.4E+03	11/27/2011 13:09	77.17	3.3E+06
11/26/2011 21:54	0.05	2.1E+03	11/27/2011 13:24	30.65	1.3E+06
11/26/2011 22:09	0.08	3.4E+03	11/27/2011 7:24	0.08	3.4E+03
11/26/2011 22:24	0.05	2.1E+03	11/27/2011 7:39	0.08	3.4E+03
11/26/2011 22:39	0.08	3.4E+03	11/27/2011 7:54	0.24	1.0E+04
11/26/2011 22:54	0.08	3.4E+03	11/27/2011 8:09	1.33	5.7E+04
11/26/2011 23:09	0.08	3.4E+03	11/27/2011 8:24	2.80	1.2E+05
11/26/2011 23:24	0.08	3.4E+03	11/27/2011 8:39	4.36	1.9E+05
11/26/2011 23:39	0.08	3.4E+03	11/27/2011 14:39	63.88	2.8E+06
11/27/2011 6:09	0.08	3.4E+03	11/27/2011 14:54	65.03	2.8E+06
11/27/2011 6:24	0.08	3.4E+03	11/27/2011 15:09	58.61	2.5E+06
11/27/2011 6:39	0.05	2.1E+03	11/27/2011 15:24	52.22	2.3E+06
11/27/2011 6:54	0.08	3.4E+03	11/27/2011 15:39	47.36	2.0E+06
11/27/2011 1:24	0.05	2.1E+03	11/27/2011 15:54	49.76	2.1E+06
11/27/2011 1:39	0.08	3.4E+03	11/27/2011 16:09	35.16	1.5E+06
11/27/2011 1:54	0.05	2.1E+03	11/27/2011 10:54	36.56	1.6E+06
11/27/2011 2:09	0.08	3.4E+03	11/27/2011 11:09	42.41	1.8E+06
11/27/2011 2:24	0.05	2.1E+03	11/27/2011 11:24	48.67	2.1E+06
11/27/2011 2:54	0.08	3.4E+03	11/28/2011 6:24	0.08	3.4E+03
11/27/2011 8:54	7.62	3.3E+05	11/28/2011 6:39	0.05	2.1E+03
11/27/2011 9:09	10.11	4.4E+05	11/28/2011 6:54	0.08	3.4E+03
11/27/2011 9:24	13.15	5.7E+05	11/28/2011 7:09	0.05	2.1E+03
11/27/2011 9:39	16.72	7.2E+05	11/28/2011 7:24	0.05	2.1E+03
11/27/2011 9:54	20.30	8.8E+05	11/28/2011 7:39	0.08	3.4E+03
11/27/2011 10:09	21.96	9.5E+05	11/28/2011 7:54	0.21	9.0E+03
11/27/2011 10:24	27.78	1.2E+06	11/28/2011 8:09	1.33	5.7E+04
11/27/2011 4:39	0.05	2.1E+03	11/28/2011 8:24	3.02	1.3E+05

Appendix B (Continued)

Table A (Continued)

Date/Time	W/m^2	j/m^2.d	Date/Time	W/m^2	J/m^2.d
11/27/2011 13:54	66.56	2.9E+06	11/28/2011 14:39	8.42	3.6E+05
11/27/2011 14:09	73.97	3.2E+06	11/28/2011 20:39	0.08	3.4E+03
11/27/2011 14:24	68.48	3.0E+06	11/28/2011 20:54	0.08	3.4E+03
11/28/2011 9:09	10.94	4.7E+05	11/28/2011 21:09	0.08	3.4E+03
11/28/2011 9:24	18.19	7.9E+05	11/28/2011 21:24	0.05	2.1E+03
11/28/2011 9:39	24.23	1.0E+06	11/28/2011 21:39	0.08	3.4E+03
11/28/2011 9:54	12.92	5.6E+05	11/28/2011 21:54	0.08	3.4E+03
11/28/2011 10:09	21.04	9.1E+05	11/28/2011 22:09	0.05	2.1E+03
11/28/2011 10:24	24.49	1.1E+06	11/28/2011 22:24	0.08	3.4E+03
11/28/2011 10:39	34.49	1.5E+06	11/28/2011 22:39	0.08	3.4E+03
11/28/2011 10:54	42.79	1.8E+06	11/28/2011 22:54	0.08	3.4E+03
11/27/2011 16:39	31.87	1.4E+06			
11/27/2011 16:54	14.07	6.1E+05			
11/27/2011 17:09	28.10	1.2E+06			
11/28/2011 12:09	13.78	6.0E+05			
11/28/2011 12:24	13.18	5.7E+05			
11/28/2011 12:39	9.41	4.1E+05			
11/28/2011 12:54	14.46	6.2E+05			
11/28/2011 13:09	9.57	4.1E+05			
11/28/2011 13:24	13.56	5.9E+05			
11/28/2011 8:54	9.06	3.9E+05			
11/28/2011 14:54	12.12	5.2E+05			
11/28/2011 15:09	13.66	5.9E+05			
11/28/2011 15:24	12.12	5.2E+05			
11/28/2011 15:39	8.64	3.7E+05			
11/28/2011 15:54	10.24	4.4E+05			
11/28/2011 16:09	6.02	2.6E+05			
11/28/2011 16:24	4.90	2.1E+05			
11/28/2011 16:39	9.28	4.0E+05			
11/28/2011 16:54	9.66	4.2E+05			
11/28/2011 17:09	7.46	3.2E+05			
11/28/2011 11:39	19.25	8.3E+05			
11/28/2011 17:54	2.25	9.7E+04			
11/28/2011 18:09	0.94	4.1E+04			
11/28/2011 18:24	0.69	3.0E+04			
11/28/2011 18:39	0.14	6.2E+03			
11/28/2011 18:54	0.08	3.4E+03			

Appendix C-Parameter Estimation

1) C_s estimation

C_s is related to the gas-phase concentration of CO_2 at air-water interface (y_s) by:

$$C_s = \frac{y_s}{H} \tag{31}$$

where H is the Henry's law constant and is equal to 1.1 for CO_2 at 20°C (Crittenden 2005). Y_s is calculated using ideal gas law:

$$Y_s = \frac{V_{CO2}}{V_{air}} . \frac{P_{air}}{RT} \tag{32}$$

where R is ideal gas constant and is equal to 0.0821 L.atm.mol^{-1}.K

Using the data in table1,

$$Y_s = 0.02 \times \frac{8.5}{0.0821 \times 303} \times 12 \ \frac{g\ CO2}{mol\ CO2} = 0.24\ kgm^{-3}$$

And from equation --, C_s was estimated to be 0.22 kgm^{-3}.

2) K_La estimation

Fair and Mersmann equations were used to calculate ϵ_G and K_La, respectively (Shah 1982).

$$K_L.a = 3.31 \frac{D_l \epsilon_G}{{d_b}^2} \left(\frac{\mu_L}{\rho_L D_l}\right)^{1/3} \left(\frac{d_b \rho_L u_G}{\mu_L \epsilon_G}\right)^{1/2} \tag{33}$$

$$\frac{\epsilon_G}{(1-\epsilon_G)^4} = 0.14 u_G \left(\frac{{\rho_L}^2}{\sigma(\rho_L - \rho_G)g}\right)^{1/4} \left(\frac{{\rho_L}^2 \sigma^3}{{\mu_L}^4 (\rho_L - \rho_G) g}\right)^{1/24} \left(\frac{{\rho_L}^2}{\rho_L - \rho_G}\right)^{1/3} \left(\frac{\rho_L}{\rho_G}\right)^{5/72} \tag{34}$$

where ρ_l is water density (kg m^{-3}), ρ_G is air density (kgm^{-3}), μ_L is viscosity of water (Pa s), g is standard gravity (m s^{-2}), db is bubble diameter (m), D_l is CO_2 diffusivity in water (m^2 s^{-1}) and σ is Water interfacial tension (N m^{-1}).

Table B shows the values of some physical characteristics of water and air at 30°C.

From equations 33 and 34, ϵ_G and K_La were calculated to be 0.01 and 3.7×10^{-3} s^{-1}.

Appendix C (Continued)

Table B-Some physical characteristics of water and air at 30°C

Water density (kgm^{-3})	Air density (kgm^{-3})	Dynamic viscosity of water (Pa.s)	CO_2 diffusivity in water (m^2s^{-1})	Water interfacial tension ($N.m^{-1}$)
995	1.16	0.0008	2.2×10^{-9} (Tamimi et al., 1994)	7.2×10^{-2}

3) Estimation of yield coefficients

Algal biosynthesis can be described by the following chemical equations where ammonium is the nitrogen sources (Dalrymple et al. 2012)

$$16NH_4^+ + 92CO_2 + 92H_2O \; + \; 14HCO_3^- + HPO_4^{2-} \xrightarrow{h\upsilon} C_{106}H_{263}O_{110}N_{16}P + 106O_2$$

The yield coefficient is defined as: (Vaccari et al., 2006:327)

$$Y_S = \frac{Mass\ of\ produced\ biomass}{Mass\ of\ consumed\ \ nitrogen} \qquad (35)$$

Therefore, the yield coefficient for nitrogen will be:

$$Y_N = \frac{3550}{14\times16} \cong 16\ \frac{\text{g biomass}}{\text{g substrate}}$$

The yield coefficient for phosphorous and carbon will be calculated the same:

$$Y_P = 115\ \frac{\text{g biomass}}{\text{g substrate}} \quad ; \quad Y_C = 2.8\ \frac{\text{g biomass}}{\text{g substrate}}$$

Appendix D- Change of S/Ks for Nitrogen, Phosphorus, Carbon and Light Intensity during Algae Cultivation

The ratio of simulated concentration of nitrogen, carbon, phosphorus and light intensity over the half saturation constants of those factors during the algae group experiment, has been shown in Table C. The values are shown for three different hours during the day (7 a.m., 12 p.m. and 9 p.m.) from November 4, 2011- November 27, 2011.

Table C-Change of S/K_s for nitrogen, phosphorus, carbon and light intensity

Date/Time	$\frac{S_N}{K_{s,N}}$	$\frac{S_P}{K_{s,P}}$	$\frac{S_c}{K_{s,c}}$	$\frac{I}{K_{s,I}}$	μ (d^{-1})
11/4/2011 7:00 a.m.	2.9	5.1	0.0	3.2	$\mu_{max,c}$
11/4/2011 12:00 p.m.	3.4	6.4	2.0	2583.0	$\mu_{max,c}$
11/4/2011 21:00 p.m.	3.3	6.3	1.9	3.2	$\mu_{max,I}$
11/5/2011 7:00 a.m.	3.1	6.2	1.9	12.0	$\mu_{max,c}$
11/5/2011 12:00 p.m.	3.6	7.3	1.9	1284.8	$\mu_{max,c}$
11/5/2011 21:00 p.m.	3.5	7.3	1.9	3.2	$\mu_{max,I}$
11/6/2011 7:00 a.m.	3.3	7.2	1.9	128.7	$\mu_{max,c}$
11/6/2011 12:00 p.m.	3.2	7.1	1.9	852.5	$\mu_{max,c}$
11/6/2011 21:00 p.m.	3.0	7.1	1.9	3.2	$\mu_{max,c}$
11/7/2011 7:00 a.m.	2.9	7.0	1.9	287.1	$\mu_{max,c}$
11/7/2011 12:00 p.m.	2.7	6.9	1.9	2216.6	$\mu_{max,c}$
11/7/2011 21:00 p.m.	2.5	6.9	1.9	3.2	$\mu_{max,c}$
11/8/2011 7:00 a.m.	3.1	7.9	1.9	498.9	$\mu_{max,c}$
11/8/2011 12:00 p.m.	3.0	7.8	1.9	539.4	$\mu_{max,c}$
11/8/2011 21:00 p.m.	2.8	7.7	1.9	1.9	$\mu_{max,c}$
11/9/2011 7:00 a.m.	2.6	7.7	1.9	819.6	$\mu_{max,c}$
11/9/2011 12:00 p.m.	2.4	7.6	1.9	659.8	$\mu_{max,I}$
11/9/2011 21:00 p.m.	2.2	7.5	1.9	3.2	$\mu_{max,c}$
11/10/2011 7:00 a.m.	2.7	6.6	1.9	1089.6	$\mu_{max,c}$
11/10/2011 12:00 p.m.	2.5	6.5	1.9	62.7	$\mu_{max,I}$
11/10/2011 21:00 p.m.	2.4	6.4	1.9	3.2	$\mu_{max,c}$
11/11/2011 7:00 a.m.	2.2	6.3	1.9	1448.4	$\mu_{max,c}$
11/11/2011 12:00 p.m.	2.0	6.3	1.9	3.2	$\mu_{max,c}$
11/11/2011 21:00 p.m.	2.5	5.5	1.9	3.2	$\mu_{max,c}$
11/12/2011 7:00 a.m.	2.4	5.4	1.9	2007.4	$\mu_{max,c}$
11/12/2011 12:00 p.m.	2.2	5.4	1.9	3.2	$\mu_{max,c}$
11/12/2011 21:00 p.m.	2.1	5.3	1.9	1.9	$\mu_{max,c}$
11/13/2011 7:00 a.m.	1.9	5.2	1.9	2518.3	$\mu_{max,N}$
11/13/2011 12:00 p.m.	1.7	5.2	1.9	3.2	$\mu_{max,N}$
11/13/2011 21:00 p.m.	2.3	4.6	1.9	1.9	$\mu_{max,c}$

Appendix D (Continued)

Table C (Continued)

Date/Time	$\frac{S_N}{K_{s,N}}$	$\frac{S_P}{K_{s,P}}$	$\frac{S_c}{K_{s,c}}$	$\frac{I}{K_{s,I}}$	μ (d^{-1})
11/14/2011 7:00 a.m.	2.1	4.6	1.9	3088.8	$\mu_{max,c}$
11/14/2011 12:00 p.m.	2.0	4.5	1.9	1.9	$\mu_{max,c}$
11/14/2011 21:00 p.m.	1.9	4.5	1.9	3.2	$\mu_{max,N}$
11/15/2011 7:00 a.m.	1.7	4.4	1.9	1804.6	$\mu_{max,N}$
11/15/2011 12:00 p.m.	1.6	4.3	1.9	3.2	$\mu_{max,N}$
11/15/2011 21:00 p.m.	2.2	3.9	1.9	3.2	$\mu_{max,c}$
11/16/2011 7:00 a.m.	2.0	3.8	1.9	1374.8	$\mu_{max,c}$
11/16/2011 12:00 p.m.	2.6	3.5	1.9	1.9	$\mu_{max,c}$
11/16/2011 21:00 p.m.	2.5	3.4	1.9	3.2	$\mu_{max,I}$
11/17/2011 7:00 a.m.	2.3	3.4	1.9	942.6	$\mu_{max,c}$
11/18/2011 7:00 a.m.	2.6	3.0	1.9	3244.7	$\mu_{max,c}$
11/18/2011 12:00 p.m.	3.0	2.8	1.9	1.9	$\mu_{max,I}$
11/18/2011 21:00 p.m.	2.9	2.7	1.9	1.9	$\mu_{max,c}$
11/19/2011 7:00 a.m.	2.8	2.7	1.9	1671.5	$\mu_{max,c}$
11/19/2011 12:00 p.m.	3.2	2.5	1.9	1.9	$\mu_{max,c}$
11/19/2011 21:00 p.m.	3.1	2.4	1.9	3.2	$\mu_{max,c}$
11/20/2011 7:00 a.m.	3.0	2.4	1.9	2498.0	$\mu_{max,c}$
11/20/2011 12:00 p.m.	2.9	2.3	1.9	3.2	$\mu_{max,c}$
11/20/2011 21:00 p.m.	2.7	2.3	1.9	3.2	$\mu_{max,c}$
11/22/2011 7:00 a.m.	3.2	2.2	1.9	678.9	$\mu_{max,c}$
11/22/2011 12:00 p.m.	3.1	2.1	1.9	1.9	$\mu_{max,c}$
11/22/2011 21:00 p.m.	3.0	2.1	1.9	18.4	$\mu_{max,c}$
11/23/2011 7:00 a.m.	3.4	2.0	1.9	749.8	$\mu_{max,c}$
11/23/2011 12:00 p.m.	3.3	1.9	1.9	3.2	$\mu_{max,c}$
11/23/2011 21:00 p.m.	3.2	1.9	1.9	199.7	$\mu_{max,p}$
11/24/2011 7:00 a.m.	3.6	1.8	1.9	1264.6	$\mu_{max,p}$
11/24/2011 12:00 p.m.	3.5	1.8	1.9	9.5	$\mu_{max,p}$
11/24/2011 21:00 p.m.	3.9	1.7	1.9	311.2	$\mu_{max,p}$
11/25/2011 7:00 a.m.	3.8	1.7	1.9	893.1	$\mu_{max,p}$
11/25/2011 12:00 p.m.	3.7	1.6	1.9	3.2	$\mu_{max,p}$
11/25/2011 21:00 p.m.	3.6	1.6	1.9	722.0	$\mu_{max,p}$
11/26/2011 7:00 a.m.	4.0	1.6	1.9	813.2	$\mu_{max,p}$
11/26/2011 12:00 p.m.	3.9	1.5	1.9	3.2	$\mu_{max,p}$
11/26/2011 21:00 p.m.	3.9	1.5	1.9	818.3	$\mu_{max,p}$
11/27/2011 7:00 a.m.	3.8	1.5	1.9	141.3	$\mu_{max,p}$
11/27/2011 12:00 p.m.	4.2	1.5	1.9	3.2	$\mu_{max,p}$
11/27/2011 21:00 p.m.	4.2	1.5	1.9	1102.3	$\mu_{max,p}$